

## Millimeterwave rotational spectrum of H<sub>2</sub>SiO

Stephane Bailleux, Marcel Bogey, Claire Demuynck, JeanLuc Destombes, and Adam Walters

Citation: *The Journal of Chemical Physics* **101**, 2729 (1994); doi: 10.1063/1.467654

View online: <http://dx.doi.org/10.1063/1.467654>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/101/4?ver=pdfcov>

Published by the AIP Publishing

---

### Articles you may be interested in

[The laboratory millimeterwave spectrum of MgCN \(X<sup>2</sup>Σ<sup>+</sup>\)](#)

AIP Conf. Proc. **312**, 297 (1994); 10.1063/1.46607

[Millimeterwave spectrum of vibrationally excited cyclopropenylidene, cC<sub>3</sub>H<sub>2</sub>](#)

J. Chem. Phys. **99**, 890 (1993); 10.1063/1.465353

[High resolution millimeterwave spectrum of methyl bromide. Spin-rotation and nuclear shielding tensors of bromine](#)

J. Chem. Phys. **67**, 254 (1977); 10.1063/1.434551

[MillimeterWave Spectrum of Hydrogen Peroxide](#)

J. Chem. Phys. **51**, 5336 (1969); 10.1063/1.1671954

[MillimeterWave Spectrum of Formic Acid](#)

J. Chem. Phys. **28**, 71 (1958); 10.1063/1.1744083

---



# Millimeter-wave rotational spectrum of $\text{H}_2\text{SiO}$

Stephane Bailleux, Marcel Bogey, Claire Demuynck, Jean-Luc Destombes, and Adam Walters

Université des Sciences et Technologies de Lille, Laboratoire de Spectroscopie Hertzienne, associé au CNRS, F-59655 Villeneuve d'Ascq Cedex, France

(Received 28 February 1994; accepted 18 April 1994)

The first high resolution rotational spectrum of  $\text{H}_2\text{SiO}$  in the gas phase has been obtained. This molecule was identified among several short-lived unknown species produced by a low power "abnormal" glow discharge in a mixture of  $\text{SiH}_4$ ,  $\text{O}_2$ , and Ar. On/off modulation of the discharge allowed lines belonging to each species to be characterized by their lifetime measured using a digitizing oscilloscope. In total 107 lines of  $\text{H}_2\text{SiO}$  were measured between 140 and 470 GHz. Evidence for a possible large amplitude motion has been found from anomalies in the fit of close lying  $K_a$  doublets.

## INTRODUCTION

Silicon-containing molecules and ions of composition  $[\text{Si}, \text{O}, \text{H}_n]$  are of interest not only because of their supposed role in ionospheric<sup>1</sup> and interstellar chemistry<sup>2</sup> but also because of recent developments in thin silicon film plasma deposition and etching technology.<sup>3,4</sup> Unlike their carbon analogues, the spectra of almost all of these silicon-containing molecules has not been measured in the gas phase. An exception is  $\text{SiOH}^+$  which has been studied by infrared laser spectroscopy.<sup>5,6</sup>

Another major interest is a comparison of silicon and carbon binding properties. The binding properties of silicon vary considerably from those of its group IV neighbor carbon.<sup>7-10</sup> All recent *ab initio* calculations<sup>7-14</sup> indicate that the three most stable isomers of  $[\text{Si}, \text{O}, \text{H}_2]$ , *trans* ( $\text{HSiOht}$ ) and *cis* ( $\text{HSiOhc}$ ) hydroxysilylene, and silanone ( $\text{H}_2\text{SiO}$ ), have approximately the same energy. In contrast, the *cis* and *trans* isomers of  $\text{HCOH}$  are more than 50 kcal/mol higher in energy than formaldehyde ( $\text{H}_2\text{CO}$ ).<sup>7</sup> Some calculations<sup>7,12</sup> suggest that  $\text{HSiOht}$  is the most stable form, others<sup>10,11,13</sup> suggest that  $\text{H}_2\text{SiO}$  is most stable. While previous calculations attribute a lower energy to the *trans* isomer of  $\text{HSiOH}$  than to the *cis* isomer, the latest calculations by Ma and Schaefer<sup>13</sup> (accompanying paper) indicate contrarily that the *cis* isomer could be the most stable. However it would seem from a practical point of view that the exact energy of each "stable" configuration is less important than the potential barrier between them.  $\text{H}_2\text{SiO}$  is separated from the other isomers by a large potential barrier (typically 69.5 kcal/mol)<sup>12</sup> indicating that it should be relatively stable once formed. The barrier between  $\text{HSiOhc}$  and  $\text{HSiOht}$  is much smaller (8.3 kcal/mol)<sup>13</sup> so there may be interconversion between these two forms. The barrier to dissociation by hydrogen elimination is relatively large (around 50 kcal/mol for  $\text{HSiOhc}$  and 90 kcal/mol for  $\text{H}_2\text{SiO}$ ).<sup>7</sup>

