Excited Vibrational Level Rotational Constants for SiC$_2$: A Sensitive Molecular Diagnostic for Astrophysical Conditions

Ryan C. Fortenberry*

Georgia Southern University, Department of Chemistry, Statesboro, GA 30460, U.S.A.

Timothy J. Lee*

Mail Stop 245-1, NASA Ames Research Center, Moffett Field, California 94035-1000, U.S.A.

Holger S. P. Müller*

I. Physikalisches Institut, Universität zu Köln, Zülpicher Str. 77, 50937 Köln, Germany

Abstract

Silacyclopropynylidene, SiC$_2$, is a known and highly abundant circumstellar molecule. Its spectrum has been established as a major component of lines observed toward the carbon-rich star IRC +10216 (CW Leonis). It has been detected in its low-lying $v_3 = 1$ and 2 vibrational states as well as in various isotopic compositions. Increasing sensitivity and spatial resolution will enable many more emission or absorption lines to be detected. In order to detect new molecular species, unassigned lines of known species must be identified. This work uses established *ab initio* quartic force fields to produce data necessary for this classification of lines related to SiC$_2$. Agreement between the theoretical vibrational frequencies and known rotational and spectroscopic constants is quite good, as good as 5 cm^{-1} and 3 MHz, respectively in some cases. Additionally, experimentally unknown vibrational frequencies and rotational constants are provided for the first overtones and combination bands in addition to $3\nu_3$, the second overtone of the low-lying antisymmetric stretch/carbide rotation mode. Frequencies of $v_3 = 3$ low-J rotational transitions of the main isotopic species are also estimated from published data for $v_3 \leq 2$. Further, we determine rotational and centrifugal distortion parameters for which in most cases vibrational effects due to the ν_3 mode were reduced to first, and in several cases also to second order. These values may approximate equilibrium values better than the ground state values. The data produced herein will aid in the experimental and observational characterization of this known astromolecule in order to identify some of the unassigned lines for a known entity.

Keywords: Rovibrational spectroscopy; quartic force fields; quantum chemistry; silicon; astrochemistry

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*Corresponding author

Email addresses: `rfortenberry@georgiasouthern.edu` (Ryan C. Fortenberry), `timothy.j.lee@nasa.gov` (Timothy J. Lee), `hspm@ph1.uni-koeln.de` (Holger S. P. Müller)

1. Introduction

SiC$_2$ was first detected in space in 1984 by Thaddeus and coworkers [1]. This was followed shortly by Cernicharo and coworkers who detected the ^{29}Si, ^{30}Si, and single-^{13}C isotopologues all toward the carbon-rich star IRC+10216 [2, 3], the stellar target toward which a significant number of other astromolecules have been originally detected [4]. Employing the high-resolution HIFI instrument on board of the *Herschel Space Observatory*, emission lines caused by the molecule were observed even beyond 1 THz [5]. SiC$_2$ was also seen in the circumstellar envelopes of several other carbon-rich late-type stars [6]. Furthermore, SiC$_2$ was detected in its excited vibrational states $v_3 = 1$ and 2 [7, 8]. Such data can be used to study the dust formation zone of late type stars, as was done recently with highly excited HNC transitions [9] and even more highly excited HCN [10]. Excited state transitions of a rapidly growing number of molecules have been detected in star-forming regions, see, e.g., Ref. [11]. Detections of minor isotopologues of SiC$_2$ are largely possible in the pre-ALMA (Atacama Large Millimeter Array) era due to the significantly high abundance of this molecule [12]. The detection of such a common circumstellar species should have taken place earlier, but there was much controversy as to the lowest energy isomer of SiC$_2$. Experimental work on the electronic properties of this carbide ultimately showed that it is cyclic (or "T"-shaped, equivalently)[13] with later corroboration for this atomic-arrangement coming from high-level quantum chemical computations [14].

The ground state rotational spectrum of SiC$_2$ has been characterized quite well for the main and singly substituted isotopologs and for the main species in its excited $v_3 = 1$ and 2 excited states [1, 15, 3, 16–18, 5]. In addition, extensive vibrational and some rovibrational data are available for the main species [19–21]. However, with the dawn of more powerful instruments such as ALMA, the number of lines observed towards various celestial objects continues to grow. Since SiC$_2$ is known to exist in circumstellar media (CSM), it is an almost certainty that features related to other vibrationally excited states or even vibrationally excited states of other isotopologues are present in the observed spectra. Assignment of these lines is essential in order to limit the number of truly unidentified lines and not those unknown lines that correspond to a known astromolecule.

