Absorption spectroscopy of SiH₂ near 640 nm

Rafael Escribano and Alain Campargue

Citation: *J. Chem. Phys.* **108**, 6249 (1998); doi: 10.1063/1.476062

View online: <http://dx.doi.org/10.1063/1.476062>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v108/i15>

Published by the AIP Publishing LLC.

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT

Goodfellow
metals • ceramics • polymers • composites
70,000 products
450 different materials
small quantities *fast*

www.goodfellowusa.com

Absorption spectroscopy of SiH₂ near 640 nm

Rafael Escribano

Instituto de Estructura de la Materia, CSIC, Serrano, 123, 28006 Madrid, Spain

Alain Campargue

Laboratoire de Spectrométrie Physique (UMR 5588), Université Joseph Fourier de Grenoble, B.P. 87, 38402 Saint-Martin-d'Hères Cedex, France

(Received 21 November 1997; accepted 13 January 1998)

The $\tilde{A}^1B_1-\tilde{X}^1A_1$ absorption spectrum of SiH₂ has been observed using intracavity laser absorption spectroscopy with an equivalent path length of up to 13.0 km and the $\tilde{A}^1B_1(0, 0, 0)-\tilde{X}^1A_1(0, 0, 0)$ band near 640 nm recorded for the first time. The silylene radical was generated in a continuous discharge in a flowing mixture of silane in argon, giving a concentration of the order of 10^{10} SiH₂/cm³. The spectrum spans the region between 15350 and 16100 cm⁻¹. Rotational transitions have been assigned to levels up to $J=16$ and $K_a=9$, with ΔK_a up to 5, ΔK_c up to 4. Perturbations have been detected in the spectrum, due to Renner-Teller and spin-orbit interactions between both electronic states and the 3B_1 state, predicted to be between them. However, the strength of the irregular perturbations affecting the rotational states of $\tilde{A}^1B_1(0,0,0)$ state is found to be much weaker than that affecting the other $(0, v'_2, 0)$ levels previously studied. The analysis of the spectrum has allowed the determination of the rotational constants of the $^1B_1(0,0,0)$ level, and a new estimation of those of the vibrational and electronic ground state. The geometry of the excited electronic level has also been determined for the first time from accurate experimental data. A change in the structure of this molecule takes place with this transition, the equilibrium angle opening from 92° to 122.4°, while the bond distance is reduced from 1.51 to 1.485 Å. © 1998 American Institute of Physics. [S0021-9606(98)01815-7]

I. INTRODUCTION

Silylene, SiH₂, is an intermediate species of importance in silicon hydride chemistry as it may play a role in the deposition of amorphous silicon films by chemical vapor deposition (CVD). The industrial applications of this very reactive species have prompted several studies on its reactivity and dynamics.¹⁻³

From the academic point of view, SiH₂ is the simplest polyatomic molecule containing silicon, it is isovalent with CH₂, and its electronic spectrum presents a challenging blend of Renner-Teller and spin-orbit couplings. It is also of the right size to enable high level *ab initio* calculations.

In the ground electronic state (1A_1), the equilibrium geometry is close to a rectangular triangle ($\theta_e=92^\circ$), very similar to the SH₂ molecule, with marked asymmetric top structure (asymmetry parameter $\kappa=0.51$). The next upper electronic state is $\tilde{a}^3B_1$, estimated to be 7000 cm⁻¹ above, although it has never been directly observed, as far as we are aware. In the next upper state, $\tilde{A}^1B_1$, situated 15500 cm⁻¹ above the ground state, the bending angle opens up drastically to an equilibrium value of $\sim 120^\circ$, giving a nearly prolate symmetric top structure ($\kappa=-0.84$). A schematic representation of these two geometrical structures is presented in Fig. 1. In both singlet states, large excitations of the bending vibration would bring the molecule near a linear configuration, thus enabling a large Renner-Teller interaction, which has been identified from the analysis of rovibronic spectra and lifetimes of excited levels.⁴⁻⁶

A number of spectroscopic studies has been devoted to

this transient species. SiH₂ was first identified by Dubois 30 years ago^{7,8} by detection of its electronic absorption spectrum in the visible range. It was produced by photolysis of phenylsilane and the spectrum was obtained with a path length of 48 m and photographed at high dispersion. The spectrum, which consists of a progression of several bands separated by about 850 cm⁻¹, shows a widely open rotational structure due to the important change of geometry. It was analyzed as an $\tilde{A}^1B_1(0, v'_2, 0)-\tilde{X}^1A_1(0, 0, 0)$ transition, each band of the progression corresponding to the excitation of the bending vibration ($v'_2=1-7$) in the $\tilde{A}^1B_1$ electronic state. The interpretation of these spectra^{8,9} led to the determination of the geometrical structure of the 1B_1 and 1A_1 states, but the rotational level structure of the excited state was found to be affected by a large number of erratic rotational perturbations. A rms observed-calculated deviation of more than 1 cm⁻¹ was obtained in the fit of the rotational parameters of the excited states for the transitions to the (010), (020) and (030) states.⁸ More recently, Duxbury, Alijah and Trieling⁴ have carried out an extensive study on these previously published data,^{8,9} showing that these perturbations arise from the combined effects of Renner-Teller interaction between the two singlet states and spin-orbit coupling with the lowest triplet $\tilde{a}^3B_1$. They also developed a model to treat these interactions simultaneously. The strong rotational perturbations in the $\tilde{A}^1B_1$ state have been related⁴ to the unusual radiative lifetimes recently measured by laser-

FIG. 1. Equilibrium geometry of SiH₂ in the $\tilde{X}^1A_1$ (full line) and $\tilde{A}^1B_1$ (dotted line) electronic states.

induced fluorescence (LIF) by Thoman, Steinfeld and coworkers.^{5,6} In the 1A_1 state, Yamada *et al.*¹⁰ studied the ν_2 band by means of an infrared diode laser spectrometer, thus providing the only high resolution infrared data available for this radical up to this moment.

Several authors have reported the LIF detection of silylene produced by multiphoton or UV dissociation of silane compounds.^{5,6,11–13} The LIF excitation and dispersed fluorescence spectra reported by Fukushima, Mayana and Obi¹³ led to the determination of both the electronic transition moment of the $\tilde{A}^1B_1-\tilde{X}^1A_1$ transition ($|\mu_e|^2 = 0.26 \text{ e}^2 \text{ a}_0^2$) and of the $(0, \nu_2', 0) - (0, \nu_2'', 0)$ Franck-Condon factors.