The infrared spectra of  $\text{HSiOH}$ ,  $\text{HSiOD}$ , and  $\text{DSiOD}$  were first recorded in matrix isolation studies of the reaction of silicon atoms with water.<sup>15</sup> For the last two isotopic species both *cis* and *trans* forms were observed but interestingly one isomer of  $\text{HSiOH}$  was missing. Ismail *et al.*<sup>15</sup> attributed the observed spectrum to the *trans* isomer and this isotopic effect was subsequently attributed to a tunneling instability

and wave function localization in  $\text{HSiOht}$ .<sup>16</sup> The results of Ma and Schaefer<sup>13</sup> (accompanying paper) would suggest that it was the *cis* and not the *trans* isomer which was observed. Experimental evidence for silanone was subsequently provided in 1985 by infrared spectra recorded after mercury-arc irradiation of argon matrices containing silane and ozone.<sup>17,18</sup> Simultaneously chemiluminescent emission in the visible region, following the reaction of ozone with silane in a beam-gas apparatus,<sup>19</sup> was attributed to this species. Evidence for the existence of both  $\text{H}_2\text{SiO}$  and  $\text{HSiOH}$  in the gas phase has recently been provided by Srinivas *et al.*<sup>20</sup> through collisional-activation and neutralization-reionization mass spectrometry. Recent attempts to observe  $\text{H}_2\text{SiO}$  through the flash vacuum thermolysis of retroene precursors<sup>21</sup> were not successful but led directly to the synthesis of  $\text{SiO}$ , resulting from an easy thermal dehydrogenation of silanone.

*Ab initio* calculations provided the molecular constants<sup>7,10,12,13,22,23</sup> we needed in order to search for  $\text{HSiOH}$  and  $\text{H}_2\text{SiO}$  in the gas phase using millimeter-wave spectroscopy. In particular we are grateful to Ma and Schaefer<sup>13</sup> (accompanying paper) and to A. G. Császár<sup>23</sup> who sent us privately the results of their calculations. Ma and Schaefer also calculated at our request the permanent dipole moment of the different isomers and found a relatively large value for that of  $\text{H}_2\text{SiO}$  [3.82 D at the TZ2P(*f*,*d*)/CCSD(T) level of theory]. Silanone is predicted to be a planar nearly symmetric prolate rotor with  $C_{2v}$  symmetry and an *a*-type spectrum;<sup>13</sup> the two isomers of hydroxysilylene should also be planar with  $C_s$  symmetry showing both *a*- and *b*-type spectra.

## EXPERIMENT

The spectrometer used in this study has been described extensively<sup>24</sup> but several modifications and improvements have recently been made.<sup>25</sup> As previously the millimeter-wave power is obtained by harmonic generation from phase-locked Varian klystrons using Schottky barrier diodes (Faran Technology) mounted in a commercial multiplier (Custom Microwave). In the submillimeter-wave region (340–470 GHz) two phase-locked Thomson C.S.F. carcinotrons give improved sensitivity. A liquid helium cooled InSb detector (QMC Instruments) allows low-noise detection over

a wide frequency band. Source modulation at 40 kHz and lock-in detection at 80 kHz for improved sensitivity give a second derivative line shape. Data acquisition is achieved by a Hewlett-Packard 9000 microcomputer-controlled microprocessor system which also ensures frequency scanning and signal processing. The molecules are produced by dc discharge in an all-glass, 2-m-long, 50-mm-i.d. absorption cell. The plane Teflon windows formerly at the entry and exit of this cell have been replaced by windows mounted at the Brewster angle. This modification has reduced significantly the well-known problem of standing waves. By using mirrors instead of lenses to match the millimeter-wave beam to the cell diameter, and to focus it subsequently on the detector, power transmission has been increased. It is now possible to modulate the discharge (on/off) and to record the absorption signal at a fixed frequency as a function of time by using a digitizing oscilloscope. In this way the lifetime of molecular states giving rise to a certain transition can be measured.

