Accurate Frequency Determination of Vibration–Rotation and Rotational Transitions of SiH$^+$

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Received 2017 August 25; revised 2017 September 26; accepted 2017 September 26; published 2017 October 31

Abstract

The fundamental $^{28}$SiH$^+$ ion has been characterized in a collaborative work, utilizing a hollow-cathode discharge laser spectrometer and a cryogenic ion trap spectrometer. Twenty-three vibration–rotation transitions around 4.75 $\mu$m have been detected with high accuracy. This has facilitated the first direct measurement of the pure rotational transition $J = 1 \leftarrow 0$ at 453056.3632(4) MHz in the trap spectrometer. The measured and accurately predicted transitions enable the search for this ion in space with IR and sub-mm telescopes.

Key words: ISM: molecules – methods: laboratory: molecular – molecular data – techniques: spectroscopic

1. Introduction

About twelve of the molecules identified in the interstellar medium (ISM) contain silicon, mostly bound to C, N, O, or S atoms. On the other hand, silane (SiH$_4$) is the only one containing hydrogen that has been securely identified (by Goldhaber & Betz 1984 in the outer envelope of IRC+10216). Merely tentative detections have been reported for SiH$_3$ (Turner 1995), SiH (Schilke et al. 2001), and SiH$_2$CN (Agúndez et al. 2014). The simplest silicon hydrides, the radical SiH (silylidyne), and the ion SiH$^+$ (silylidynium) have only been identified in the Sun’s photosphere (Sauval & Greaves 1997; Grevesse & Sauval 1970), and SiH also in the atmosphere of some cool stars (see, e.g., Merrill 1953, 1959).

In diffuse and translucent clouds, hydrides can usually be observed by their electronic absorptions at visible and ultraviolet wavelengths superposed on the spectra of bright background stars. Unlike the chemically similar CH$_2$, this is not the case for SiH$_2$. At the time of the discovery of SiH$^+$ in the Sun, it was expected to be found in the ISM on the grounds of the relatively high abundance of Si, the similarity to CH$^+$, and the ionization potential of Si being lower than that of C, which would allow Si to remain ionized to larger optical depths (Douglas & Lutz 1970; de Almeida & Singh 1978). The gas-phase chemistry of Si in diffuse clouds was discussed by Turner & Dalgarno (1977), who noted radiative association as the main formation process, and dissociative recombination with electrons, photodissociation, and reactions with H and O as destruction mechanisms. Unlike the case of CH$^+$, H$_2$ does not destroy SiH$^+$, which could favors a higher SiH$^+$/CH$^+$ abundance ratio than that of Si/C. Since radiative association of Si$^+$ with H and H$_2$ is very slow (Stancil et al. 2000), in cold dense clouds the ion–molecule silicon chemistry is initiated by the exothermic reaction H$_3^+$ + Si $\rightarrow$ SiH$^+$ + H$_2$. The reaction of SiH$^+$ with H$_2$ is endothermic, so the main destruction pathway for silylidynium is mainly collisions with C, N, and O (Herbst et al. 1989). In dark clouds most gas-phase Si is supposed to be in the form of SiO, for which extremely low upper limits have been derived and for which models predict a much higher abundance, leading to the conclusion that Si has to be heavily depleted into grains. MacKay (1996) has noted that depletion would not need to be so high if SiH$_4$ were the major Si-bearing species. The formation reaction Si$^+$ + H$_2$ $\rightarrow$ SiH$^+$ + H is highly endothermic (by $\sim$14,200 K, from the thermochemical data of Curtiss & Pople 1988), therefore, and similarly to the formation mechanisms suggested for the ubiquitous CH$^+$ or SH$^+$, a warm chemistry is necessary, and this reaction would only proceed in shocked or turbulent regions or if the hydrogen molecules were vibrationally excited ($v > 3$). It is worth noting that sulfanylium (the SiH$^+$ radical) was searched for, and not found, in the absorption in the UV (Millar & Hobbs 1988; Magnani & Salzer 1991) until it was recently identified in the sub-mm range by Menten et al. (2011). The endothermicity of the reaction Si$^+$ + H$_2$ $\rightarrow$ SH$^+$ + H is 9860 K, more than twice of that involving CH$^+$ (4280 K), and vibrationally excited H$_2$ (in $v > 1$ and $v \geq 2$, respectively) has been invoked in both cases as a way to overcome the energy barriers (Zanchet et al. 2013; Gerin et al. 2016).