Most of the SiH₂ detection experiments using lasers^{5,6,11–21} have been performed on the $\tilde{A}^1B_1(0, 2, 0) - \tilde{X}^1A_1(0, 0, 0)$ transition near 580 nm because of favorable Franck-Condon access and of the availability of an excellent dye in the corresponding range (Rhodamine 6G). Jasinski and coworkers^{14–16} used frequency modulation and direct absorption techniques to monitor SiH₂ by detecting some rovibronic transitions of this band near 17250 cm⁻¹. The same transition was observed by ICLAS^{19–21} and LIF¹⁷ in order to evaluate the SiH₂ concentration produced in a RF plasma²⁰ or in reacting high temperature mixtures of disilane.²¹ The estimation of the absolute concentration of SiH₂ was possible only by indirect comparative methods^{17,20} or by making an assumption on the reaction kinetic model leading to the formation of SiH₂.²¹ For *in situ* and real time diagnostic of CVD plasma, absorption techniques are much more suitable than LIF, resonantly enhanced multiphoton ionization (REMPI) or four wave mixing. We have very recently²² obtained the Doppler limited absorption spectrum of the $\tilde{A}^1B_1(0, 2, 0) - \tilde{X}^1A_1(0, 0, 0)$ transition using two highly sensitive techniques equivalent to classical absorption: intracavity laser absorption spectroscopy (ICLAS)²³ and the newly developed cw-cavity ring down spectroscopy (CW-CRDS) technique.²⁴ From the results of Ref. 13 and using the rotational assignments given by Dubois,⁸ it was possible to calculate the absolute line intensity of some specific rovibronic transitions and then deduce the SiH₂ concentration from the measured absorption coefficient. To our knowledge, this study was the first direct and absolute concentration measurement of SiH₂. A detectivity

of the order of 10⁸ SiH₂/cm³ was achieved.²²

First Dubois,⁸ and later Yamada *et al.*,¹⁰ determined the ground state rotational constants of SiH₂, and hence the r_0 structure, by making ground state combination differences from their respective data. Based on the similar structure of SiH₂ and SH₂, Yamada *et al.* extended their calculation to derive the equilibrium geometrical structure of silylene by means of the rovibrational constants α_i^B of the SH₂ molecule, which had been reported before.¹⁰

Allen and Schaefer²⁵ have performed the most comprehensive theoretical calculation on the geometrical structure, force constants and vibrational spectra of SiH₂ (as well as SiH, SiH₃ and SiH₄) for all three electronic states mentioned above. They report also the estimated rovibrational constants α_i^B for each state. Using these constants, they successfully reduce the uncertainty in the geometrical structure found in the determination of two parameters (r_e and θ_e) from three pairs of constants (A_e , B_e and C_e , taken two by two). The agreement between experimental and theoretical results is very good in the ground 1A_1 state, but less good in the 1B_1 state, where the rotational constants of the $\nu_2'=0$ state had never been determined before. The *ab initio* potential energy surfaces of the three low lying states of SiH₂ have been calculated by Kosecki and Gordon.²⁶

In the present work, we report the observation and rovibrational analysis of the $\tilde{A}^1B_1(0, 0, 0) - \tilde{X}^1A_1(0, 0, 0)$ transition, recorded by ICLAS between 15350 and 16100 cm⁻¹. The only previous report concerning this transition is the fluorescence excitation spectrum recorded at medium resolution between 15540 and 15580 cm⁻¹ and displayed without rotational analysis in Fig. 4 of Ref. 6. This transition, which is weaker than those previously studied, is particularly important as it allows the determination of the geometry and of the energy of the vibrationless level of the $\tilde{A}^1B_1$ electronic state. We have also determined the equilibrium r_e structure of silylene in this singlet excited state. The accuracy of the line positions is about 0.01 cm⁻¹, which is intermediate between the high resolution infrared experiment of Yamada *et al.*¹⁰ and the previous data from Dubois.^{7,8} We also present a more comprehensive determination of the rotational constants of the (0,0,0) level in the electronic ground state, performed by combining all three sets of data with appropriate weights in a single refinement process.

Another interest and motivation of the present study is that the $\tilde{A}^1B_1(0, 0, 0) - \tilde{X}^1A_1(0, 0, 0)$ transition near 640 nm corresponds to a range where diode lasers are available. Following the same procedure as described in our recent study of the $\tilde{A}^1B_1(0, 2, 0) - \tilde{X}^1A_1(0, 0, 0)$ transition,²² it is then possible to use some specific rovibronic transitions of this band for *in situ* and real time monitoring of SiH₂ in CVD reactors using the newly developed CW-CRDS technique.²⁴

II. EXPERIMENT

A. The discharge cell

The silylene radical was generated by a continuous discharge (40 mA, 1 kV) in a slowly flowing mixture of silane

(5%) in argon. The total pressure was about 1 Torr and gases were pumped out with a mechanical pump. The plasma tube (80 cm length, 3.6 cm diameter) was fitted by Brewster angle windows. The flow of argon entered the cell close to the two windows while silane was injected through an inlet close to the center of the cell. This arrangement prevents deposition of silicon films on the Brewster windows as observed on the walls of the cell. The distance between the two cylindrical electrodes was 60 cm.

B. ICLAS spectrometer

The ICLAS experimental method has been described before.²³ Briefly, the ICLAS technique is based on the high sensitivity of a broadband laser to intracavity losses namely absorption. The absorption lines appear superimposed on the broadband spectrum of the dye laser (DCM) pumped by an argon laser. The spectrum dispersed by a high resolution grating spectrograph (resolving power up to 800 000) is recorded by a 1024 photodiode array. Furthermore, the dye spectrum is time resolved by using two synchronized acousto-optic modulators and the generation time, t_g , between the start of the laser and the recording of the spectrum gives directly the equivalent path length:

$$l_{eq} = (l/L)ct_g,$$

where (l/L) is the ratio of the length of the cell to the optical length of the dye laser cavity.

In the present study, we have inserted the plasma tube in the dye laser cavity and used generation times ranging between 20 and 70 μ s (absorption equivalent path lengths between 3.7 and 13.0 km). The occupation ratio of the cavity by the cell was 62%.

In order to reduce the number of elementary spectra needed to cover the whole band (750 cm^{-1}), we did not use in this work our spectrograph in its higher resolution configuration. As a consequence, the observed linewidth [half width at half-maximum (HWHM) of about 0.05 cm^{-1}] is mainly determined by the apparatus function of the spectrograph, the Doppler linewidth (HWHM of about 0.017 cm^{-1}) being almost negligible.

The wave number calibration was achieved by simultaneous recording of the iodine absorption spectrum.²⁷ We estimate the wave number accuracy in the SiH_2 line positions to be about 0.01 cm^{-1} . We have checked the quality of our wave number calibration on some absorption lines from excited states of Ar which appear in our spectra, and from some rovibronic transitions of NH_2 which are observed near 15900 cm^{-1} .²⁸ This species is probably produced in the discharge from N_2 present as a sample impurity.