In order to search for  $\text{H}_2\text{SiO}$  we set up an abnormal glow discharge, using conditions which had previously given a good production of  $\text{Si}_2\text{H}_2$ ,<sup>25,26</sup> but with the addition of oxygen into the mixture of  $\text{SiH}_4$  and argon. As previously, the discharge cell was cooled to liquid nitrogen temperature and  $\text{SiH}_4$  mixed with argon was introduced into the cell through an axial glass tube, in order to avoid condensation at the cell entrance. To prevent the blockage of this tube due to the formation of  $\text{SiO}_2$ , oxygen was introduced separately into the cell. Since  $\text{SiO}$  is expected to be produced simultaneously with  $\text{H}_2\text{SiO}$  and  $\text{HSiOH}$  we first verified that it was formed in the discharge. We then began a frequency scan around 200 GHz and almost immediately found unidentified lines. However, after a short time of operation the discharge became strongly noisy making signal detection difficult. Consecutively we noticed a white deposit (attributed to the formation of amorphous  $\text{SiO}_2$ ) on the cathode. The noise appeared to be correlated with sparking at the cathode which was situated at the end of the cell close to the pump. By placing the cathode downstream of the pump and introducing additional argon at the end of the cell in order to reduce deposit formation we were able to reduce the noise. The following conditions were found to give the best signal-to-noise ratio:  $P(\text{SiH}_4)=30$  mTorr,  $P(\text{O}_2)=30$  mTorr (all pressures measured at room temperature), and  $I=5$  mA. The partial argon pressure had to be adjusted during the course of the experiment. The total pressure in the cooled cell never exceeded 70 mTorr.

## IDENTIFICATION OF THE MOLECULE

We first measured around 100 lines in the frequency range 165–220 GHz and eliminated all known lines of  $\text{SiO}$  and a few lines corresponding to stable species. A few lines observed after replacing  $\text{SiH}_4$  by  $\text{SiD}_4$  (a test for molecules without H atoms) were also eliminated. All of the remaining lines showed the same variation when the gas mixture or discharge conditions were altered. However, the distribution of frequencies obtained seemed too complicated for a single molecule and we were unable to identify the spectrum of silanone or one of the hydroxysilylene isomers. In order to obtain more information, we decided to study the decay of

the absorption signal following extinction of the discharge and rapidly came to the conclusion that there were in fact three series of lines, each one with a characteristic lifetime (1.2, 1.4, and 2.4 ms, respectively, to decay to  $1/e$  of the steady state signal). The lines corresponding to the shortest lifetime were arranged in a typical  $a$ -type  $R$  branch pattern with an intensity alternation 1:3 corresponding to spin statistics characteristic of two interchangeable H atoms. It was straightforward to calculate the molecular constants giving rise to these lines and by comparison with the *ab initio* results to attribute them most probably to  $\text{H}_2\text{SiO}$ . The prediction and subsequent measurement of further transition frequencies confirmed the initial rotational quantum number attribution.

The lines of longer lifetime remain as yet unidentified but it is tempting to assume that they result from one or both of the two low lying  $\text{HSiOH}$  isomers. Identification of their spectra is more difficult because the strongest lines are predicted to be of  $b$  type and because of the very low barrier which could allow interconversion between the two isomers.

## TRANSITION FREQUENCIES AND MOLECULAR CONSTANTS

The spectrum of  $\text{H}_2\text{SiO}$  has been extensively measured. In total 107 transitional frequencies between 137 and 471 GHz have been determined (Table I). Most resolvable transitions with  $J''$  from 4 to 13 were measured. However, all transitions with  $K_a \geq 9$ , some transitions with  $K_a = 8$ , and one transition with  $K_a = 6$  were not sufficiently intense. Two transitions ( $9_{1,9}-8_{1,8}$  and  $9_{0,9}-8_{0,8}$ ) were not accessible using our available millimeter-wave sources. The frequency of these missing transitions can easily be calculated using the determined molecular constants given in Table II. In order to provide a complete list of frequencies for radioastronomy the nine nonmeasured transitions below 141.5 GHz have been calculated using the experimental constants and are included in Table I.

