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Improved rest frequencies for the submillimetre-wave spectrum of SiN*

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ABSTRACT

The submillimetre-wave spectrum of the SiN radical has been investigated in the laboratory using a source-modulation microwave spectrometer equipped with a negative glow discharge cell. SiN was produced in a $SiCl_4/N_2$ discharge plasma. Twenty-one new fine and hyperfine components up to $N = 17-16$ were observed reaching a frequency as high as 740 GHz. The new laboratory measurements provide much improved rest frequencies in the submillimetre spectral region useful for the identification of SiN lines in hot core sources and circumstellar shells.

Key words. molecular data – methods: laboratory – techniques: spectroscopic – radio lines: ISM

1. Introduction

Silicon-bearing molecules are particularly elusive for astronomical detection in the interstellar medium (ISM) because of the extremely low abundance of this element in the gas phase. It is well known that silicon and other refractory elements are heavily depleted in both diffuse and dense clouds, and they are thought to be condensed onto silicate dust grains (see for example Walmsley et al. 2002, and reference therein). Silicon-containing species are typically found in regions associated with the occurrence of energetic processes (e.g. outflows or photon dominated regions, Ziurys 1991; Greenhill et al. 1998; Schilke et al. 2001) where atomic silicon or silicon-bearing material is returned to the gas phase via evaporation of ice grain mantles (MacKay 1995) or sputtering of the grain cores produced by shocks (Caselli et al. 1997; Schilke et al. 1997). As far as the silicon nitride radical (SiN) is concerned, models of Si ion-molecule gas-phase chemistry (Herbst et al. 1989) predicted a very low abundance of this species in the ISM due to its rapid destruction by reaction with atoms of nitrogen or oxygen or ionized carbon.

The presence of this radical in the interstellar space was inferred by Lovas (1974) who indicated SiN as a possible source of some unidentified molecular lines, but the early searches for this species in the ISM were unsuccessful (Ziurys et al. 1984). SiN was identified in space for the first time by Turner (1992), who observed five transitions in the 1 mm and 3 mm spectral ranges in the circumstellar envelope IRC +12016. In this C-rich object, SiN is thought to be produced by reaction between ionized Si and NH_3 in the outer part of the envelope, followed by dissociative electron recombination of the intermediate product. More recently Schilke et al. (2003) reported the detection of the $N = 2-1$, $J = 2.5-1.5$ transition of SiN in absorption toward the star forming core Sgr B2(M), close to the galactic centre. This object is characterized by a very massive, shock-heated envelope (Flower et al. 1995) in which several other refractory species have been identified, perhaps even FeO (Walmsley et al. 2002, tentative detection).

In laboratory, the SiN radical has been the subject of numerous spectroscopic investigations in the visible and ultraviolet regions, as well as of a number of theoretical studies mainly focused on the ground state $X^2\Sigma^+$ and on the low-lying excited state $A^2\Pi_i$ (see Cai et al. 1998, and reference therein). In the infrared, Yamada & Hirota (1984) investigated the 1, 0 band of the electronic transition $A^2\Pi_i - X^2\Sigma^+$ in the 5 μm region by diode laser spectroscopy. The rotational spectrum of SiN in its $^2\Sigma^+$ ground state was measured by Saito et al. (1983), who recorded the three rotational transitions $N = 2-1$, 3–2, and 4–3 in the frequency range from 87 to 175 GHz using a source modulation millimetre-wave (mm-wave) spectrometer. The rotational parameters, the electron spin-rotation coupling constant, and the hyperfine structure parameters obtained in the latter study have been employed to generate the set of rest frequencies through which the SiN radical was then identified in space (Turner 1992; Schilke et al. 2003).

Although the accuracy of these rest frequencies is well suited for radioastronomical observations in the 1, 2, and 3 mm spectral ranges, it appears inadequate for higher frequency studies since the predicted line positions in the submillimetre-wave (submm-wave) and far infrared (FIR) regions are affected by uncertainties of several MHz. It should be pointed out that observation of these lines does not produce only redundant information: emissions in the submm-wave region originate from higher energy levels, thus they are useful for tracing gas with higher densities and temperatures. This observational trend is further enhanced by the small beam sizes typically achievable at higher frequencies, which allow a more efficient coupling to very small, high density, hot sources. The availability of very accurate rest frequencies in the submm-wave and FIR ranges will become more critical in the near future, since air- and space-borne missions like SOFIA and

* Table 3 is only available in electronic form at the CDS via anonymous ftp to cdsarc.u-strasbg.fr (130.79.128.5) or via http://cdsweb.u-strasbg.fr/cgi-bin/qcat?J/A+A/455/1161

HERSCHEL will make observations in these spectral regions much more feasible.