Our previous study of the $\tilde{A}^1B_1(0, 2, 0) - \tilde{X}^1A_1(0, 0, 0)$ band²² allowed us to calculate the SiH_2 concentration in the discharge cell. We obtained a value of the order of $10^{10}\text{ SiH}_2/\text{cm}^3$ and estimated our detection limit to be about $10^8\text{ SiH}_2/\text{cm}^3$. From the Franck-Condon factors reported in Ref. 13, we calculate that the intensity of the presently studied $\tilde{A}^1B_1(0, 0, 0) - \tilde{X}^1A_1(0, 0, 0)$ transition is 22% of that of the $\tilde{A}^1B_1(0, 2, 0) - \tilde{X}^1A_1(0, 0, 0)$ transition.

FIG. 2. The ICLAS spectrum of SiH_2 generated in a continuous discharge (40 mA, 1 kV) in a mixture of silane (5%) in argon. The total pressure was about 1 Torr and the absorption equivalent path length was about 11 km ($t_g=60\text{ }\mu\text{s}$). The band origin ν_0 of the $\tilde{A}^1B_1(0, 0, 0) - \tilde{X}^1A_1(0, 0, 0)$ transition is indicated as well as some absorption lines from excited states of Ar.

III. RESULTS AND DISCUSSION

The ICLAS spectrum of SiH_2 was recorded between 15350 and 16100 cm^{-1} . Figure 2 shows an overview of the spectrum between 15350 and 15800 cm^{-1} . The excellent agreement between our ICLAS spectrum²² and the spectrum reported by Dubois⁸ for the $\tilde{A}^1B_1(0, 2, 0) - \tilde{X}^1A_1(0, 0, 0)$ transition, left no doubt about the assignment of this spectrum to the SiH_2 species and was confirmed by ground state combination differences.

A. Assignments

The central region of the spectrum provided a clue to start the assignment process. This band is of c type, with selection rules ΔK_a odd, ΔK_c even (see Fig. 1 for the definition of the axis labels). However, we use symmetric top formalism, with the K subindex representing K''_a , to label those series for which there is no possibility of confusion. Figure 3 presents the spectrum of this central region, showing also a computer simulation of the spectrum. The pQ_1 and

FIG. 3. Comparison of the ICLAS spectrum of SiH_2 with the simulated spectrum obtained using the rotational constants of Table II.

rQ_0 branches stand out clearly. Note that in the present case, it is safe to use this notation because of the lack of asymmetry splitting when K'_a or K''_a are equal to zero. The J assignment for each of these two branches was facilitated by the spin statistical weights of the rotational levels of this radical: $K''_a + K''_c$ odd lines have three times as much weight as $K''_a + K''_c$ even. Thus, consecutive lines in the above-mentioned series have alternating weights, those with J even being the stronger in pQ_1 , while those with J odd are the stronger in rQ_0 . This figure can be compared to Fig. 3 in Ref. 16, where the central region of the 020-000 band is shown. Both figures are quite similar, the main differences being that in our spectrum the rQ_0 branch is folded over at a lower J value, and that the bandhead of pQ_1 is less complex.

To ensure our initial assignments, we searched for transitions reaching the same excited levels in order to provide the appropriate ground state combination differences. We thus found the pP_1 and pR_1 series to accompany pQ_1 , and the pP_2 series (with $K'_c = K''_c = 1$) to confirm rQ_0 . Once a few initial assignments were thus settled, we proceeded in a cautious way, looking gradually for series with higher K_a values, accepting only those transitions which we could check by combination differences (unless the assignment was indisputable), and refining the excited state rotational constants after each assignment step. We have assigned transitions up to $J = 16$ and $K_a = 9$, with ΔK_a up to 5, ΔK_c up to 4.

The only previously available parameters for the excited state of this transition came from a graphical extrapolation carried out by Dubois⁸ from his data on higher v'_2 states. We used Dubois' parameters in our initial prediction, which gave a reasonable agreement with the observation, apart from a shift of 14 cm^{-1} in the band origin wave number, which was immediately noticed.

B. Perturbations

Even for low K_a transitions, we soon found that large perturbations were present in the spectrum. Pairs of strong lines, which gave good ground state combination differences, were poorly reproduced in a fit to the excited state parameters, with observed-calculated deviations up to a few tenths of a wave number. The perturbations had a very localized nature, affecting just some J levels in a given K_a, K_c series. Already Dubois⁸ had found perturbations in his spectra of higher v'_2 vibrational states, which were later interpreted by Dubois, Duxbury and Dixon⁹ and Duxbury, Alijah and Trieling.⁴ Figures 3 and 4 of this last study illustrate the effect of these perturbations for several K values in $v'_2 = 2$ while Table IX gives observed and calculated energies for several rotational levels for v'_2 up to 8. These authors developed a model to describe the Renner-Teller interactions and could explain the relatively smaller value of the perturbations for $v'_2 = 1$ to 4, and their increasing effect for higher v'_2 values. They concluded that the local perturbations observed for $v'_2 = 2, 3$ and 4 must be due to spin-orbit coupling between the 1B_1 state and the 3B_1 state.

We present in Table I a summary of the perturbations observed in our spectra, indicating the rotational assignment

TABLE I. Energy of the perturbed ($J' K'_a K'_c$) rotational states of the $\tilde{A} {}^1B_1(0,0,0)$ state, and energy shift Δ (in 10^{-2} cm^{-1}) due to the perturbation.

J'	K'_a	K'_c	E'_v (cm^{-1})	Δ (10^{-2} cm^{-1})	N^a
3	1	3	15610.33	9	2
4	1	4	15642.34	-15	3
5	1	5	15682.75	-6	3
3	2	1	15655.63	15	4
4	2	2	15691.13	37	5
7	2	5	15851.58	-53	3
8	2	6	15924.12	-59	3
3	2	2	15655.74	60	3
5	2	4	15732.75	-12	4
8	2	7	15912.90	14	2
4	3	1	15914.98	14	4
6	3	3	15853.22	-59	5
8	3	5	15984.83	-52	2
4	3	2	15758.19	38	4
5	3	3	15801.02	-31	4
7	3	5	15914.37	-16	5
6	4	2	15946.46	53	5
7	4	3	16005.38	50	2
6	4	3	15946.05	13	2
8	4	5	16076.27	-23	3
5	5	0	16008.55	-12	2
6	5	1	16061.19	20	3
8	5	3	16192.36	68	4
5	5	1	16008.53	-14	3
6	5	2	16061.23	26	2
7	5	3	16122.53	16	4

^aNumber of observed transitions used to calculate the upper state energy level.

and an approximate value of the perturbation induced displacement. Whereas in some cases the perturbation presents the typical look of a 2 by 2 interaction, in other cases the pattern is much more complex, which would indicate that several levels are interacting simultaneously. An example of the former is given by the 3_{13} and 4_{14} levels, which are pushed down (to lower energy) and pushed up (to higher energy), respectively, while the 5_{15} level is pushed up with a smaller displacement. Besides, the $3_{13} \leftarrow 3_{03}$ transition, displayed in Fig. 3, appears not only displaced from its predicted position, but with an intensity loss of almost 30% of its expected value. This intensity must have been transferred to a transition to the perturber level. Indeed, the comparison of the experimental and calculated spectra (Fig. 3) shows that a number of lines carrying significant intensity remain unassigned.