The data were fitted by using a standard Watson's  $A$ -reduced Hamiltonian<sup>27</sup> in the  $I'$  representation. First fits gave a standard deviation much poorer than expected. Although most transitions were calculated to experimental accuracy certain close lying  $K_a$  doublets with  $K_a = 2, 3$ , and 4 were poorly predicted. Attempts to resolve the problem by changing the fitted constants and by using an  $S$ -reduced Hamiltonian were unsuccessful. Finally we fitted only the central frequency of these doublets which gave good agreement and a standard deviation of only 16 kHz. The observed minus calculated values given in Table I derive from the constants determined from this average fit. For comparison we also give the measured frequency of each  $K_a$  component and its deviation from the value calculated using the derived constants.

The problem with the  $K_a$  doublets occurs when they just start to be resolved and disappears when the difference between the two frequencies becomes large. The greatest effect is seen for doublets which are poorly resolved by our spectrometer (we had linewidths of around 400 kHz). The results cannot however be explained by an instrumental effect since other fully resolved lines are also affected, e.g., two  $K_a = 2$

TABLE I. Rotational frequencies of H<sub>2</sub>SiO with the differences  $\Delta f = f_m - f_c$  (in MHz).<sup>a</sup> The standard deviation of the fit is  $\sigma = 16$  kHz.