The main objective of the present laboratory work is to provide very accurate rest frequencies useful for unambiguous identification of the SiN lines in the submm-wave region. New laboratory measurements of the SiN rotational spectrum have been carried out reaching a frequency as high as 741 GHz: twenty-one new fine and hyperfine components, corresponding to ten rotational transitions from $N = 5{-}4$ to $N = 17{-}16$, have been recorded and analysed yielding much more precise values of the rotational and centrifugal distortion constants. The improved set of spectroscopic constants derived in the present investigation allows for the prediction of the rotational line position of SiN, with an uncertainty of few thousandths of km s^{-1} in the 300 μm spectral region.

2. Experiment

The rotational spectrum of SiN was recorded in the frequency range 218–741 GHz employing a source modulation millimetre-wave spectrometer (Cazzoli & Dore 1990) equipped with a negative glow discharge cell (Dore et al. 1999). The radical SiN was produced directly in the absorption cell by a DC glow discharge in a mixture of silicon tetrachloride and nitrogen: optimal conditions were attained using partial pressures of 1.3 Pa and 4 Pa of $SiCl_4$ and N_2, respectively, and a discharge current of about 60 mA. Phase locked Gunn oscillators working in the frequency region 55–115 GHz were used as primary radiation sources and the submillimetre-wave power was obtained using harmonic multiplication. Source frequency modulation at 16.7 kHz was applied and the signal was demodulated at $2f$ by a lock-in amplifier, thus obtaining the second derivative of the actual spectrum profile. A liquid helium-cooled InSb hot electron bolometer was used as detector. Measurement accuracy of the line positions lies in the range 10–20 kHz, depending on the signal-to-noise ratio.

3. Analysis

Silicon nitride is a radical conforming to the Hund's case ($b_{\beta J}$) (Townes & Schawlow 1975) coupling scheme in its $X^2\Sigma^+$ ground electronic state. Each rotational level, denoted by the quantum number N, is doubled by the spin-rotation coupling produced by the unpaired electron. Hyperfine interaction due to the ^{14}N ($I = 1$) nucleus results in further splitting of these fine components into three sublevels denoted by the quantum number F. The overall vector coupling scheme is:

$$\boldsymbol{J} = \boldsymbol{N} + \boldsymbol{S}\,; \qquad \boldsymbol{F} = \boldsymbol{J} + \boldsymbol{I}. \tag{1}$$

The measured spectrum was analysed using an effective Hamiltonian expressed as

$$H_{\rm eff} = H_{\rm rot} + H_{\rm sr} + H_{\rm hfs} \tag{2}$$

where $H_{\rm rot}$ represents the rotational kinetic energy, $H_{\rm sr}$ the electron spin-rotation coupling, and $H_{\rm hfs}$ the nuclear spin hyperfine interaction. The detailed forms of the various terms are (Brown & Carrington 2003):

$$H_{\rm rot} = B\,\boldsymbol{N}^2 - D\,\boldsymbol{N}^4 \tag{3}$$

$$H_{\rm sr} = \gamma\,\boldsymbol{N}\cdot\boldsymbol{S} + \gamma_D\,\boldsymbol{N}^2\,(\boldsymbol{N}\cdot\boldsymbol{S}) \tag{4}$$

$$H_{\rm hfs} = b_{\rm F} T^1(\boldsymbol{I})\cdot T^1(\boldsymbol{S}) + \frac{\sqrt{6}}{3} c T^2_{q=0}(\boldsymbol{I},\boldsymbol{S}) + T^2(\boldsymbol{q})\cdot T^2(\boldsymbol{Q}). \tag{5}$$