The rotational structure of the (0,0,0) state studied here is much less perturbed than that of the $(0, v'_2, 0)$ states observed by Dubois. For comparison, we have performed a fit of the rotational constants of the (0,0,0) state to reproduce the whole set of assigned transitions, including those given in Table I, whose upper state is clearly perturbed. The standard deviation of this fit was 0.18 cm^{-1} , to be compared to the values from 2 to 8 cm^{-1} obtained for the standard deviation of fits to Dubois' data for $(0, v'_2, 0)$ levels, with $v'_2 = 1$ to 5.^{4,8} The maximum individual perturbation shift observed in our data is 0.6 cm^{-1} for the 3_{22} level, where deviations of several wave numbers were detected in the study of higher bending levels. Duxbury, Alijah and Trieling⁴ concluded that

the local perturbations (and the anomalous radiative lifetimes) in the 1B_1 state of SiH_2 were due to indirect spin-orbit coupling between the 1B_1 and 3B_1 states, mediated by the Renner–Teller coupling between 1A_1 and 1B_1 . According to these authors, a direct coupling of the 1B_1 with either 3B_1 or 1A_1 could not reproduce the observed erratic perturbations: the direct spin-orbit coupling between the 1B_1 and 3B_1 states would be very weak because of the strong similarity of the bending potential energy curves of these two states; and the direct Renner–Teller coupling between 1A_1 and 1B_1 would produce smooth perturbations for v_2' less than 5 and not irregular perturbations as observed.⁴ In the frame of this model, we believe that the decrease of the strength of the perturbations in (0,0,0) compared to the other (0, v_2' , 0) states, must be attributed to the weakening of the Renner–Teller coupling when v_2' decreases, which consequently softens the effect of the indirect spin-orbit coupling with 3B_1 . It would be interesting to check if the Hamiltonian describing the Renner–Teller coupling given in Ref. 4 should reproduce quantitatively the large decrease (about one order of magnitude) in the strength of the perturbation going from (0,1,0) to (0,0,0).

Since we have been unable to identify transitions to the “dark” band (or bands), we cannot add more to the interpretation of the perturbations at this stage. Our present results could perhaps be used in the future, if more data become available, especially from the 3B_1 state, to enable a more comprehensive understanding of these perturbations.

C. Vibronic parameters

Although the perturbed data cannot be used to estimate the rovibrational parameters of the excited state within the standard Watson rotational model, they can still provide information on the parameters of the ground state, *via* the appropriate ground state combination differences. Thus, we have at our disposal data from three sources (Refs. 8, 10 and this work), with different degrees of accuracy, which can be used together in the most comprehensive fit of the ground state constants of silylene.

We first checked the data from Dubois relative to the (010), (020) and (030) levels,⁸ band by band, in order to eliminate eventual missassignments or misprints in the publication of the tables. To these we added our data from this work, and those of Yamada *et al.*¹⁰ on the ν_2 fundamental. Considering the different accuracy of each data set, we gave relative weights of 0.1, 1 and 10 to individual transitions belonging to each set, respectively. A few lines that were assigned as blends of two or more SiH_2 transitions were given a weight of one tenth of that of the pure unblended lines (0.1 for our data). The program was designed to search for ground state combination differences within each set. Weights for the combination differences were taken as the mean of the individual weights of each transition. Altogether we had a set of 851 combinations of non-null weight, from which we refined the ground state parameters. We performed several fits for different choices of parameters. Our aim was to obtain a set of parameters giving a reasonable fit of all data, being well determined in the fit, and which were not highly correlated among them. Our final choice is shown in

TABLE II. The rovibrational parameters of the $(v_1, v_2, v_3) = (0,0,0)$ level of the $\bar{X} {}^1A_1$ and $\bar{A} {}^1B_1$ electronic states of SiH_2 . The ground state parameters were fitted from the data of Yamada *et al.* (Ref. 10), Dubois (Ref. 8) and our present data.^a Parameters without uncertainties were constrained to 0. All values in cm^{-1} .

	$\bar{X} {}^1A_1$	$\bar{A} {}^1B_1$
ν_0	0	15547.7730(93)
A	8.09617(25)	18.3241(21)
B	7.02262(25)	4.89951(87)
C	3.70058(21)	3.76611(31)
δ_J	$0.20238(89) \times 10^{-3}$	$0.412(28) \times 10^{-4}$
δ_K	0	0
Δ_J	$0.4341(22) \times 10^{-3}$	$0.895(53) \times 10^{-4}$
Δ_{JK}	$-0.14013(89) \times 10^{-2}$	$-0.337(63) \times 10^{-3}$
Δ_K	$0.22995(86) \times 10^{-2}$	$0.3516(14) \times 10^{-1}$
Φ_J	0	0
Φ_{JK}	0	$-0.399(70) \times 10^{-5}$
Φ_{KJ}	0	$0.235(12) \times 10^{-4}$
Φ_K	0	$0.1843(28) \times 10^{-3}$
L_K	0	$-0.816(19) \times 10^{-6}$
rms	0.045	0.038

^aThe total number of data included in the fit is 1315 corresponding to 54 transitions of Ref. 10 affected with weight 10, 988 data of Ref. 8 with a weight 0.1 and 273 transitions of our work with weight 1. With these data, 851 ground state combination differences were formed.

Table II. We found that the best results were obtained when up to quartic centrifugal distortion constants only were taken, and even in this case the off-diagonal δ_K was not well determined and we fixed it to zero. This choice is in contrast with that of Yamada *et al.*,¹⁰ which used a much larger parameter set for a limited number of combination differences. They needed to release up to ten constants in order to reproduce their very accurate data within experimental accuracy. We have preferred not to force such a reproducibility of the highly accurate data, with the aim of reproducing a very large set of data with a limited number of well defined, correlation free parameters.

Our rotational constants A , B and C are closer to those of Dubois⁸ than to those of Yamada *et al.*,¹⁰ because of the effect of the larger data set we used. The quartic centrifugal distortion constants are very close to those of Yamada *et al.*, indicating that they are well determined by the data. Dubois used the τ_{abcd} parameters instead of the Δ 's and δ 's more frequently used today, which makes the comparison less straightforward. Although our results are not very different from those previously published, we believe that the parameters of Table II provide a reliable and accurate representation of the rotational constants of SiH_2 in the electronic and vibrational ground state.