<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	—	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	Obs. freq. <sup>b</sup>	$\Delta f$	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	—	<i>J</i>	<i>K<sub>a</sub></i>	<i>K<sub>c</sub></i>	Obs. freq. <sup>b</sup>	$\Delta f$
1	0	1	—	0	0	0	35 422.094 <sup>c</sup>	0.001	(9	4	6	—	8	4	5	318 757.221	0.228 <sup>d</sup>
2	1	2	—	1	1	1	68 906.460 <sup>c</sup>	0.002	9	4	*	—	8	4	*	318 757.221 <sup>e</sup>	0.002
2	0	2	—	1	0	1	70 824.944 <sup>c</sup>	0.001	(9	4	5	—	8	4	4	318 757.221	-0.224 <sup>d</sup>
2	1	1	—	1	1	0	72 776.254 <sup>c</sup>	0.002	(9	3	7	—	8	3	6	318 941.784	0.051 <sup>d</sup>
3	1	3	—	2	1	2	103 347.113 <sup>c</sup>	0.003	9	3	*	—	8	3	*	318 968.022 <sup>e</sup>	-0.003
3	0	3	—	2	0	2	106 189.321 <sup>c</sup>	0.002	(9	3	6	—	8	3	5	318 994.318	-0.058 <sup>d</sup>
3	2	2	—	2	2	1	106 287.777 <sup>c</sup>	0.001	9	2	7	—	8	2	6	320 594.505	-0.004
3	2	1	—	2	2	0	106 287.777 <sup>c</sup>	0.001	9	1	8	—	8	1	7	326 871.517	-0.010
3	1	2	—	2	1	1	109 151.440 <sup>c</sup>	0.003	10	1	10	—	9	1	9	343 768.451	0.003
4	1	4	—	3	1	3	137 772.835	0.000	10	0	10	—	9	0	9	351 117.208	0.007
4	0	4	—	3	0	3	141 496.060	0.000	10	8	3	—	9	8	2	353 454.275	0.002
(4	2	3	—	3	2	2	141 650.586	0.148 <sup>d</sup>	10	2	9	—	9	2	8	353 634.416	0.009
(4	3	2	—	3	3	1	141 678.233	0.339 <sup>d</sup>	10	7	4	—	9	7	3	353 654.131	0.007
4	2	*	—	3	2	*	141 744.498 <sup>e</sup>	0.005	10	6	5	—	9	6	4	353 837.823	0.008
4	3	*	—	4	3	*	141 678.233 <sup>e</sup>	-0.003	10	5	5	—	9	5	4	354 013.588	-0.002
(4	3	1	—	3	3	0	141 678.233	-0.346 <sup>d</sup>	10	5	6	—	9	5	5	354 013.588	0.003
(4	2	2	—	3	2	1	141 838.410	-0.138 <sup>d</sup>	(10	4	7	—	9	4	6	354 202.154	0.487 <sup>d</sup>
4	1	3	—	3	1	2	145 510.937	-0.002	10	4	*	—	9	4	*	354 202.154 <sup>e</sup>	-0.002
5	1	5	—	4	1	4	172 178.916	0.002	(10	4	6	—	9	4	5	354 202.154	-0.492 <sup>d</sup>
5	0	5	—	4	0	4	176 726.193	0.007	(10	3	8	—	9	3	7	354 426.509	0.053 <sup>d</sup>
5	2	4	—	4	2	3	177 036.697	0.023	10	3	*	—	9	3	*	354 471.470 <sup>e</sup>	0.000
5	4	2	—	4	4	1	177 046.859	-0.008	(10	3	7	—	9	3	6	354 516.431	-0.054 <sup>d</sup>
5	4	1	—	4	4	0	177 046.859	-0.008	10	2	8	—	9	2	7	356 667.783	0.003
(5	3	3	—	4	3	2	177 112.587	1.237 <sup>d</sup>	10	1	9	—	9	1	8	363 011.388	-0.012
5	3	*	—	4	3	*	177 112.587 <sup>e</sup>	0.039	11	1	11	—	10	1	10	377 973.846	0.003
(5	3	2	—	4	3	1	177 112.587	-1.159 <sup>d</sup>	11	0	11	—	10	0	10	385 546.042	0.012
5	2	3	—	4	2	2	177 412.483	-0.059	11	2	10	—	10	2	9	388 862.994	0.016
5	1	4	—	4	1	3	181 849.259	0.004	11	7	5	—	10	7	4	389 019.773	0.012
6	1	6	—	5	1	5	206 560.874	0.007	11	6	6	—	10	6	5	389 227.391	-0.001
6	0	6	—	5	0	5	211 861.151	0.009	11	5	7	—	10	5	6	389 430.208	0.007
6	5	1	—	5	5	0	212 382.745	-0.022	11	5	6	—	10	5	5	389 430.208	-0.006
6	2	5	—	5	2	4	212 405.372	0.035	(11	4	8	—	10	4	7	389 655.001 <sup>f</sup>	0.202 <sup>d</sup>
6	2	4	—	5	2	3	213 061.986	-0.034	11	4	*	—	10	4	*	389 655.780 <sup>e</sup>	0.002
6	4	3	—	5	4	2	212 465.797	0.014	(11	4	7	—	10	4	6	389 656.559 <sup>f</sup>	-0.198 <sup>d</sup>
6	4	2	—	5	4	1	212 465.797	0.014	11	3	9	—	10	3	8	389 921.861	0.028
(6	3	4	—	5	3	3	212 553.582	0.078 <sup>d</sup>	11	3	8	—	10	3	7	390 067.851	-0.023
6	3	*	—	5	3	*	212 556.662 <sup>e</sup>	-0.036	11	2	9	—	10	2	8	392 865.516	0.007
(6	3	3	—	5	3	2	212 559.743	-0.149 <sup>d</sup>	11	1	10	—	10	1	9	399 090.230	0.002
6	1	5	—	5	1	4	218 160.664	-0.001	12	1	12	—	11	1	11	412 135.579	0.002
7	1	7	—	6	1	6	240 914.459	-0.028	12	0	12	—	11	0	11	419 806.861	0.013
7	0	7	—	6	0	6	246 883.118	-0.032	12	2	11	—	11	2	10	424 053.253	-0.006
7	2	6	—	6	2	5	247 752.934	0.009	12	8	5	—	11	8	4	424 137.520	-0.006
7	5	3	—	6	5	2	247 785.912	-0.001	12	7	6	—	11	7	5	424 385.432	-0.026
(7	4	4	—	6	4	3	247 889.908	0.041 <sup>d</sup>	12	6	7	—	11	6	6	424 618.603	-0.016
7	4	*	—	6	4	*	247 889.908 <sup>e</sup>	0.007	12	5	8	—	11	5	7	424 851.169	0.000
(7	4	3	—	6	4	2	247 889.908	-0.028 <sup>d</sup>	12	5	7	—	11	5	6	424 851.169	-0.029
(7	3	5	—	6	3	4	248 005.645	0.163 <sup>d</sup>	(12	4	9	—	11	4	8	425 117.296 <sup>f</sup>	0.167 <sup>d</sup>
7	3	*	—	6	3	*	248 012.665 <sup>e</sup>	0.001	12	4	*	—	11	4	*	425 118.938 <sup>e</sup>	-0.025
(7	3	4	—	6	3	3	248 019.685	-0.162 <sup>d</sup>	(12	4	8	—	11	4	7	425 120.581 <sup>f</sup>	-0.216 <sup>d</sup>
7	2	5	—	6	2	4	248 800.802	-0.013	12	3	10	—	11	3	9	425 426.979	0.001
7	1	6	—	6	1	5	254 439.168	0.012	12	3	9	—	11	3	8	425 653.640	0.004
8	1	8	—	7	1	7	275 235.892	-0.002	12	2	10	—	11	2	9	429 187.599	-0.002
8	0	8	—	7	0	7	281 775.736	0.009	12	1	11	—	11	1	10	435 099.680	-0.002
8	7	2	—	7	7	1	282 923.008	-0.004	13	1	13	—	12	1	12	446 251.943	-0.003
8	6	3	—	7	6	2	283 063.014	-0.005	13	0	13	—	12	0	12	453 900.482	-0.013
8	2	7	—	7	2	6	283 075.957	0.012	13	2	12	—	12	2	11	459 201.920	-0.010
8	5	4	—	7	5	3	283 191.844	0.009	13	8	6	—	12	8	5	459 477.633	-0.001
(8	4	5	—	7	4	4	283 320.106	0.109 <sup>d</sup>	13	7	7	—	12	7	6	459 751.238	0.020
8	4	*	—	7	4	*	283 320.106 <sup>e</sup>	0.015	13	6	8	—	12	6	7	460 011.659	0.015
(8	4	4	—	7	4	3	283 320.106	-0.079 <sup>d</sup>	13	5	9	—	12	5	8	460 276.919	0.037
(8	3	6	—	7	3	5	283 468.173	0.092 <sup>d</sup>	13	5	8	—	12	5	7	460 276.919	-0.025
8	3	*	—	7	3	*	283 482.423 <sup>e</sup>	-0.014	(13	4	10	—	12	4	9	460 589.465 <sup>f</sup>	0.124 <sup>d</sup>
(8	3	5	—	7	3	4	283 482.423	-0.118 <sup>d</sup>	13	4	*	—	12	4	*	460 592.607 <sup>e</sup>	0.008
8	2	6	—	7	2	5	284 641.462	0.005	(13	4	9	—	12	4	8	460 595.749 <sup>e</sup>	-0.107 <sup>d</sup>
8	1	7	—	7	1	6	290 678.374	0.007	13	3	11	—	12	3	10	460 940.515	-0.012
9	7	3	—	8	7	2	318 288.540	-0.002	13	3	10	—	12	3	9	461 279.537	0.011
9	2	8	—	8	2	7	318 370.930	0.007	13	2	11	—	12	2	10	465 629.086	0.013
9	6	4	—	8	6	3	318 449.753	0.012	13	1	12	—	12	1	11	471 030.827	-0.005
9	5	5	—	8	5	4	318 600.928	0.000									