Laboratory spectroscopic information on SiH$^+$ is surprisingly scarce. The electronic spectrum in the vis–UV region (A’’’’ $\rightarrow$ X3$^+$ transition) was recorded by Douglas & Lutz (1970), leading to its identification in the Sun’s photosphere (Grevesse & Sauval 1970). Based on those data, Singh & Vanladingham (1978) estimated line positions for rotational and vibration–rotational lines of SiH$^+$. In particular, the predicted frequency for the $J = 1 \leftarrow 0$ transition in $v = 0$ was 453037 MHz, with no estimation of the uncertainty. Carlson et al. (1980) identified two new bands of the electronic transition, and improved the molecular constants. Davies & Martineau (1988) detected the fundamental vibration–rotation band of SiH$^+$ in a silane plasma with diode laser spectroscopy. Most likely due to the patchy coverage of lead-salt diode lasers, they could only measure seven lines in the R-branch and just one in the P-branch, with a quoted accuracy of $\sim$0.003 cm$^{-1}$. From a fit to their data we obtain 453121(40) MHz for the $J = 1 \leftarrow 0$ rotational line. Until now there was no direct measurement of the rotational transitions. Regarding transition dipole moments, Singh & Vanladingham (1978) estimated the transition dipole moment for the $v = 1 \leftarrow 0$ band to be $\mu_{v=0} = 0.1081$ D, and the permanent electric dipole moment has been calculated by Park & Sun (1992) to be $\mu_0 = 0.5314$ D, while Müller & Woon (2013) give $\mu_0 = 0.388 - 0.454$ D with higher level calculations.

In this work we have measured 23 vibration–rotation lines of the $v = 1 \leftarrow 0$ band of SiH$^+$ with high accuracy ($\sim$10 MHz, 3$\sigma$),
using a difference frequency laser spectrometer coupled to a hollow-cathode discharge. Besides providing a more accurate and complete set of infrared frequencies than previously available, it has allowed for an accurate prediction of the $J = 0 - 1$ rotational transition. The frequency of the latter has been measured with sub-ppb accuracy in a cold ion trap using the method of state-dependent attachment of helium atoms.

2. Experimental Setup and Results

The vibration–rotation spectrum was measured in Madrid with a difference frequency laser spectrometer coupled to a hollow-cathode discharge, using a double modulation of the discharge current (i.e., concentration modulation) and the infrared beam power. This setup has been used recently for the measurement of the $\nu_4$ band of the NH$_3$D$^+$ ion (Cernicharo et al. 2013; Doménech et al. 2013), the measurement of the fundamental vibration–rotation bands of $^{36}$ArH$^+$, $^{38}$ArH$^+$ (Cueto et al. 2014), and H$^{35}$Cl$^+$, and H$^{37}$Cl$^+$ (Doménech et al. 2016). Since it has already been described in those works, only the details relevant to the present experiment will be given here. The accuracy of the frequency scale relies on an Ar$^+$ laser which is frequency-locked to a hyperfine transition of $^{127}$I$_2$. The same laser is also used to calibrate a high-accuracy wavemeter (10 MHz, 3σ) that measures the frequency of the dye laser at each data point, leading to an absolute accuracy of the IR frequencies limited by the wavemeter (10 MHz), and an internal precision on the order of 1 MHz. The precursor gases were silane and hydrogen. Since the pyrophoric nature of silane poses major difficulties for its handling, we decided to use a premixed sample of 0.5% SiH$_4$ in He (Alphagaz (0.50 ± 0.01)% SiH$_4$ UHP in He N46). Adding H$_2$ to the flowing mixture was found to increase SiH$^+$ signals. To our surprise, we found that, after some hours of operation, the SiH$_4$/He was not necessary at all, and that the signal level was maintained for rather long periods with only H$_2$ in the discharge. Since a deposit of amorphous Si was forming on the cathode walls, this suggested that the electron impact was removing Si atoms from the cathode and that the reaction Si + H$_2$ $\rightarrow$ SiH$^+$ + H$_2$ was efficient in the production of SiH$^+$. This was in agreement with the observation of Davies & Martineau (1988), although they did not observe such a marked persistence of the signal. Finally, the experiments were run at 1 mbar total pressure with 0.5 mbar each of H$_2$ and the SiH$_4$/He mixture and at room temperature. The discharge was maintained at 375 mA and 800 V. In the present experiment the discharge modulation frequency could be increased up to 15 kHz, and it was found that $\sim$10 kHz provided a good compromise between signal intensity and discrimination of ion signals against interferences of other species (neutral SiH$_4$ and likely other polysilanes). A total of 23 lines was measured, from $P(11)$ to $R(11)$, spanning the range 1902–2236 cm$^{-1}$. Between 100 and 500 scans were averaged for each line, reaching signal-to-noise ratios between 100 and 10, depending on the signal intensity. Two examples of the detected lines are shown in Figure 1. The initial search was facilitated by the wavenumbers listed in Davies & Martineau (1988), although, as the number of detected lines increased, our own data were used to predict the next lines. Gaussian fits to the line profiles were used to extract the line centers. Table 1 lists the observed wavenumbers, their 1σ uncertainty (calculated as the quadratic sum of the center frequency uncertainty derived from the fit and the 1σ accuracy of the wavemeter), and the comparison with the measured frequencies of Davies & Martineau (1988). Our frequencies were fit using the program PGOPHER (Western 2017) for the case of a linear molecule in a $^1\Sigma^+$ state. Up to the sextic centrifugal distortion constants could be derived with statistical significance, both for $v = 0$ and $v = 1$. For the $J = 1–0$ fundamental rotational transition, a frequency prediction of 453057.7 MHz, with 3σ = 1.5 MHz, was obtained.