The hyperfine Hamiltonian $H_{\rm hfs}$, Eq. (5), is expressed adopting spherical tensor notation; it involves the two magnetic hyperfine coupling constants $b_{\rm F}$ (Fermi contact interaction) and c (direct dipolar interaction), and the nuclear electric quadrupole coupling constant eQq. The molecular parameters were determined using the nonlinear least-squares fitting program SPFIT developed by Pickett (1991). Twenty-one new line frequencies belonging to 10 rotational transitions ranging from $N = 5{-}4$ to $N = 17{-}16$ have been analysed together with the 19 millimetre-wave lines previously reported by Saito et al. (1983). Different weights $w = 1/\sigma^2$ were given to the two sets of data in order to take into account the different measurement precisions: σ values of 30 kHz and 16 kHz, were estimated for the previous millimetre-wave measurements (Saito et al. 1983) and for the data of the present work, respectively. The overall standard deviation of the fit relative to experimental uncertainties was 0.973. The complete list of the analysed transition frequencies along with the corresponding least-squares residuals is reported in Table 1. The spectroscopic parameters derived by the analysis are listed in Table 2, where the previous results of Saito et al. (1983) are also reported for comparison. The inclusion of the new submillimetre-wave transitions allowed for a considerable refinement of the rotational constant B and of the quartic centrifugal distortion constant D whose uncertainties have been reduced by factors of 10 and 170, respectively. In addition, the centrifugal correction to the electron spin-rotation coupling constant γ_D had to be included in the fit in order to reproduce the observed high-N spin doublings within experimental accuracy. The magnetic and quadrupole coupling constants $b_{\rm F}$, c, and eQq have been just slightly improved since only three new nonblended hyperfine component frequencies have been added to the data set.

4. Discussion

This paper extends to the submm-wave region the study of the rotational spectrum of SiN. Most of the lines observed in the present investigation span N values from 7 to 16; for these transitions the three $\Delta F = +1$ hyperfine components (accounting for the majority of the total line intensity) are very close in frequency and give rise to a single blended line. As a consequence, each $N + 1 \leftarrow N$ transition appears as a spin-doublet with a frequency separation of $\approx\gamma$. The hyperfine structure could be only resolved for the line $N = 5{-}4$, $J = 4.5{-}3.5$, occurring at ca. 218 GHz. This transition was observed in IRC+10216 by Turner (1992), but no hyperfine splittings could be resolved due to the large linewidth ($\Delta v = 29$ km s^{-1}) and the partial superposition with the $10_{0,10} - 9_{0,9}$ transition of ^{29}SiCC. The laboratory recording of the three $\Delta F = +1$ components of the $N = 5{-}4$, $J = 4.5{-}3.5$ transition is shown in Fig. 1.

The improved set of spectroscopic constants derived from the present analysis makes it possible to predict submm-wave line frequencies with uncertainties of a few tens of kHz in the Terahertz region; in comparison with previous results (Saito et al. 1983), the line position accuracy has been improved by more than two orders of magnitude. The present uncertainties evaluated at 1σ level in radial equivalent velocity are 3×10^{-3} km s^{-1} and 10^{-2} km s^{-1} at 600 GHz and 1 THz, respectively.

Table 3, available in electronic form at the CDS, presents a list of rest frequencies between 200 GHz and 1 THz calculated from the spectroscopic data of Table 2 including also the estimated uncertainty of each hyperfine component as determined statistically by the least-squares fit (Albritton et al. 1976) and the values of the corresponding line strengths S_{ij}, defined as

Table 1. Observed transition frequencies (MHz) and least-squares residuals (MHz) for SiN.

N'–N	J'–J	F'–F	observed	obs–calc
2–1	1.5–0.5	1.5–1.5	87045.357[a]	0.005
		2.5–1.5	87049.857[a]	0.011
		0.5–0.5	87076.960[a]	0.003
		1.5–0.5	87080.691[a]	0.011
	2.5–1.5	3.5–2.5	87559.811[a]	0.013
		2.5–1.5	87567.496[a]	0.051
		1.5–0.5	87571.654[a]	0.012
3–2	2.5–1.5	3.5–2.5	130707.096[a]	0.008
		2.5–1.5	130713.185[a]	0.020
		1.5–0.5	130716.834[a]	0.023
	3.5–2.5	4.5–3.5	131213.980[a]	0.042
		3.5–2.5	131217.196[a]	−0.014
		2.5–1.5	131219.097[a]	−0.018
4–3	3.5–2.5	4.5–3.5	174358.872[a]	0.032
		3.5–2.5	174361.453[a]	−0.001
		2.5–1.5	174363.374[a]	−0.055
	4.5–3.5	5.5–4.5	174864.893[a]	0.025
		4.5–3.5	174866.632[a]	−0.060
		3.5–2.5	174867.744[a]	−0.074
5–4	4.5–3.5	5.5–4.5	218006.406	0.012
		4.5–3.5	218007.848	−0.006
		3.5–2.5	218009.084	−0.011
8–7	7.5–6.5		348919.282	0.023
	8.5–7.5		349425.012	0.019
9–8	8.5–7.5		392544.001	−0.012
	9.5–8.5		393049.911	0.023
10–9	9.5–8.5		436161.117	0.011
	10.5–9.5		436667.143	−0.002
12–11	11.5–10.5		523368.898	−0.011
	12.5–11.5		523875.334	−0.009
13–12	12.5–11.5		566957.888	−0.030
	13.5–12.5		567464.574	−0.007
14–13	13.5–12.5		610535.863	−0.002
	14.5–13.5		611042.779	0.002
15–14	14.5–13.5		654101.914	0.014
	15.5–14.5		654609.064	−0.017
16–15	15.5–14.5		697655.180	0.007
	16.5–15.5		698162.639	−0.004
17–16	16.5–15.5		741194.835	0.002
	17.5–16.5		741702.626	0.015