<sup>a</sup> $f_m$ : measured frequencies,  $f_c$ : calculated frequencies.<sup>b</sup>The experimental accuracy was better than 50 kHz.<sup>c</sup>These frequencies of astrophysical interest are calculated values and the variance is given instead of  $\Delta f$ .<sup>d</sup>For these  $K_a$  doublets, the measured frequency which was not used in the fit is compared to the value calculated from the constants given in Table II.<sup>e</sup>These frequencies correspond to the center of the  $K_a$  doublets (\*). Only these values were used in the fit.<sup>f</sup>Frequencies obtained from fit to experimental line shape.

TABLE II. Experimental and *ab initio* molecular constants of H<sub>2</sub>SiO in its vibrational ground state.

	Experimental	Schaefer and Ma <sup>a</sup> (TZ2P/CCSD)	Császár <sup>b</sup> (DZP/SCF)
A (MHz)	166657.3 (19)	167742	168774
B (MHz)	18679.3897(63)	18576	18890
C (MHz)	16742.7743(63)	16724	16938
$\Delta_J$ (kHz)	17.5216(24)		15.1
$\Delta_{JK}$ (kHz)	602.486 (23)		504
$\Delta_K$ (kHz)	7500. (940)		7650
$\delta_J$ (kHz)	2.0811(25)		1.7
$\delta_K$ (kHz)	413.0 (32)		316
$\Phi_{JK}$ (Hz)	4.757 (73)		6.0
$\Phi_{KJ}$ (Hz)	-47.74 (31)		-42.6

<sup>a</sup>Reference 13.<sup>b</sup>Reference 23.

lines 94 MHz apart are each shifted by around 150 kHz. For the poorly resolved doublets ( $\Delta\nu \leq 6$  MHz) we attempted a deconvolution using a least-squares fit to the experimentally determined line shape. This has allowed us where successful to include a frequency for each component in Table I. Even where not successful this line profile fitting shows that the splitting between components must be smaller than that predicted using the determined constants. For this reason we include in Table I for certain nonresolved doublets the deviation of the measured center frequency from the predicted values.