Once these parameters were fixed, we aimed to determine a set of rotational parameters for the vibrational ground state of the 1B_1 electronic state. In order to do this, we extracted from the data set used for the determination of the ground state parameters, those transitions which were clearly perturbed, and which could not be reproduced without the adequate model to treat the spin-orbit or Renner–Teller perturbations. It may be somewhat subjective to decide the threshold within which a line can be labeled as perturbed or not. Looking for a more objective way, we decided to carry out a refinement process in which lines whose observed

TABLE III. Rotational assignments and wave numbers of the $\tilde{A}^1B_1(0,0,0)-\tilde{X}^1A_1(0,0,0)$ rovibronic transitions of SiH₂ (obs.-calc.) values are given in 10^{-3} cm^{-1} . The lines marked by an asterisk or two asterisks were given a weight 0.1 and 0, respectively, in the fit of the upper state rotational constants. A weight of unity was attributed to the other lines. The last column gives the calculated line intensities in arbitrary units.

J'	K'_a	K'_c	J''	K''_a	K''_c	$\sigma \text{ (cm}^{-1}\text{)}$	o.-c.	Int.	J'	K'_a	K'_c	J''	K''_a	K''_c	$\sigma \text{ (cm}^{-1}\text{)}$	o.-c.	Int.
6	0	6	7	3	4	15367.674	13	83	5	0	5	5	1	5	15545.264	-13	537
6	1	5	7	4	3	15374.060	-6	219	2	1	1	2	2	1	15546.312	20	317
8	1	7	9	2	7	15401.606	0	74	4	3	2	5	4	2	15546.598**	404	220
9	1	9	10	2	9	15404.825	-47	67	6	0	6	6	1	6	15546.852	-1	1595
7	2	5	8	3	5	15408.342**	-507	24	5	3	2	6	2	4	15547.745	-5	56
7	1	6	8	2	6	15415.069	4	38	12	1	11	12	2	11	15548.632**	631	134
8	0	8	9	1	8	15415.821*	54	94	7	0	7	7	1	7	15548.632	-4	495
8	1	8	9	2	8	15418.854*	80	34	8	0	8	8	1	8	15550.518	14	1300
4	0	4	5	3	2	15427.650	-7	187	6	4	2	7	5	2	15551.940**	500	206
6	1	5	7	2	5	15429.728	-6	181	9	0	9	9	1	9	15552.408	5	358
7	1	7	8	2	7	15433.050	37	148	6	1	6	6	0	6	15552.570*	41	637
4	1	3	5	4	1	15437.441	10	223	5	1	5	5	0	5	15552.570*	-76	2032
6	0	6	7	1	6	15441.980	14	181	7	1	7	7	0	7	15552.835	-2	1694
8	0	8	8	3	6	15444.796	57	70	4	1	4	4	0	4	15553.079**	-174	669
5	1	4	6	2	4	15445.894	22	98	8	1	8	8	0	8	15553.527	16	475
8	1	7	8	4	5	15446.031	2	75	0	0	10	10	1	10	15554.322	-4	840
5	0	5	6	1	5	15455.390*	39	80	9	1	9	9	0	9	15554.526*	28	1142
3	0	3	4	3	1	15456.900	-32	58	3	1	3	3	0	3	15554.526**	101	1791
7	1	7	7	2	5	15462.209	33	64	4	2	2	4	3	2	15555.340**	370	185
5	1	5	6	2	5	15462.660	-53	286	10	1	10	10	0	10	15555.791	38	292
4	1	3	5	2	3	15463.878	11	488	11	0	11	11	1	11	15556.302*	16	208
4	0	4	5	1	4	15469.144	-23	318	2	1	2	2	0	2	15556.302*	9	445
7	3	5	8	4	5	15470.983**	-140	187	11	1	11	11	0	11	15557.275	32	641
6	0	6	6	3	4	15471.248	17	92	10	2	9	10	1	9	15557.569**	402	120
6	3	3	7	4	3	15473.113**	-573	150	11	2	10	11	1	10	15557.670**	472	253
6	1	5	6	4	3	15473.706*	-1	80	12	0	12	12	1	12	15558.322	16	443
4	1	4	5	2	4	15478.153**	-132	125	2	0	2	1	1	0	15558.525	-13	192
5	2	4	6	3	4	15478.886**	-142	431	12	1	12	12	0	12	15558.973*	34	150
2	0	2	3	3	0	15481.948	-53	77	1	1	1	1	0	1	15559.105*	40	669
3	0	3	4	1	3	15483.700	-19	141	4	0	4	3	1	2	15559.186*	16	304
3	1	2	4	2	2	15484.176	4	243	8	2	7	8	1	7	15559.308**	157	214
5	0	5	5	3	3	15484.570	11	29	3	0	3	2	1	1	15559.492	-5	103
4	2	2	5	3	2	15485.466**	385	527	5	0	5	4	1	3	15559.692	27	75
6	3	4	7	4	4	15495.460	-73	105	13	0	13	13	1	13	15560.400*	-9	100
2	0	2	3	1	2	15499.471	-22	552	13	1	13	13	0	13	15560.828	5	303
2	1	1	3	2	1	15505.664	-4	823	6	0	6	5	1	4	15560.950*	40	159
8	1	7	7	4	3	15509.271	-56	159	6	4	3	7	5	3	15560.950**	101	109
2	1	2	3	2	2	15510.789	51	180	7	2	6	7	1	6	15561.426	64	802
3	2	1	4	3	1	15513.185**	132	230	7	0	7	6	1	5	15562.373	-89	37
1	0	1	2	1	1	15516.515	-10	192	14	0	14	14	1	14	15562.536	-77	194
6	0	6	5	3	2	15519.317	-83	90	14	1	14	14	0	14	15562.882	1	65
3	2	2	4	3	2	15519.953**	595	723	7	1	6	6	2	4	15563.922	27	92
5	3	3	6	4	3	15520.555**	-303	482	8	0	8	7	1	6	15564.126	-2	79
1	1	0	2	2	0	15525.385	19	246	6	1	5	5	2	3	15564.269	-12	427
1	1	1	2	2	1	15526.707	10	568	6	2	5	6	1	5	15564.493*	-21	314
7	2	5	7	3	5	15527.056**	-578	32	8	1	7	7	2	5	15564.963*	-32	177
6	3	3	7	2	5	15528.772**	-582	151	15	1	15	15	0	15	15564.983**	-121	121
8	2	6	7	5	2	15529.642**	-579	167	15	0	15	15	1	15	15564.983*	52	40
7	4	4	8	5	4	15530.148	16	184	3	2	1	3	3	1	15565.515**	126	52
0	0	0	1	1	0	15532.605	-9	434	6	1	6	5	2	4	15566.538	-10	36
5	0	5	4	3	1	15532.925	47	30	8	2	6	7	3	4	15566.682**	-617	229
6	1	5	6	2	5	15534.214	-1	495	7	1	7	6	2	5	15566.682*	24	90
7	1	6	7	2	6	15534.498	52	144	5	1	4	4	2	2	15566.682*	-3	192
5	1	4	5	2	4	15535.36*	29	181	8	5	3	9	6	3	15567.092**	657	42
8	1	7	8	2	7	15535.838	6	365	8	1	8	7	2	6	15567.092	-42	23
2	2	0	3	3	0	15537.585	21	799	4	1	4	3	2	2	15567.092**	-150	33
4	1	3	4	2	3	15537.887*	-9	555	16	0	16	16	1	16	15567.441	66	72
6	1	5	5	4	1	15537.887*	42	153	16	1	16	16	0	16	15567.441	-44	24
9	1	8	9	2	8	15538.149	11	100	5	2	4	5	1	4	15568.571**	-136	1024
2	2	1	3	3	1	15539.077	28	268	3	3	0	4	4	0	15569.253	-42	262
10	1	9	10	2	9	15541.123	18	239	3	3	1	4	4	1	15570.093*	-48	817
4	3	1	5	4	1	15541.631**	139	543	4	1	3	3	2	1	15570.093*	36	549
3	0	3	3	1	3	15543.495	-30	447	1	1	0	0	0	0	15570.943	24	157
2	0	2	2	1	2	15543.699	-37	1053	3	1	2	2	2	0	15571.505	38	102
4	0	4	4	1	4	15544.068	-25	1526	7	2	5	6	3	3	15573.352**	-601	132
1	0	1	1	1	1	15544.592	-7	221	9	3	7	9	2	7	15574.635	7	182
11	1	10	11	2	10	15544.753**	283	61	2	1	1	1	0	1	15578.675	16	671