Quantum chemical analysis has long been viewed as a useful tool in the detection of new molecules in CSM going as far back as the 1970s [22]. In the intervening years, theoretical predictions of vibrational frequencies and spectroscopic constants have improved leading even leading to the detection of C$_5$N$^-$ in CSM without the use of experimentally-determined values [23]. The most consistent means of producing highly-accurate rovibrational data has utilized quartic force fields (QFFs), fourth-order Taylor series exapansions of the potential piece of the nuclear Hamiltonian and are of the form

$$V = \frac{1}{2}\sum_{ij}F_{ij}\Delta_i\Delta_j + \frac{1}{6}\sum_{ijk}F_{ijk}\Delta_i\Delta_j\Delta_k + \frac{1}{24}\sum_{ijkl}F_{ijkl}\Delta_i\Delta_j\Delta_k\Delta_l. \qquad (1)$$

The Δ_i, Δ_j, ... represent the displacements with respect to the symmetry-internal coordinates while $F_{ij...}$ are the force constants. Modern composite energy schemes [24–27] have been developed where the complete-basis set (CBS) limit energies are further corrected for core correlation, scalar relativity, and, often, higher-order electron correlation for every point on the surface defined from the Δ_is in Eq. 1. The hydride stretches, in

particular, have showed exceptionally good agreement with experiment getting as close as better than 1 cm^{-1} [26, 28–31]. Other fundamentals have been within 5-15 cm^{-1} with rotational constants often matching to within 15-20 MHz [27, 32, 33], especially for those cases where vibrational-averaging of the rotational constants is not as necessary [33, 34].

The unknown lines of the known SiC_2 need to be identified in order for their contributions to the spectrum of this star and other astronomical environments of interest to be removed. Additionally, since the ν_3 frequency is so low, SiC_2 can be used as a sensitive diagnostic to determine the physical conditions of a particular astronomical environment. Further insight into its spectrum must be produced in order for SiC_2 to function in such a manner. Due to the complexities of analyzing this molecule in the laboratory [14, 18], analysis of only the rovibrational nature of the ν_3, Si$-$C antisymmetric stretch, has been attempted [17, 20] beyond the pure rotational transitions in the vibrational ground state. The present study brings to light more of the full rovibrational nature of SiC_2 for the vibrational fundamentals, the two-quanta modes, and $3\nu_3$ in the standard istopologue as well as that for $^{29}SiC_2$ and $SiC^{13}C$.

2. Computational Details

The coupled cluster singles, doubles, and perturbative triples [CCSD(T)] method [35] along with the restricted Hartree-Fock reference [36] are used for all of the computations. When the aug-cc-pVXZ basis set family is utilized for the carbon atoms, the reader should understand that the aug-cc-pV(X+d)Z sets are employed for the silicon atoms [37–39].

The geometries are optimized at the 5ζ level with further modifications coming from core electron correlation. The difference in the optimized geometric parameters computed from the Martin-Taylor core correlating [40] basis set for one structure computed with core electrons frozen and one without is added to the aug-cc-pV5Z results. This reference geometry is then displaced by 0.5 pm for the bond lengths and 0.005 radians for the bond angle by way of the following coordinates:

$$S_1(a_1) = \frac{1}{\sqrt{2}}[(Si - C_1) + (Si - C_2)] \tag{2}$$

$$S_2(a_1) = \angle(C_1 - Si - C_2) \tag{3}$$

$$S_3(b_1) = \frac{1}{\sqrt{2}}[(Si - C_1) - (Si - C_2)] \tag{4}$$

to create 69 symmetry-unique points. At each point on the constructed geometry grid, the three-point extrapolated [41] CCSD(T)/aug-cc-pVXZ (X=T, Q, 5) CBS energy is further corrected once more for core correlation as well as scalar relativity [42]. The latter correction is additive for the difference between the inclusion of relativistic effects within the cc-pVTZ-DK basis and the exclusion of relativity within the same basis set. This creates the so-called CcCR QFF with terms for the CBS energy ("C"), core correlation ("cC"), and relativity ("R") [27]. All electronic structure computations make use of the MOLPRO 2012.1 quantum chemistry program [43].

