Free Jet Millimeter Wave Torsion-Rotation Spectrum of a Silicon containing Molecule: Dimethylsilane

Andrea Maggio, Wentao Song, Assimo Maris, Luca Evangelisti, Sonia Melandri
Dipartimento di Chimica “Giacomo Ciamician”, Via Selmi 2 , I-40126 Bologna

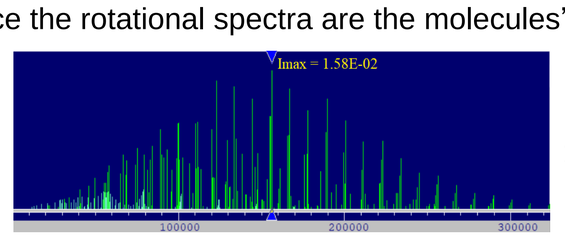
Introduction

More than 270 molecules have been identified in the interstellar and circumstellar regions; 14 of the molecules discovered so far are silicon-based.

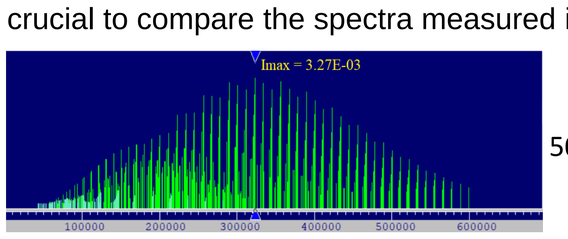
Relatively little is known about the chemistry of molecules containing silicon in the interstellar medium (ISM), so the identification of new species is fundamental for building theoretical models regarding their formation and reaction pathways.

The research of molecular species in the ISM requires the measure, analysis and modelization of the rotational spectra of the molecule itself.

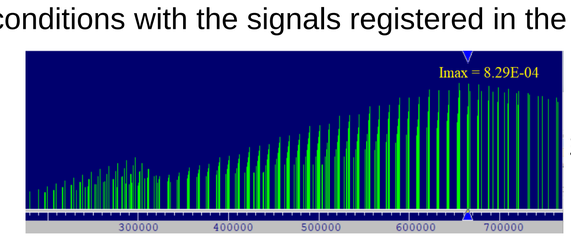
Since the rotational spectra are the molecules’ fingerprint, it is crucial to compare the spectra measured in standard conditions with the signals registered in the ISM.



10 K



50 K



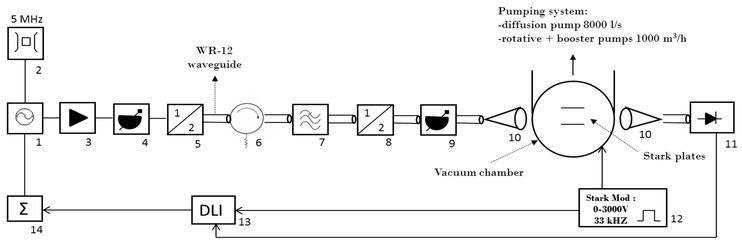
300 K

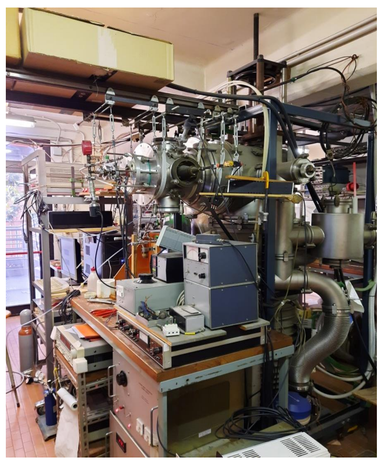
A reliable model allows for accurate prediction of transitions’ frequencies and intensities in different conditions, adaptable for the research in different astronomical objects, at different temperatures.

Methods

Free Jet Absorption MilliMeter (FJAMMW) Spectroscopy

Range: 60-78 GHz
Sweep rate: 5 GHz per day
Sensitivity: 10^{-7}-10^{-8} cm^{-1}
Resolution : 200 kHz
Accuracy of frequency measurements < 0.05 MHz.





Theoretical calculations

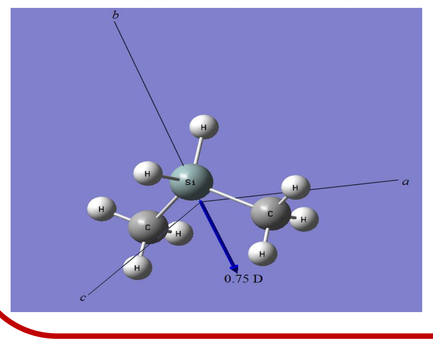
Quantum mechanical calculations were performed to predict the relative energies of plausible conformations and the molecular properties relevant to the interpretation of the rotational spectra. The Gaussian package of programs was used.