TABLE III. (Continued.)

J'	K'_a	K'_c	J''	K''_a	K''_c	σ (cm $^{-1}$)	o.-c.	Int.	J'	K'_a	K'_c	J''	K''_a	K''_c	σ (cm $^{-1}$)	o.-c.	Int.
3	2	2	3	1	2	15581.571**	589	722	7	4	4	6	5	2	15704.058	6	167
8	3	6	8	2	6	15581.571**	-119	88	4	4	0	4	3	2	15714.369*	-16	199
3	1	2	2	0	2	15587.355	25	181	8	4	5	8	1	7	15722.635**	-271	105
5	4	1	6	5	1	15587.890	-2	144	6	3	3	5	0	5	15723.147**	-621	253
8	2	7	7	3	5	15588.405**	126	54	9	4	6	9	1	8	15723.393	-6	265
6	4	2	7	3	4	15589.044**	527	161	7	4	4	7	1	6	15723.773	13	336
2	2	1	2	1	1	15589.332	55	108	7	6	1	8	7	1	15725.369	33	72
7	3	5	7	2	5	15589.931**	-157	361	6	4	3	6	1	5	15726.115**	151	102
7	2	6	6	3	4	15590.695	68	204	7	6	2	8	7	2	15726.264	54	229
5	4	2	6	5	2	15590.922	45	512	5	4	2	5	1	4	15729.597	68	215
5	2	4	4	3	2	15597.008	-78	192	6	4	2	5	3	2	15740.788**	532	259
4	1	3	3	0	3	15597.970	10	375	7	5	3	7	4	3	15741.977**	154	111
2	2	0	2	1	2	15599.349	51	300	8	5	3	8	4	5	15748.869**	701	208
4	2	2	3	3	0	15599.473**	371	245	8	3	5	7	0	7	15751.047**	-518	147
6	3	4	6	2	4	15599.843	-77	151	5	4	1	4	3	1	15751.276	16	188
3	2	1	3	1	3	15599.843**	198	178	9	4	6	8	3	6	15752.408	37	81
4	2	2	4	1	4	15601.886**	369	646	7	4	4	6	3	4	15753.042	17	333
5	1	4	4	0	4	15610.324	25	89	5	4	2	4	3	2	15757.958	49	860
5	3	3	5	2	3	15611.131**	-302	485	4	4	0	3	3	0	15758.475	-42	936
2	2	0	1	1	0	15614.142	42	667	4	4	1	3	3	1	15760.029	-42	358
3	2	1	2	1	1	15615.750**	132	243	6	6	0	7	7	0	15760.933	-26	379
8	5	3	9	4	5	15616.185**	716	93	6	6	1	7	7	1	15761.029	-15	127
4	2	2	3	1	2	15616.957**	363	532	7	5	2	7	4	4	15763.839*	-53	80
7	5	3	8	6	3	15617.480**	154	202	9	7	3	10	8	3	15772.044*	36	62
4	4	0	5	5	0	15618.296	-55	690	4	4	0	3	1	2	15775.970	-39	180
4	4	1	5	5	1	15618.715	-53	236	5	4	1	4	1	3	15778.059	12	127
9	3	7	8	4	5	15618.999	-53	149	8	4	4	8	1	8	15779.879	50	95
6	1	5	5	0	5	15624.143	-5	197	6	5	1	6	4	3	15780.686**	197	219
4	3	2	4	2	2	15625.289**	325	127	6	4	2	5	1	4	15782.284**	518	410
3	2	2	2	1	2	15625.831**	606	685	8	7	1	9	8	1	15812.697	-1	131
8	2	6	8	1	8	15627.398**	-581	295	8	7	2	9	8	2	15813.082	-41	45
8	3	5	8	2	7	15631.216**	-525	495	5	5	1	5	2	3	15818.611**	-162	62
8	4	5	8	3	5	15633.043**	-205	40	7	5	3	6	4	3	15841.627**	164	417
6	3	3	6	2	5	15633.230**	-605	691	6	5	1	5	4	1	15844.825**	198	502
7	3	5	6	4	3	15633.870**	-191	236	6	5	2	5	4	2	15849.625**	277	239
6	3	3	5	4	1	15636.858**	-607	319	10	6	4	9	7	2	15850.006**	366	64
3	3	1	3	2	1	15639.267*	-31	194	8	6	2	8	5	4	15850.680	-49	123
4	3	1	4	2	3	15642.107**	149	524	7	7	1	8	8	1	15851.087	18	242
5	2	4	4	1	4	15643.500**	-133	478	7	7	0	8	8	0	15851.087	55	80
7	4	4	7	3	4	15649.468	13	187	5	5	0	4	4	0	15854.842**	-116	312
6	5	1	7	6	1	15650.034**	188	320	5	5	1	4	4	1	15855.676**	-131	1013
6	5	2	7	6	2	15651.778**	242	119	7	6	2	7	5	2	15863.206	32	72
6	2	5	5	1	5	15654.397	-43	122	8	5	3	7	2	5	15867.818**	684	279
8	1	7	7	0	7	15655.606	-50	113	7	5	2	6	2	4	15868.236	-43	121
6	3	3	5	2	3	15663.305**	-596	123	9	6	4	9	3	6	15869.732*	5	129
7	2	6	6	1	6	15666.296	47	271	7	5	3	6	2	5	15902.140**	168	172
4	3	2	4	0	4	15668.975**	397	61	9	6	4	8	5	4	15929.127	-26	111
5	3	3	5	0	5	15670.986**	-314	258	8	6	2	7	5	2	15932.893	-82	144
8	4	4	8	3	6	15674.139	75	348	8	8	0	9	9	0	15951.359	-7	141
4	3	1	3	2	1	15674.287**	168	636	8	8	1	9	9	1	15951.359	-23	47
6	3	4	6	0	6	15675.290	-69	96	7	6	1	6	5	1	15951.909	47	143
3	3	0	2	2	0	15677.455	-5	280	7	6	2	6	5	2	15954.890	42	544
3	3	1	2	2	1	15679.912	-9	983	6	6	0	5	5	0	15964.678	-21	821
7	3	5	7	0	7	15680.582**	-167	280	6	6	1	5	5	1	15965.131	15	284
8	4	4	7	5	2	15682.100	29	189	8	6	2	7	3	4	15970.001	-51	251
5	5	0	6	6	0	15682.712**	-128	180	8	7	1	8	6	3	15977.321	-8	68
7	4	3	7	3	5	15682.897**	498	139	7	6	1	6	3	3	15979.563	64	74
4	3	2	3	2	2	15682.897**	330	300	9	7	3	9	4	5	15984.676	78	66
5	5	1	6	6	1	15682.897**	-135	546	6	6	0	5	3	2	15990.796	-48	85
8	6	2	9	7	2	15684.124	-82	89	9	6	4	8	3	6	16003.394	2	146
5	3	3	4	2	3	15685.148**	-314	701	7	6	2	6	3	4	16003.874	53	142
8	3	6	8	0	8	15687.368	-80	81	10	7	3	10	4	7	16011.691**	-91	57
5	4	2	5	3	2	15688.093	74	206	8	6	2	7	1	6	16044.334	-23	57
6	3	4	5	2	4	15689.324	-55	161	9	7	2	8	6	2	16049.526	-17	36
8	4	5	7	5	3	15691.211**	-230	61	9	6	3	8	1	7	16052.237*	-40	20
6	4	2	6	3	4	15692.656**	569	434	9	7	3	8	6	3	16056.147	49	174
7	3	5	6	2	5	15694.438**	-132	313	9	9	0	10	10	0	16059.664	6	25
7	4	3	6	5	1	15701.578**	498	68	9	9	1	10	10	1	16059.664	-1	75
4	3	1	3	0	3	15702.195**	173	265	8	7	1	7	6	1	16070.766	-58	332
5	4	1	5	3	3	15702.968	27	120									