The fundamental rotational transition of SiH$^+$ was then measured in the Köln laboratories exploiting the rotational state-dependent attachment of the He atoms to cations (Brüken et al. 2014, 2017; Jusko et al. 2017). The experiment was performed in the 4 K trapping machine COLTRAP described by Asvany et al. (2010) and Asvany et al. (2014). The $^{28}$SiH$^+$ ions were generated in a storage ion source by bombarding the SiH$_4$ precursor gas (Linde AG, 2% silane in He) with 30 eV electrons. A pulse of several ten thousand mass-selected ions ($m = 29$ u) was injected into the 22-pole ion trap filled with about $10^{14}$ cm$^{-2}$ He. During the trapping time of 700 ms, the complexes SiH$^+(\text{He})_n$ ($n = 1–4$) formed by three-body collisions, as shown in Figure 2. The detection of the resonant absorption of the sub-mm wave by the naked ion ($n = 0$) was achieved by observing the decrease of the counts of the complex with $n = 1$ (mass 33 u). The sub-mm wave radiation was supplied by an atomic clock referenced synthesizer (Agilent E8257D) driving a multiplier chain source (Virginia Diodes, Inc.) covering the range of 80–1100 GHz. The nominal sub-mm power of the source at the fundamental rotational transition of SiH$^+$ was about 160 μW. This power was attenuated by a factor of about three (with further losses by the transport to the trap) in order to avoid power broadening. In this case, the spectral profile is a pure Gaussian with a
corresponding Doppler temperature of $T = 13$ K, as seen in Figure 3. The final value for the fundamental $J = 1 \rightarrow 0$ after eleven measurements is 453056.3632(4) MHz ($1\sigma$) and is also listed in Table 1. The resulting uncertainty of 400 Hz corresponds to a relative precision of better than 1 ppb. Also, the good agreement with the prediction from the IR-only data is noteworthy. Interestingly, we were not able to detect the $J = 2 \rightarrow 1$ transition, even though the corresponding line for, e.g., CD$^+$, has been observed with the same method. The joint effect of the small dipole moment for SiH$^+$, lower available power, small population in $J = 1$, and, most probably, a small difference in He attachment rate coefficients for $J = 1$ and $J = 2$ can explain this non-observation. Therefore, only a prediction based on all our data is given in Table 1.

We also searched for the fundamental transitions of isotopologues of SiH$^+$. Although $^{30}$Si is less abundant than $^{29}$Si (3.1% and 4.7%, respectively), we choose it for the search scan because it has a nuclear spin of $I = 0$ and therefore, a potential signal dilution due to hyperfine effects can be excluded. Our predicted frequency value (based on the mass scaling of the spectroscopic parameters) was about 452014 MHz. We integrated in the range of 451970–452030 MHz, and did not find any rotational signal of $^{30}$SiH$^+$. This non-detection is caused by the high ion mass ($m = 35$ u) being heavily dominated by $^{28}$SiH$^+$. He, with the desired $^{30}$SiH$^+$. He ions making up less than 3.1% of that mass.