Some barely resolved doublets showed an unusual pattern, which could not be reproduced by fitting to two or even three lines. It was, however, possible to fit to four lines, two intense and two weak. The most likely explanation is that the two weak lines correspond to the two forbidden transitions in the four-level system. The discrepancies between measured and calculated frequencies together with the observation of forbidden transitions could be due to a nondiagonal Coriolis-type coupling term in the Hamiltonian. This term could be related to a large amplitude out-of-plane motion. This problem will be analyzed and discussed in a future paper.<sup>28</sup>

It should be stressed that in spite of the problems encountered the determined molecular constants give very good agreement with the measured center frequency of close lying doublets and with the exact frequency of other transitions. We would expect to have hence determined the true molecular constants and not arbitrary fitted values. These experimentally determined molecular constants are compared in Table II with the *ab initio* predictions for the silanone molecule from Ma and Schaefer<sup>13</sup> and from Császár.<sup>23</sup> Only the  $\Phi_{JK}$  and  $\Phi_{KJ}$  sextic centrifugal distortion constants were determinable; the others were constrained to zero. There is good agreement with the equilibrium values of Ma and Schaefer who made high level [CCSD(T)] calculations using a large TZ2P(*f,d*) basis set. Although at a lower level of theory and using a smaller basis set, the calculations of Császár give good agreement with the experimental quartic and sextic centrifugal distortion constants. An inertial defect of 0.094 uÅ<sup>2</sup>, and centrifugal defect of only -795 Hz, determined using the experimental constants, indicate clearly that the molecule is planar. These results strongly suggest

that we have observed the C<sub>2v</sub> isomer H<sub>2</sub>SiO. Further evidence is the detection of lines corresponding to the predicted spectra for the isotopic species <sup>29</sup>Si and <sup>30</sup>Si of this molecule.<sup>28</sup> These spectra were predicted using "scaled" values of the rotational constants deduced from the *ab initio* structure<sup>13</sup> with the empirical relation<sup>29</sup>

$$\frac{X(^{29}\text{Si})_{\text{scal}}}{X(^{29}\text{Si})_{\text{ab in}}} = \frac{X(^{28}\text{Si})_{\text{exp}}}{X(^{28}\text{Si})_{\text{ab in}}} \quad (X=A, B, C).$$

For heavy atom substitution, this relation gives an accurate value of the rotational constants. The observation of small lines near the predicted frequencies conclusively confirms our identification. The measurement of these spectra is now in progress and will be followed by that of the dideuterated and <sup>18</sup>O species in order to determine a precise experimental structure.

## CONCLUSION

The high resolution rotational spectrum of the elusive molecule H<sub>2</sub>SiO has been measured for the first time in the gas phase and a complete list of frequencies necessary for an astronomical search for this molecule provided. Certain anomalies in the fit and in the observed pattern of poorly resolved K<sub>a</sub> doublets suggest a large amplitude motion in this molecule. The experimental procedure of modulating the discharge on/off allows the lifetime of a transient species to be accurately measured by millimeter-wave spectroscopy and thus provides an invaluable tool in its subsequent identification.

## ACKNOWLEDGMENTS

The present study was partially supported by the European Communities through Project No. 892 001 59/OP1 and by the C.N.R.S. (G.D.R. "Physico-Chimie des Molécules et des Grains Interstellaires"). The authors wish to thank H. F. Schaefer for providing before publication the *ab initio* structure and A. G. Császár for calculating the centrifugal distortion constants, necessary for the experimental search for H<sub>2</sub>SiO. They are also grateful to J. Demaison for his advice concerning the anomalous results obtained in fitting the experimental frequencies.

<sup>1</sup>E. E. Ferguson, D. W. Fahey, F. C. Fehsenfeld, and D. L. Albritton, *Planet. Space Sci.* **23**, 1621 (1975).

<sup>2</sup>J. L. Turner and A. Dalgarno, *Astrophys. J.* **213**, 386 (1977).