TABLE IV. Rotational constants (in cm^{-1}) and geometrical structures for the $\tilde{X}^1A_1$ and $\tilde{A}^1B_1$ states of SiH_2 . The rotational constants at equilibrium were calculated using the α_i^B rovibrational constants computed by Allen and Schaefer (Ref. 25) (set A in Table 15 and Table 20 for $\tilde{X}^1A_1$ and $\tilde{A}^1B_1$, respectively). The r_e (Si-H) and θ_e (H-Si-H) values were derived from the three pairs of rotational constants and are given in Å and degrees, respectively.

	$\tilde{X}^1A_1$			$\tilde{A}^1B_1$		
	A_e	B_e	C_e	A_e	B_e	C_e
	8.09813	7.04917	3.77198	17.71856	4.94926	3.84201
	r_e	θ_e		r_e	θ_e	
(A,B)	1.51446	91.9807		1.48184	122.6231	
(B,C)	1.51377	92.0348		1.48725	121.8658	
(A,C)	1.51382	91.9336		1.48688	122.8359	
Average	1.51402	91.9830		1.48532	122.4416	
Dubois	1.51408 ^a	91.990 ^a		1.4871 ^c	121.83 ^c	
<i>ab initio</i>	1.51477 ^b	92.42 ^b		1.48328 ^d	122.53 ^d	

^aValues obtained in Ref. 25 (Set A of Table 15) from the ground state rotational constants given by Dubois in Ref. 8.

^bB2 2R CISD *ab initio* calculations (Table 10 of Ref. 25).

^cValues obtained in Ref. 25 (Table 20) from the extrapolated values of the rotational constants given by Dubois in Ref. 8.

^dB2 CISD *ab initio* calculations (Table 18 of Ref. 25).

minus calculated value was larger than 2.5 times the standard deviation of the previous cycle, would be excluded from the present iteration. The next choice was again that of the set of parameters to be released in the fit. After several trials, we finally chose a set which included basically quartic and sextic centrifugal distortion constants, with the exclusion of δ_K and H_J , which were poorly determined, and the inclusion of L_K , which was necessary to reproduce the higher K transitions: $9_{9,0} \leftarrow 10_{10,0}$ and $9_{9,1} \leftarrow 10_{10,1}$. The parameters resulting from this procedure are quoted also in Table II, with their fitting uncertainty in parentheses.

These values are the first experimental determination of the parameters of the (0,0,0) vibrational level of the 1B_1 electronic state. Dubois⁸ had estimated these parameters by extrapolation from his data on higher bending states, and Duxbury, Alijah and Trieling⁴ had obtained calculated values for these parameters through their Renner–Teller model. Whereas the extrapolation⁸ was not accurate for the A constant (17.75 compared to the experimental value of 18.32 cm^{-1}), which changes largely from one bending state to the next, the extrapolated results for B and C were quite good (4.9 and 3.8 compared to 4.899 and 3.766 cm^{-1} , respectively), as these constants are much less sensitive to the bending excitation. On the other hand, the Renner–Teller model⁴ gives a value for the A constant (18.30 cm^{-1}) which is very close to the experimental one, while the B and C parameters are calculated with less precision (4.722 and 3.651 cm^{-1} , respectively). Duxbury, Alijah and Trieling⁴ also estimated the vibrational band origin of this transition at 15546 cm^{-1} from the LIF excitation spectra of the $^pP_1(1)$ rotational line observed by Fukushima, Mayana and Obi.¹³ Their value agrees with the present band origin within 1.7 cm^{-1} . From our band origin and that of the (0,1,0) state from Dubois (Table IV of Ref. 8), we obtain a value of 856.53

cm^{-1} for the bending wave number in $\tilde{A}^1B_1$. This value is fairly different from the *ab initio* result of Allen and Schaefer (Table 18 of Ref. 25), 888 cm^{-1} . The spacing between consecutive bending states as measured by Dubois is quite irregular, probably because of the Renner–Teller perturbations, which has refrained us from attempting to evaluate anharmonicity constants.

We present in Table III a list of all observed and assigned transitions, with the observed-calculated deviations and an indication of the lines that were left out of the fit, because of the perturbations. It is hoped that these line positions will help future investigations aimed, for example, at monitoring silylene in plasmas. We add also in this Table a calculated value of the intensity of each line, which is necessary for concentration measurements of silylene (see Ref. 22). As another example of the importance of the inclusion of intensities in such tables, we would mention the difficulty that we sometimes had in identifying NH_2 lines in our spectrum; their wave number was given in Ref. 28, but since no intensities were given in that reference, it was difficult at times to ascertain whether a weak line could be due to an NH_2 absorption or to an unassigned silylene line.

