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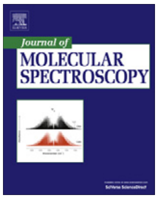

Spectroscopic parameters for silacyclopropynylidene, SiC_2, from extensive astronomical observations toward CW Leo (IRC +10216) with the *Herschel* satellite ☆,☆☆

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ABSTRACT

A molecular line survey has been carried out toward the carbon-rich asymptotic giant branch star CW Leo employing the HIFI instrument on board of the *Herschel* satellite. Numerous features from 480 GHz to beyond 1100 GHz could be assigned unambiguously to the fairly floppy SiC_2 molecule. However, predictions from laboratory data exhibited large deviations from the observed frequencies even after some lower frequency data from this survey were incorporated into a fit. Therefore, we present a combined fit of all available laboratory data together with data from radio-astronomical observations.

1. Introduction

Silacyclopropynylidene, SiC_2, somewhat better known as silicon dicarbide, is a fascinating molecule for spectroscopists, structural and quantum chemists as well as astronomers. In 1926, uncataloged bands near 500 nm were discovered in the spectra of several carbon-rich asymptotic giant branch (AGB) stars [1,2]. These are late-type stars which produce elements heavier than helium and which eject large quantities of gaseous material as well as dust which form a circumstellar envelope (CSE). Thirty years later, laboratory spectroscopy established that the molecule SiC_2 is the carrier of these bands [3]. It was assumed that the molecule has a linear SiCC structure (silapropadienediylidene) in analogy with the isoelectronic propadienediylidene, C_3. Although some later studies cast doubt on the linear structure of the molecule, it took almost another 30 years until the analysis of the rotational structure of the electronic origin band unmistakably determined the structure as silacyclopropynylidene [4]. In the course of their analysis, the authors instigated quantum chemical calculations which provided evidence that the cyclic isomer of SiC_2 may be lower in energy than the linear form [5].

A plethora of quantum chemical calculations on various properties of SiC_2 have been published later, yielding energy differences between the linear and the cyclic form which depended strongly on the level of the calculation and the size of the basis set. A high level ab initio calculation concluded that the cyclic isomer of SiC_2 is the only minimum on the potential energy surface and that the linear transition state is 24.3 kJ/mol higher in energy [6]. However, the authors attached a caveat to this value as an anharmonic force field calculation provided a much too small value for the vibrational energy of $\upsilon_3 = 1$ and much too large anharmonicity constants. Therefore, some of the authors revisited the problem of the energy difference between the two SiC_2 structures, the last time in 2003 when very high level calculations combined with very large basis sets, basis set extrapolation to infinite size as well as additional corrections yielded a value of 26.5 kJ/mol [7].

☆ We dedicate this work to the memory of Gisbert Winnewisser, a pioneer of *Herschel* and of astrochemistry.

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The SiC_2 molecular parameters obtained in Ref. [4] laid the foundation for progress in laboratory spectroscopy. The $J = 1 - 0$ rotational transition frequencies of the three isotopologs SiC_2,[1] $^{29}SiC_2$, and $^{30}SiC_2$, as well as the permanent electric dipole moment were measured using Fourier transform microwave spectroscopy [8]. Subsequently, 34 additional transition frequencies were measured for the main isotopic species between 93 and 370 GHz [9]. Even though a comparatively large number of 15 spectroscopic parameters of a standard Watson-type Hamiltonian in the *A*-reduction, all parameters up to sixth order, were employed in the fit, the transition frequencies were reproduced on average to only four times the experimental uncertainties.

Similarly large bodies of laboratory transition frequencies were obtained for $SiC^{13}C$ between 339 and 405 MHz [10] and, only very recently, for $^{29}SiC_2$ and $^{30}SiC_2$ between 140 and 360 GHz [11].

Higher excited vibrational states have been studied for the main isotopolog. Rotational transitions in its low-lying $\upsilon_3 = 1$ vibrational state between 186 and 399 GHz [12] and in $\upsilon_3 = 1$ and 2 were obtained between 140 and 400 GHz [13]. The symmetry of $\upsilon_3 = 1$ is b_2 and can be viewed as an asymmetric bending state which facilitates internal rotation of the C_2 unit with respect to the Si atom. Its vibrational energy has been determined as 196.37 cm^{-1} from an investigation into the laser-induced and the dispersed fluorescence of a jet-cooled sample of SiC_2 [14].

Several attempts have been made to model rotational and sometimes also rovibrational data to a varying extent and accuracy. A semirigid bender (SRB) Hamiltonian was employed [16] to reproduce $\upsilon_3 = 0$ and 1 rotational transition frequencies [9,12] as well as rovibrational data from their previous [14] and present work [16]. The analysis suggested that the linear configuration is not a local minimum, and the cyclic form is 22.5 kJ/mol lower than the linear form; the estimated uncertainty was 2.4 kJ/mol. They found the energy difference to be in good agreement with results from their own ab initio calculations; their highest level value being 21.8 kJ/mol. The reproduction of the vibrational data was reasonable, that of the rotational data was only qualitative and thus of no use for radio-astronomical purposes.