[a] From Saito et al. (1983).

the square of the reduced matrix elements of the rotation matrix (Brown & Carrington 2003)

$$S_{ij} = \left|\langle N'J'F' \left\| \mathscr{D}^{(1)}_{\cdot q}(\omega)^* \right\| NJF\rangle\right|^2. \tag{6}$$

The intensity of a line in absorption can be obtained by multiplying the line strength S_{ij} by the square of the dipole moment μ, by the transition frequency and by the population factor of the lower level. The Einstein A-coefficients for spontaneous emission from state i to j can also be calculated from the line strengths by use of

$$A_{i\to j} = \frac{16\pi^3\nu_{ij}}{3\epsilon_0 hc^3}\frac{1}{2F_i+1}S_{ij}\mu^2. \tag{7}$$

SiN has proven to be an extremely elusive molecule for the astronomical detection in the ISM. However, models of "shock" or high-temperature chemistry often predict an increase in the abundance of silicon compounds, as a results of high temperature (Ziurys 1991); also grain destruction might aid in producing silicon and other refractory species. This property makes silicon-bearing molecules extremely sensitive and selective tracers for hot interstellar gas. Calculations of the spectral intensity for rotational temperature T_R ranging from 100 to 200 K, using a partition function $2(hB/kT)$, show that the optimal region for the observation of SiN spectrum occurs in the 500–750 GHz frequency interval ($\approx$500 μm). The high-accuracy rest frequencies provided by the present investigation may be of help in guiding the search for silicon nitride radical in this spectral region.

Table 2. Ground state spectroscopic constants of SiN[a].

Constant	Unit	This work	Saito et al. (1983)
B	MHz	21827.79116(42)	21827.7987(45)
D	kHz	35.4240(10)	35.44(17)
γ	MHz	505.029(11)	505.109(17)
γ_D	kHz	3.142(23)	
b_F	MHz	50.968(76)	50.95(12)[b]
c	MHz	94.483(85)	94.47(11)
eQq	MHz	3.047(73)	3.05(10)

[a] Standard uncertainties in units of the last quoted digits are given in parentheses. [b] Derived from the reported b and c constants through the relation $b_F = b + c/3$.

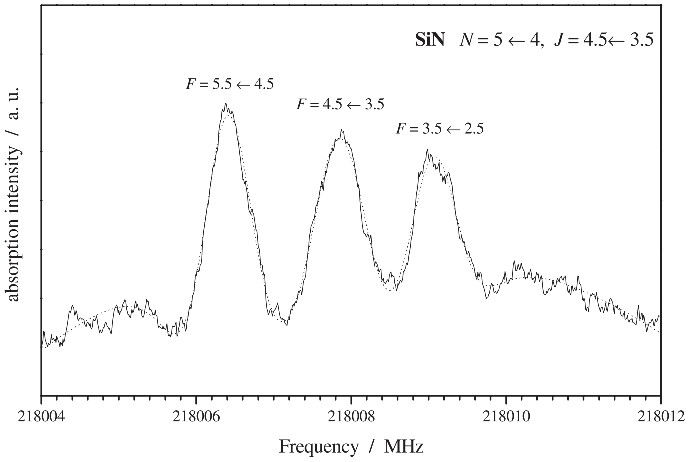

Fig. 1. Recording of the three $\Delta F = +1$ hyperfine components the $N = 5 \leftarrow 4$, $J = 4.5 \leftarrow 3.5$ transition. Their profile (continuous line) has been fitted to a model lineshape (dotted line) to recover the respective line positions.

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