D. Equilibrium geometry

With the new rotational constants for the vibrational ground states derived in this work, it is possible to recalculate the equilibrium value of the rotational constants, and hence the equilibrium geometry of the molecule in both electronic states involved. In the 1A_1 state, the rotational constants A_0 , B_0 and C_0 calculated here are very close to those of Dubois,⁸ which makes the value of the inertial defect of the (0,0,0) vibrational state of this work to be coincident with the values observed and calculated by Dubois⁸ (0.0073 and 0.0074 uÅ^2 , respectively). We have derived the equilibrium values of the rotational constants A_e , B_e and C_e by adding the calculated values of the vibrational dependence of the rotational constants (the α_i^B parameters) calculated by Allen and Schaefer.²⁵ From A_e , B_e and C_e it is possible to estimate the equilibrium geometry of SiH_2 , given by the two parameters r_e and θ_e , either by taking two rotational constants at a time, or by making a mean average of all three values. Our results are collected in Table IV, together with those derived by Allen and Schaefer,²⁵ from the experimental values of Dubois⁸ using the same procedure, and from their own *ab initio* calculations. Although all three sets are in good agreement, our values are closer to those of the experimental work of Dubois.⁸

For the 1B_1 state, the inertial defect in the (0,0,0) vibrational level calculated from our rotational constants is fairly high: 0.115 uÅ^2 . This may be a consequence of the perturbations still remaining in our data, although this number may be comparatively normal for the electronic configuration of the molecule in this state, where the bonds have a weaker nature. We have transformed the rotational constants into their equilibrium values by means of the α_i^B parameters calculated by Allen and Schaefer²⁵ for this electronic level. The geometrical parameters obtained in this way are also given in Table IV. It is interesting to note that our values are closer

now to the theoretical results of Allen and Schaefer than to those of Dubois, which were in fact estimated by extrapolation from observations of higher bending states. Allen and Schaefer questioned the reason of the less good agreement between their theoretical results and the experimental ones for this electronic state. Our results seem now to confirm the high quality of their calculation.

IV. CONCLUSION

The new experimental measurements presented here allow a more accurate determination of the energy and geometrical structure of the 1B_1 electronic state of silylene. These results complement previous observations of excited bending levels in this electronic state.^{4,8} The transitions observed here could be used for monitoring this species in silicon plasmas. Local perturbations affecting the spectra are probably due to crossings with rovibrational levels of the 3B_1 electronic state, which has not yet been experimentally observed. The detection of silylene in the triplet state would be of great interest to clarify the energy level structure of this radical.

ACKNOWLEDGMENTS

The expert help of Ludovic Biennier (Grenoble) was appreciated for the recording of the ICLAS spectrum. Daniele Romanini and Nader Sadeghi (Grenoble) are thanked for helpful discussions and for their contribution in the designing of the intracavity discharge cell. R.E.'s work is supported by the Spanish DGES, Project No. PB96-0881.

¹A. Matsuda and N. Hata, *Glow-discharge Hydrogenated Amorphous Silicon*, edited by K. Tanaka (KTK, Tokyo, 1989).

²T. Shirafuji, K. Tachibana, and Y. Matsui, Jpn. J. Appl. Phys., Part 1 **34**, 4239 (1995).

- ³J. R. Doyle, D. A. Doughty, and A. Gallagher, J. Appl. Phys. **68**, 4375 (1990).
- ⁴G. Duxbury, A. Alijah, and R. R. Trieling, J. Chem. Phys. **98**, 811 (1993).
- ⁵J. W. Thoman and J. I. Steinfeld, Chem. Phys. Lett. **124**, 35 (1986).
- ⁶J. W. Thoman, J. I. Steinfeld, R. I. McKay, and A. E. W. Knight, J. Chem. Phys. **86**, 5909 (1987).
- ⁷I. Dubois, G. Herzberg, and R. D. Verma, J. Chem. Phys. **47**, 4262 (1967).
- ⁸I. Dubois, Can. J. Phys. **46**, 2485 (1968); Depository for unpublished data, National Science Library, Ottawa, Canada (1968).
- ⁹I. Dubois, G. Duxbury, and R. N. Dixon, J. Chem. Soc. Faraday Trans. 2 **71**, 799 (1975).
- ¹⁰C. Yamada, H. Kanomori, E. Hirota, N. Nishiwaki, N. Itabashi, K. Kato, and G. Goto, J. Chem. Phys. **91**, 4582 (1989).
- ¹¹G. Inoue and M. Suzuki, Chem. Phys. Lett. **105**, 651 (1984); **122**, 361 (1985).
- ¹²D. M. Rayner, R. P. Steer, P. A. Hackett, C. L. Wilson, and P. John, Chem. Phys. Lett. **123**, 449 (1986).
- ¹³M. Fukushima, S. Mayana, and K. Obi, J. Chem. Phys. **96**, 44 (1992).
- ¹⁴J. M. Jasinski, E. A. Whittaker, G. C. Bjorklund, R. W. Dreyfus, R. D. Estes, and R. E. Walkup, Appl. Phys. Lett. **44**, 1155 (1984).
- ¹⁵J. M. Jasinski, J. Phys. Chem. **90**, 555 (1986).
- ¹⁶J. M. Jasinski and J. O. Chu, J. Chem. Phys. **88**, 1678 (1988).
- ¹⁷A. Kono, N. Koike, K. Okuda, and T. Goto, Jpn. J. Appl. Phys., Part 2 **32**, 543 (1993).
- ¹⁸H. Nomura, K. Akimoto, A. Kono, and T. Goto, J. Phys. D **28**, 1977 (1995).
- ¹⁹J. J. O'Brien and G. H. Atkinson, Chem. Phys. Lett. **130**, 321 (1986).
- ²⁰K. Tachibana, T. Shirafuji, and Y. Matsui, Jpn. J. Appl. Phys., Part 1 **31**, 2588 (1992).
- ²¹M. W. Markus and P. Roth, J. Quant. Spectrosc. Radiat. Transf. **52**, 783 (1994).
- ²²A. Campargue, D. Romanini, and N. Sadeghi, J. Phys. D (accepted).
- ²³A. Campargue, F. Stoeckel, and M. Chenevier, Spectrochim. Acta Rev. **13**, 69 (1990).
- ²⁴D. Romanini, A. A. Kachanov, N. Sadeghi, and F. Stoeckel, Chem. Phys. Lett. **264**, 316 (1997).
- ²⁵W. D. Allen and H. F. Schaefer III, Chem. Phys. **108**, 243 (1986).
- ²⁶S. Koseki and M. S. Gordon, J. Mol. Spectrosc. **123**, 392 (1987).
- ²⁷S. Gerstenkorn and P. Luc, *Atlas du spectre d'absorption de la molécule d'iode* (Edition du CNRS, Paris, 1978).
- ²⁸S. C. Ross, F. W. Birss, M. Vervloet, and D. A. Ramsay, J. Mol. Spectrosc. **129**, 436 (1988).