The $\upsilon_3 = 0$ and 1 state rotational data [9,12] were also modeled with a dedicated internal rotation Hamiltonian [15]. A greatly improved reproduction, within 1.5 times the experimental uncertainties, was achieved for the ground vibrational state, albeit at the expense of 16 spectroscopic parameters compared to 15 previously [9]. The barrier to linearity was derived as ~54 kJ/mol, more than twice the value from ab initio calculations of that time.

A reasonably successful result has been obtained by employing a conventional Watson-type Hamiltonian in the *S*-reduction [17]. The reproduction of the ground state rotational data [8,9] was converged after varying 17 spectroscopic and keeping one fixed. The data were reproduced on average as well as in the fit which employed an internal rotation Hamiltonian [15]; the number of varied parameters, however, was larger by still another one. After scaling of the parameters, the transition frequencies of $^{29}SiC_2$ and $^{30}SiC_2$ available at that time, mostly from astronomical observation [10,17], could be reproduced well after releasing only 5 spectroscopic parameters [17]; 13 parameter were released in the fit for $SiC^{13}C$ because of the large amount of accurate laboratory data [10].

The unambiguous assignment of a spectroscopic feature observed in space relies on reliable predictions which are usually based on laboratory data which, for the most part, have been obtained in approximately the same frequency domain. The predictions may also be based in part on data from astronomical observations, recent examples include $H^{13}CO^+$ [18], DCO^+ [19,20], DNC and $HN^{13}C$ [20], C_2H [21], and $C^{13}CH$ [22]. Sometimes, identifications are even possible in the absence of laboratory data, as demonstrated recently by the detection of C_5N^- in the CSE of CW Leo [23]. Frequencies have to be predicted with accuracies better than around one tenth of the line width to permit extraction of dynamical information. Some type of intensity information, such as that at a certain temperature, the line strength, or the Einstein *A*-value is needed as is additional auxiliary information such as quantum numbers, lower or upper state energies etc. Pickett's SPCAT and SPFIT programs [24] have been developed for that purpose and have evolved over time, see e.g. Ref. [25]. These programs are routinely used in the Cologne Database for Molecular Spectroscopy,[2] CDMS [26,27], to provide in its catalog section[3] predictions of (mostly) rotational spectra of molecules which may be found in various environments in space.

The spectroscopic parameters from the first rotational analysis of the electronic spectrum of SiC_2 [4] were accurate enough to identify nine unassigned emission features, previously observed between 93 and 171 GHz toward the carbon-rich AGB star CW Leo, also known as IRC +10216, as belonging to SiC_2 and improved the SiC_2 structural parameters [28]. Using the structural parameters from that work, the three $J = 4 - 3$, $\Delta K_a = 0$ transitions of $^{29}SiC_2$ and $^{30}SiC_2$ were detected toward the same source very soon thereafter [29]; two of these transitions were marginally detected for $SiC^{13}C$. Extensive sets of transition frequencies of $^{29}SiC_2$, $^{30}SiC_2$, and $SiC^{13}C$ were obtained from radio-astronomical observation between 90 and 241 GHz together with laboratory rest frequencies for the latter isotopolog [10].

Radio lines of SiC_2 have also been detected in the CSEs of other C-rich AGB stars, e.g. toward II Lup, which is also known as IRAS 15194-5115 [30]. However, SiC_2 features are particularly strong toward CW Leo, which, to a large extent, is due to its proximity to our Solar system. CW Leo has been studied extensively, and many molecular species, such as CN^- [31] and FeCN [32], have been detected toward its CSE exclusively or for the first time, including many Si-containing ones, such as SiCN and SiNC [33]. The source is a subject of observations in several key projects carried out with the recently launched *Herschel* satellite [34]. One of these projects is a molecular line survey carried out with the Heterodyne Instrument for the Far-Infrared (HIFI) [35]. This high-resolution instrument covers, in several bands, the 480–1250 and 1410–1910 GHz regions. A preliminary analysis of a lower frequency region (554–637 GHz) revealed that a rather small number of molecules account for a large fraction of the emission features [36]. These molecules are CS, SiO, SiS, HCN, and, in particular, SiC_2. Predictions of the rotational spectrum based on Ref. [17] turned out to be very good for transitions with higher values of K_a, but showed increasing deviations of up to 10 MHz for transitions with decreasing K_a, contrary to common expectations. A combined fit of these transitions frequencies together with those from laboratory spectra [8,9] required only one additional parameter [36] to reproduce the astronomical data within uncertainties, and the laboratory data about as well as before [17]. Predictions of the SiC_2 rotational spectrum based on these results are currently available as version 2 in the CDMS.[4] Since they were still not appropriate to predict the observed emission features satisfactorily to high frequencies (beyond 1100 GHz), we present here a combined fit using these as well as laboratory data, supplemented with data from additional astronomical observations.

2. Observed spectrum

Silacyclopropynylidene, SiC_2, is a triangular, fairly asymmetric rotor with $\kappa = (2B - A - C)/(A - C) = -0.7117$. Its dipole moment

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[1] Unlabeled atoms refer to ^{12}C and ^{28}Si.

[2] Internet address: http://www.astro.uni-koeln.de/cdms.

[3] Internet address: http://www.astro.uni-koeln.de/cdms/catalog.

[4] http://www.astro.uni-koeln.de/cgi-bin/cdmssearch?file=c052527.cat; see http://www.astro.uni-koeln.de/cgi-bin/cdmsinfo?file=e052527.cat for the documentation.