Nonclassical Double-Bridged Structure in Silicon-Containing Molecules: Experimental Evidence in Si_2H_2 from Its Submillimeter-Wave Spectrum

M. Bogey, H. Bolvin, C. Demuynck, and J. L. Destombes
Laboratoire de Spectroscopie Hertzienne, Université des Sciences et Techniques de Lille I,
59655 Villeneuve d'Ascq CEDEX, France

(Received 1 November 1990)

The first spectroscopic evidence of a double-bridged silicon molecule is reported. The submillimeter-wave rotational spectrum of the disilyne Si_2H_2 has been observed in a low-power silane plasma cooled at liquid-nitrogen temperature, with argon as buffer gas. These measurements led to the determination of the r_0 structure, which is in good agreement with *ab initio* calculations. This nonclassical structure is confirmed by the observation of the ^{29}Si and ^{30}Si monosubstituted forms.

PACS numbers: 33.10.Ev, 33.20.Bx, 35.20.Dp, 35.20.Pa

There is presently a growing interest in the study of small unsaturated silicon compounds, related to the vapor deposition of amorphous silicon films.[1-3] Detection of some monosilicon intermediate species [SiH_n (Ref. 4); SiH_n^+ (Ref. 5), $n \leq 3$] by high-resolution spectroscopy has already led to the development of nonintrusive diagnostic techniques of silane plasmas.[2,3,6] In contrast, experimental data on unsaturated disilicon hydrides are very scarce, although recent mass-spectrometry investigations[7] have shown that Si_2H_2 and Si_2H_4 can be abundant in SiH_4 plasmas and therefore can play a key role in deposition processes (Refs. 1-3, and 8, and references therein).

The study of these highly reactive species also has its own interest, for a fundamental comparison between carbon and silicon bonding properties. For example, *ab initio* calculations have shown that the simplest unsaturated hydrides Si_2H_2 and Si_2H_4 exhibit geometries very different from the analogous C-containing molecules, and that the smaller basis sets are not adequate to properly describe the structures and the relative stabilities of the various isomers.[9-15] In particular, it has been shown that addition of Si *d* functions and of electron correlation makes the nonclassical bridged structure of the disilyne $Si(H_2)Si$ in its singlet ground state more stable than the silasilene H_2SiSi classical structure, which is the minimum-energy structure at the HF/3-21G level.[14] The energy difference between the two structures is rather small, in the range of 7-13 kcal/mol.[9-12,14] In fact, bridged structures are well known in molecules involving electron-deficient atoms such as boron.[16] Nevertheless, very little is experimentally known regarding the existence of such three-center bonds in the group-IV compounds. Protonated acetylene, recently investigated by ir spectroscopy[17] and Coulomb-explosion experiments,[18] is the only example of such a situation. The nonclassical bridged form $HC(H)CH^+$ is calculated to be lower in energy than the classical form H_2CCH^+ by about 4-7 kcal/mol,[19,20] which is consistent with the experiments. However, no complete structural information on $C_2H_3^+$ can be deduced from these experiments at the moment. In this Letter, we present the first spectroscopic evidence of the disilyne Si_2H_2, and the first determination of a bridged structure for a silicon-containing molecule.

In the course of an investigation of a silane plasma by submillimeter-wave spectroscopy, some unidentified lines were observed around 450 GHz. The submillimeter-wave spectrometer used in this study has been described elsewhere.[21] It consists mainly of phase-locked carcinotrons (Thomson CSF) covering the 340-475-GHz frequency range. Detection was achieved with a liquid-helium-cooled InSb detector (QMC Instr.). A weak electric discharge (which is known to produce good-quality hydrogenated amorphous silicon films[7] was ignited in SiH_4 with Ar as buffer gas, in an all glass, 2-m-long, 50-mm-i.d. absorption cell which was cooled at liquid-N_2 temperature. A confinement axial magnetic field of 200 G was used to extend the negative glow to the whole length of the cell, as in the millimeter-wave spectroscopy of molecular ions.[21-23] To avoid immediate condensation at the entrance of the cell, silane was introduced through an axial glass tube (1.5 m long, 6 mm i.d.), with small holes drilled every 20 mm. The best conditions were $P(\mathrm{Ar}) \approx 20$ mTorr, $P(\mathrm{SiH_4}) \approx 30$ mTorr (measured at room temperature), $I \approx 10$ mA. In these conditions, signal-to-noise ratios of about 10 were obtained for a single scan of 1 s with a 10-ms lock-in time constant. The lifetime of the molecule appeared to be far below 0.1 s.