A fitting of the points via a least-squares formula determines the minimum, equilibrium geometry. Refitting the points guarantees zero gradients and properly described force constants. The symmetry-internal coordinate force constants are transformed [44]

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into Cartesian coordinates via the INTDER program [45] for subsequent analysis. Vibrational second-order perturbation theory (VPT2) [46, 47] and rotational second-order perturbation theory [48] produce the vibrational frequencies and A-reduced Hamiltonian spectroscopic constants through the SPECTRO program [49]. SPECTRO requires input of the resonances, but this small system only possesses a $2\nu_2 = \nu_1$ type-1 Fermi resonance in all of its examined isotopolgoues.

3. Results and Discussion

3.1. Vibrational Frequencies

Table 1 contains the 19 CcCR force constants produced for SiC_2. Since the potential is constructed within the Born-Oppenheimer approximation, the QFF remains the same for each isotopologue. The vibrational frequencies are presented in Table 2. The correspondence between the standard isotopologue fundamental vibrational frequencies and the experimental values reported in the literature is quite good, especially for non-hydride motions. The CcCR ν_1 C−C stretch at 1750.5 cm^{-1} differs from experiment [20] at 1746.0 cm^{-1} by less than 5 cm^{-1}. The experimental ν_2 Si−C symmetric stretch has slightly better and still excellent agreement with the theoretical 844.7 cm^{-1} value 4.1 cm^{-1} higher. The CcCR ν_3 antisymmetric stretch at 175.4 cm^{-1} is lower than experiment at 196.37 cm^{-1}. Even though a difference of 21.0 cm^{-1} is not ideal for such a low frequency mode, it is a significant improvement over previous harmonically computed values [14]. The CcCR harmonic frequency is actually closer to experiment in this case, but that is not a systematic result.

Since experimental data are not available for the other isotopologues of SiC_2 discussed here, the CcCR frequencies for the fundamental modes of these other molecules can be scaled from the theoretical comparison to experiment of the known modes. These are given in the "Experiment" section of Table 2. The relative masses do not change significantly in moving from ^{12}C to ^{13}C and certainly when moving from ^{28}Si to ^{29}Si indicating that such a procedure should be fairly robust. Explicitly, the differences between the CcCR fundamentals and experiment in standard SiC_2 are added to the other isotopologues' respective frequencies to produce an estimate of what the experimental results should be. It can be inferred, therefore, that ν_1 and ν_3 will not change much for ^{29}SiC$_2$ as compared to standard SiC_2, and ν_2 will likely drop by 6 cm^{-1}. The changes are more extreme for $SiC^{13}C$ since the relative mass differences are greater between isotopes of carbon, but ν_2 and ν_3 only decrease by 10.4 cm^{-1} and 2.8 cm^{-1}, respectively, compared to the standard isotopologue. The ν_1 mode, however, decreases to 1712.7 cm^{-1}, a shift of 33.3 cm^{-1} from the standard form.

Additionally, the two quanta mode frequencies, both overtones and combination bands, are also provided in Table 2 in addition to $3\nu_3$. The correlation to experiment here for the known $2\nu_3$ is not exceptional where the CcCR 296.9 cm^{-1} frequency is proportionately significantly less than the experimental 352.85 cm^{-1} value determined previously for SiC_2 [20]. However, this is largely the result of a compounding of errors from the one-quantum mode manifesting itself to a greater degree in the present overtone. Similar behavior is known [44] and highlights the need for high-accuracy in the fundamentals. The ν_1 and ν_2 modes are much more accurate than ν_3 indicating that the overtones associated with these CcCR mode frequencies should be more accurate, as

well. Indeed, this is the case. The $2\nu_1$ CcCR frequency at 3476.2 cm^{-1} is 10.4 cm^{-1} above experiment, and $2\nu_2$ at 1683.5 cm^{-1} is 15.7 cm^{-1} above. The combination bands will also be affected by the VPT2 treatment of ν_3 in a related way with those bands involving ν_3 being likely less accurate than the $\nu_1 + \nu_2$ band. The latter is computed to be 2591.9 cm^{-1}, again above the 2579.2 cm^{-1} experimental value. From these comparisons, scalings of the combination bands and overtones for the ^{29}SiC$_2$ and SiC^{13}C isotopologues are again provided in order to give some expected experimental values for these frequencies.