<sup>3</sup>G. Lucovsky, D. Tsu, R. Rudder, and R. Markunas, in *Thin Film Processes II*, edited by J. L. Vossen and W. Kern (Academic, Boston, 1991), pp. 565-619, and references therein.

<sup>4</sup>M. J. Kushner, *J. Appl. Phys.* **74**, 6538 (1993).

<sup>5</sup>H. F. Warner, A. Fox, T. Amano, and D. K. Bohme, *J. Chem. Phys.* **91**, 5310 (1989).

<sup>6</sup>N. Moezzen-Ahmadi, A. R. W. McKellar, H. E. Warner, and T. Amano, *J. Chem. Phys.* **91**, 531 (1989).

<sup>7</sup>T. Kudo and S. Nagase, *J. Phys. Chem.* **88**, 2833 (1984).

<sup>8</sup>G. Rabbe and J. Michel, *Chem. Rev.* **85**, 419 (1985).

<sup>9</sup>T. Kudo and S. Nagase, *Chem. Phys. Lett.* **128**, 507 (1986).

<sup>10</sup>B. T. Luke, J. A. Pople, M.-B. Krogh-Jespersen, Y. Apeloig, M. Karni, J. Chandrasekhar, and P. von Ragué Schleyer, *J. Am. Chem. Soc.* **108**, 270 (1986).

<sup>11</sup>M. S. Gordon and L. A. Pederson, *J. Phys. Chem.* **94**, 5527 (1990).

<sup>12</sup>S. Sakai, M. S. Gordon, and K. D. Jordan, *J. Phys. Chem.* **92**, 7053 (1988).

- <sup>13</sup>B. Ma and H. F. Schaefer III, *J. Chem. Phys.* **101**, 2734 (1994).  
<sup>14</sup>C. L. Darling and H. B. Schlegel, *J. Phys. Chem.* **97**, 8207 (1993).  
<sup>15</sup>Z. K. Ismail, R. H. Hague, L. Fredin, J. W. Kauffman, and J. L. Margrave, *J. Chem. Phys.* **77**, 1617 (1982).  
<sup>16</sup>A. Tachibana, H. Fueno, M. Koizumi, T. Yamabe, and K. Fukui, *J. Phys. Chem.* **92**, 935 (1988).  
<sup>17</sup>R. Withnall and L. Andrews, *J. Am. Chem. Soc.* **107**, 2567 (1985).  
<sup>18</sup>R. Withnall and L. Andrews, *J. Phys. Chem.* **89**, 3261 (1985).  
<sup>19</sup>R. J. Glinski, J. L. Cole, and D. A. Dixon, *J. Am. Chem. Soc.* **107**, 5891 (1985).  
<sup>20</sup>R. Srinivas, D. K. Böhme, D. Sülzle, and H. Schwarz, *J. Phys. Chem.* **95**, 9836 (1991).  
<sup>21</sup>M. Bogey, A. Walters, A. Chivé, V. Lefèvre, M. Letulle, A. Systermans, and J. L. Ripoll, Phosphorous, Sulfur, Silicon, in press.  
<sup>22</sup>D. A. Dixon and J. L. Gole, *Chem. Phys. Lett.* **125**, 179 (1986).  
<sup>23</sup>A. G. Császár (private communication, 1993).  
<sup>24</sup>J. L. Destombes, C. Demuynck, and M. Bogey, *Philos. Trans. R. Soc. London, Ser. A* **324**, 127 (1988).  
<sup>25</sup>M. Cordonnier, M. Bogey, C. Demuynck, and J. L. Destombes, *J. Chem. Phys.* **97**, 7984 (1992).  
<sup>26</sup>M. Bogey, H. Bolvin, C. Demuynck, and J. L. Destombes, *Phys. Rev. Lett.* **66**, 413 (1991).  
<sup>27</sup>J. K. G. Watson, in *Vibrational Spectra and Structure*, edited by J. R. Durig (Elsevier, Amsterdam, 1977), Vol. 6, p. 2.  
<sup>28</sup>M. Bogey, B. Delcroix, C. Demuynck, J. L. Destombes, and A. Walters, *J. Mol. Spectrosc.* (to be published).  
<sup>29</sup>M. Cordonnier, M. Bogey, C. Demuynck, and J. L. Destombes, *J. Chem. Phys.* **97**, 7984 (1992).