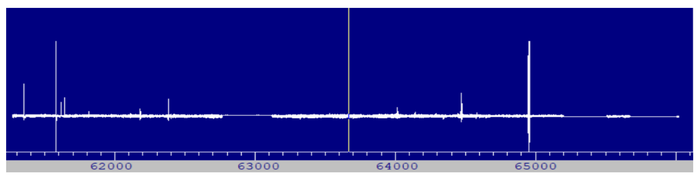
Programs employed

The CALPGM software[2] has been employed for the semirigid rotor fitting, while methyl internal rotation has been taken into account with the program XIAM[3].

Dimethylsilane

The isotopologues containing the isotopes ^{28}Si, ^{29}Si, ^{30}Si and ^{13}C were studied, recording the spectra in the frequencies region between 60 and 78 GHz, expanding the work conducted by Pierce et al.[1] in 1961 in the frequency region between 11.8 – 22.5 GHz.



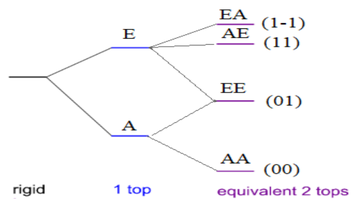


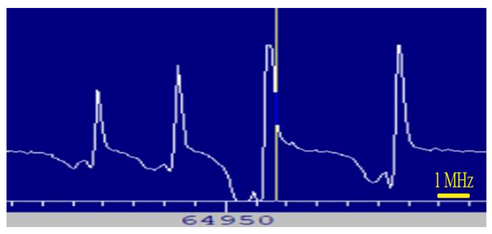
Spectra recorded in the frequency interval 61270-66022 MHz

.

Internal rotation

All the spectral lines observed were split in four components, labeled AA, EE, AE and EA according to simmetry, due to the effects of the internal rotation of the methyl groups.





Detail of the quartet of the $3_{22} \leftarrow 2_{11}$ transition of the species $(CH_3)_2{}^{30}SiH_2$.
From left to right, the components AE, EA, EE and AA can be observed.

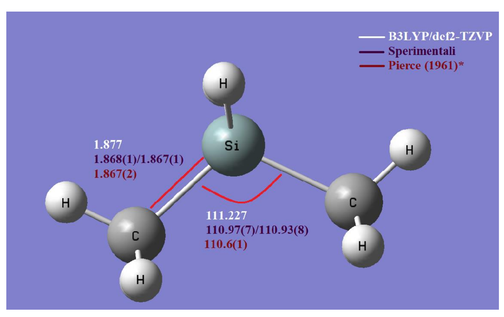
Results

A total of 180 lines, between all isotopologues, were measured, allowing the fitting of the rotational constants, the quartic centrifugal distortion constants and the internal rotation parameters.

	B3LYP/ def2TZVP	Pierce (1961)[1]	^{28}Si	^{29}Si	^{30}Si	^{13}C
A /MHz *B* /MHz *C* /MHz	16747.42 5889.63 4863.36	16754.24 5945.44 4896.50	16754.30(1) 5945.851(5) 4895.872(4)	16607.06(7) 5946.00(2) 4883.245(2)	16467.35(5) 5946.00(2) 4870.97(1)	16605.19(4) 5786.12(2) 4774.70(2)
D_J /kHz D_{JK} /kHz D_K /kHz	5.22 -35.81 0.17	-	5.22(4) -35.2(1) 162.9(4)	5.9(2) -33 (2) 163(8)	5.0(1) -34.7(3) 162(2)	[5.22] -31(1) 180(5)
d_J /kHz d_K /kHz	-1.68 -0.06	-	-1.735(6) -0.059(1)	[-1.735] [-0.059]	[-1.735] [-0.059]	[-1.735] [-0.059]
μ_b/D	0.75					
N	-	24	84	32	36	28
σ /MHz	-	-	0.059	0.124	0.093	0.078
F_0 /GHz	-	159.75	159.2(4)	[159.2]	[159.2]	[159.2]
V_3 /cm^{-1}	514	576(1)	573(1)	[573]	[573]	[573]
δ /rad	±0.600	-	±0.609(2)	[±0.609]	[±0.609]	[±0.609]
F /GHz	-	174.95	174.39	[174.39]	[174.39]	[174.39]
s	-	43.95	43.80	[43.80]	[43.80]	[43.80]

Structural Analysis

By studing different isotopologues it was possible to use the Kraitchman equations to derive the structural parameters.



Conclusions

With the determined model it is possible to make accurate predictions of frequencies and intensities of the rotational transitions up to 100 GHz (BAND 3 of ALMA), extending the spectral interval for astronomical investigations.

BAND	Frequency (GHz)	Wavelength (mm)
1	31.3-45	6.7-9.5
2	67-90	3.3-4.5
3	84-116	2.6-3.6
4	125-163	1.8-204
5	163-211	1.4-1.8
6	211-275	1.1-1.4
7	275-373	0.8-1.1
8	385-500	0.6-0.8
9	602-720	0.4-0.5
10	787-950	0.3-0.4

References

1. Pierce, L. (1961) J. Mol. Spectrosc. 34(2), 498-506.
2. Pickett, H. M. (1991) J. Mol. Spectrosc. 148, 371-377.
3. Hartwig, H. and Dreizler, H. (1996) *Z.* Naturforsch, 923-932.