The unidentified lines had a typical behavior, being maximum in intensity in the abnormal regime of the discharge and disappearing almost completely in the positive column regime. However, they did not show the intensity evolution characteristic of ionic lines when the confinement magnetic field was varied.[21-23] As they did not exhibit any Zeeman splitting, we concluded they were due to a *closed-shell neutral molecule containing only silicon and hydrogen atoms,* since Ar could be discarded because the lines were also observed (although much weaker) at room temperature in pure SiH_4.

As shown on the stick diagram of Fig. 1, the submillimeter-wave spectrum of this unknown molecule

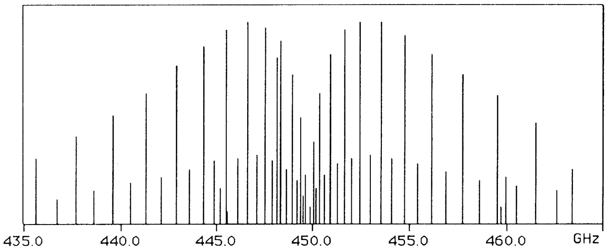

FIG. 1. Stick diagram of the ^{c}Q branch observed in SiH_4+Ar discharge. Note the 1:3 intensity alternation. The rotational temperature of ≈ 110 K deduced from the relative intensities of the lines is very close to the wall temperature, as observed by Itabashi *et al.* in the case of SiH_3 (Ref. 6).

TABLE I Molecular constants derived from the fit of the experimental spectrum (sextic centrifugal distortion constants other than H_{JK} and H_{KJ} could not be determined and were fixed to zero). Rotational constants are compared with *ab initio* predictions. All constants are in MHz.

	This work	Ref. 9	Ref. 13	Ref. 14
A	157 198.821(17)	156 137	161 113	158 602
B	7281.3268(27)	7455	7447	7518
C	7199.7342(26)	7375	7367	7434
Δ_J	$5.6966(32)\times 10^{-3}$			
Δ_{JK}	$-61.677(55)\times 10^{-3}$			
Δ_K	8.8308(38)			
δ_J	$-4.237(78)\times 10^{-6}$			
δ_K	$62.58(83)\times 10^{-3}$			
H_{JK}	$0.6072(24)\times 10^{-6}$			
H_{KJ}	$-57.(10)\times 10^{-6}$			

is completely dominated by a very characteristic *c*-type Q branch pattern. The assignment of the lines by first and second frequency difference methods was straightforward[24] and showed that the observed lines belong to the $^{R}Q_1$ branch ($K_{-1}=1\rightarrow 2$). Extension of the initial search to a wider frequency range allowed some P and R lines to be observed. Finally, a total of 87 lines were measured in the 347–472-GHz range. They are characterized by $J\leq 38$ and $K_{-1}\leq 2$. Their frequencies are available upon request to the authors. The spectrum was fitted using Watson's A reduced Hamiltonian,[25] with a standard deviation of 20 kHz. The determined molecular constants are presented in Table I. Note that the molecule is accidentally a nearly prolate symmetric top with $I_b \approx I_c$, and unusual situation previously met in H_2S_2 (Ref. 24) and $C(NH)_2$ (Ref. 26).

More can be learned about this unknown molecule by carefully examining the values of the rotational constants A, B, and C.

(i) Comparison of B and C (≈ 7250 MHz) with those of molecules having similar masses [$B(S_2)\approx 8.8$ GHz, $B(SiCl)\approx 7.6$ GHz, $B(Si_2)\approx 7.2$ GHz (Ref. 27)] clearly indicates that the molecule contains two heavy atoms.

(ii) The relatively high value of A (≈ 157 GHz) shows that A is mainly determined by a few H atoms out of the heavy-atom axis. Comparison with known molecules suggests that most likely $n(H)\leq 3$.

(iii) The 1:3 alternation in the intensity of adjacent lines indicates that the molecule contains one pair of exchangeable hydrogen atoms. This result is consistent with (ii) and then suggests that the unknown molecule is the disilyne Si_2H_2, a fundamental molecule never observed spectroscopically.

(iv) In a silane plasma very similar to ours (low pressure, low current), mass-spectroscopic investigations showed that a peak at $m/e=58$, which was attributed to Si_2H_2,[7] was predominant when Ar was used as buffer gas.

The identification of the molecule is consistent with the available *ab initio* calculations.[9–15]

(v) As already discussed above, the ground state of Si_2H_2 has a singlet nonclassical bridged structure (Fig. 2). The C_{2v} symmetry implies the existence of a permanent dipole moment which has not yet been calculated to our knowledge. However, Luke *et al.*[14] showed that Si and H have opposite charges, which would lead to a substantial dipole moment. Moreover, all *ab initio* structures show that this dipole moment lies along the *c* axis, in agreement with the experiment.

(vi) The A,B,C values calculated from the various *ab initio* structures available are very close to the experimental ones (see Table I). In particular, the $B-C$ value (≈ 81 MHz), which gives the submillimeter-wave spectrum its highly characteristic pattern, is very well accounted for by the theory.