### 3. Spectroscopic Parameters

The measured frequency of the pure rotational line $J = 1 \rightarrow 0$ was added to the fit, rendering the final set of constants given in Table 2. The frequency predictions for the higher rotational transitions in Table 1 have been calculated with these constants.

### 4. Conclusion and Outlook

We have measured 23 lines of the fundamental vibration–rotation band of $^{28}$SiH$^+$, with an absolute accuracy better than...
Table 2
Derived Spectroscopic Parameters (in cm$^{-1}$) from a Fit to All of the Measured Transitions

| Parameter | $v = 0$ | $v = 1$ |
|-----------|---------|---------|
| $v$       | 2088.689199(67) |         |
| $B_0$     | 7.556933267(160) | 7.35616891(602) |
| $D_0 \times 10^4$ | 3.832640806 | 3.78803123 |
| $H_0 \times 10^8$ | 1.5188595 | 1.3620685 |

Note. Numbers in parentheses are one standard deviation in units of the last digit.

10 MHz ($3.3 \times 10^{-4}$ cm$^{-1}$). Fifteen of these lines have been measured for the first time. This has facilitated the first direct and accurate measurement of the pure rotational transition $J = 1 \leftarrow 0$ at 453056.3632(4) MHz, and a prediction for the $J = 2 \leftarrow 1$ transition at 905837.055(60) MHz. It is gratifying to see how well high-resolution IR spectroscopy can guide laboratory (and astronomical) searches for rotational transitions.

Although current astrochemical models do not predict a high abundance of SiH$^+$ (see, e.g., Herbst et al. 1989), the importance of the molecule together with the ever increasing sensitivity and resolution of radio and IR telescopes, warrant the interest of providing precise values for the transition frequencies.

The $J = 0 \leftarrow 1$ transition was outside the bands covered by Herschel. An examination of Herschel’s data toward SgrB2 and Orion has not revealed any signature that could be attributed to the $J = 2 \leftarrow 1$ line. Now that the Herschel mission has ended, other alternatives may be ALMA, APEX, or SOFIA. The $J = 1 \leftarrow 0$ line lies within ALMA band 8, and within the range covered by the instrument APEX-3, but it is close to a telluric water line. With a total precipitable water vapor (pwv) of 0.5 mm, the calculated transmission of the atmosphere at the ALMA site is 0.38, while for the average 1 mm pwv it drops to 0.15. The $J = 2 \leftarrow 1$ line lies within ALMA band 10, and the instrument CHAMP+ at APEX, although also with limited atmospheric transparency (calculated transmission is 0.28 and 0.07 for 0.5 mm and 1 mm pwv, respectively). Observations of the $J = 0 \leftarrow 1$ transition could be attempted in dry weather with both ALMA or APEX if enough integration time was available. However, given the not so favorable atmospheric conditions, and the larger Einstein coefficients of the vibration–rotation transitions, observations in the mid-IR (around 4.75 µm) can also be a good alternative to detect this molecule. The instruments EXES onboard SOFIA, iSHELL at IRTF, or the future CRIRES+ at VLT could offer good opportunities to detect absorptions by this molecule in the ISM. The lines of sight would be those of the diffuse medium, shock regions, or supernova ejecta against bright IR sources.

This work (including the research stay of J.L.D. in Köln) has been supported by the Deutsche Forschungsgemeinschaft (DFG) via SFB 956 project B2 and the Gerätezentrum “Cologne Center for Terahertz Spectroscopy.” J.L.D. acknowledges partial financial support from the Spanish MINECO through grant FIS2016-77726-C3-1-P and from the European Research Council through grant agreement ERC-2013-SyG-610256-NANOCOSMOS. We thank Holger Müller for stimulating discussions. We also thank P. Schilke, J. Cernicharo, and V. Ossenkopf-Oka for checking their observations made with Herschel for the SiH$^+$ 2 – 1 line. The authors gratefully acknowledge the work done over the last years by the electrical and mechanical workshops of the I. Physikalisches Institut, as well as by the technicians at the Molecular Physics department of IEM-CSIC and CFMAC-CSIC workshops.

Software: PGOPHER (Western 2017).

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