(vii) The silasilene polar isomer H_2SiSi can be excluded because it would give rise to an *a*-type spectrum. Other potential molecules can be excluded by the same type of argument. For example, Si_2H_4, which could marginally fulfill (ii) and (iii), has a *trans*-bent geometry in its ground state with a center of symmetry,[14,15] and then no permanent dipole moment and no

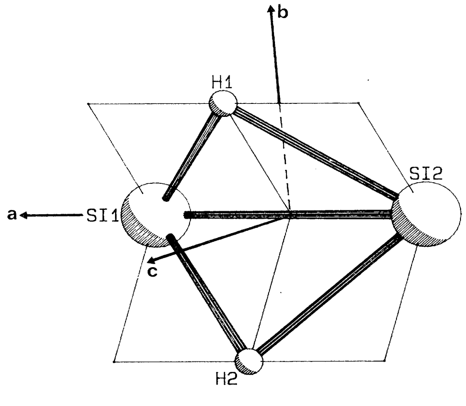

FIG. 2. Geometrical structure of the double-bridged Si_2H_2. For clarity only the *a*,*b*,*c* axes, which are parallel to the principal axes, have been drawn.

TABLE II. The experimental r_0 structure of Si_2H_2 compared with *ab initio* calculations.

	This work	Ref. 9	Ref. 13	Ref. 14
Si-Si (Å)	2.2079	2.181	2.183	2.172
Si-H (Å)	1.6839	1.678	1.664	1.668
η (deg)	103.18	102.2	102.7	102.4

pure rotational spectrum. The polar silysilylene isomer SiH_3SiH, which is ≈ 5–6 kcal/mol higher in energy,[15] has quite different *ab initio* rotational constants and would exhibit a completely different spectral pattern, with *a*- and *b*-type transitions, incompatible with the observed spectrum.

Because of the symmetry of Si_2H_2, only three geometrical parameters (Si-H, Si-Si distances, dihedral angle η, see Fig. 2) are needed to describe its structure. Relations between the principal moments of inertia and these parameters were easily derived and were used to calculate the r_0 structure of the molecule. The results are given in Table II where they are compared with the *ab initio* predictions. As expected for a r_0 structure, the experimentally determined bond lengths are slightly longer than the theoretical equilibrium values. Nevertheless, the agreement is very good. The Si-Si bond length appears to be 0.05 Å longer in Si_2H_2 than in substituted disilenes,[28] but still 0.124 Å shorter than the distance found in substituted disilanes.[29] The Si-H distance is about 12% longer than a normal Si-H bond. Such a long bond length is characteristic of a three-center bond, which has already been proposed to exist in hydrogenated amorphous silicon.[30] Similar changes have been observed in boron compounds[16] and are predicted for the C-H bonds in $C_2H_3^+$.[17]

In order to experimentally confirm the identification and the geometry of the molecule, this r_0 structure was used to predict the *A*,*B*,*C* values of the ^{29}Si and ^{30}Si monosubstituted forms (isotopomers). These predictions should be rather accurate, since the isotopic changes on the vibrational effects are expected to be very small. Because of the low natural abundance of these isotopes (4.7% and 3%, respectively), the signals expected were at the limit of the spectrometer sensitivity. Nevertheless, a total of 31 isotopic lines were observed leading to a preliminary determination of the rotational constants. They are given in Table III and compared with the predictions. The agreement is excellent and definitively confirms the identification. The observation of the monodeuterated species, which is planned in the near future, will lead to the determination of the substitution structure, a better approximation of the true equilibrium structure. Another interesting development is the investigation of the evolution of the bridged structure when the H atoms are replaced by bulkier atoms or groups.

This work was partially supported by the Centre National de la Recherche Scientifique (Groupe de Recherche "Physico-Chimie des Molecules Interstellaires"). Laboratoire de Spectroscopie Hertzienne is associated with CNRS.

TABLE III. Rotational constants of ^{29}Si and ^{30}Si isotopomers of Si_2H_2 (in MHz).

	$^{29}Si(H_2)^{28}Si$		$^{30}Si(H_2)^{28}Si$	
	Predicted	Observed	Predicted	Observed
A	157 162.0	157 160.54	157 128.9	157 124.86
B	7157.7	7157.94	7042.4	7042.83
C	7078.9	7079.14	6966.2	6966.60

Note added.—After this paper was submitted, recent theoretical results by Colegrove and Schaefer[31] came to our attention. They confirm that the minimum-energy structure is the C_{2v} dibridged geometry. The rotational constants deduced from their *ab initio* structure ($A = 163\,446$ MHz, $B = 7236$ MHz, $C = 7154$ MHz) are in very good agreement with our experimental results (see Table I).

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