3.2. Rotational and Centrifugal Distortion Parameters

The geometries, spectroscopic constants, and vibration-rotation interaction constants are provided for this same set of SiC$_2$ isotopologues in Table 3. Vibrational averaging (R_α) the geometries leads to unique shifts in each isotopologue. However, the Si$-$C bond length is always lengthened by roughly 1.3 pm to a fairly long 184.3761 pm bond distance between the silicon atom and either of the carbons in SiC$_2$. The unbalanced nature of the SiC^{13}C isotopologue produces two bond lengths that bookend around the standard SiC$_2$ value. The bond angle decreases for the zero-point structure to 40.309° for SiC$_2$ and ^{29}SiC$_2$ and to 40.313° for SiC^{13}C. Even though the C$-$C bond is redundant with these geometric parameters, it is reported here, 127.0543 pm for SiC$_2$, in order to provide a straightforward picture of this molecule and to highlight the difference of the C$\equiv$C bond over either of the much longer Si$-$C bonds. The atomic arrangement is very similar to that found in 1 $^2B_1$ CCSiN, where the silicon atom has been nitrogenated in the same cyclic SiC$_2$ construction [50].

Except for the rotational constants, the spectroscopic parameters produced in Table 3 are all computed at the equilibrium level meaning that the current potential surface is not manipulated to produce spectroscopic constants for vibrationally excited modes. Even so, the CcCR A-reduced Hamiltonian constants give fairly good agreement with with experimental ground state values [15, 3, 17, 18, 5]. All of the Δ_Js (which are not to be confused with the QFF displacements of Δ_j) are within 2.0 kHz of experiment. The Δ_K values are not quite as robust, but the worst CcCR values are still within 40 % or so, which is only 0.6 MHz in these ranges. The other quartic terms are equally reliable as the Δ_J values across the isotopologues with δ_j correlating nicely in each case between theory and experiment. The sextic term, Φ_J, differs considerably throughout, but it is a rather small value. Φ_K is difficult to determine in a rotational spectrum of a near-prolate asymmetric top rotor with a-type selection rules. Therefore, it is hard to draw any conclusion from the deviation between the calculated and measured values for the SiC^{13}C species.

The vibrationally-averaged vibrational ground and excited state rotational constants, however, perform much better and provide useful, novel insight into other states for potential observation in CSM. The C values give excellent agreement with experiment. For instance, the standard isotopologue's C_0 of 10 444.75 MHz is within 3.2 MHz of experiment at 10 442.619 MHz [15]. B_0 is within 14 MHz at 13 145.82 MHz, but A_0 gives the poorest correlation to experiment being 128.79 MHz higher than experiment at 52 602.45 MHz. However, these values bring the spectrum for this state within focus. Similar behavior and differences are also produced for these principle rotational axes constants for ^{29}SiC$_2$ and SiC^{13}C. The known ν_3 vibrationally-excited rotational constants vary from experiment in similar ways with differences of 117.54 MHz, 25.49 MHz, and

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-8.71 MHz, respectively for A_3, B_3, and C_3. Hence, the overcorrection for anharmonicity within the ν_3 fundamental and $2\nu_3$ overtone is not forcing the errors for these constants to skew in as an extreme fashion. An equivalent scaling scheme as that done for the vibrational frequencies is also done here for the A_3, B_3, and C_3 constants of the other two isotopologues to produce expected experimental rotational constants for those molecular systems, as well. Since each fundamental behaves uniquely, similar scaling is not possible for the rotational constants of the combination bands.

In order to produce as much useful data for the identification of the relatively less populated circumstellar lines of SiC_2, the rotational constants for the two quanta vibrationally excited modes as well as $3\nu_3$ are given in Table 4. For a given vibrational state, the rotational constants behave qualitatively the same as they do for the ground and fundamental vibrational states across the isotopologues. Comparison to experiment [17] for the $2\nu_3$ bands corroborates this statement. Granted, the values correlate less well with experiment since the vibrational-averaging can compound inaccuracies, but these data will enhance astronomically-minded studies of this molecule. The $SiC^{13}C$ $v_1 = 2$ A constant is the smallest of the set for its class. Increasing levels of vibrational excitation decrease the ν_3 B and C rotational constants systematically while A increases. Furthermore, it appears as though the errors for rotational constants computed here for the higher overtones of the ν_3 mode increase with higher quanta. The $\nu_3 = 1$ B-type constant, for example, is more than 35 MHz less than exmperiment. For the $\nu_3 = 2$ B-type constant, this discrepancy increases to 54.45 MHz. Hence, the $\nu_3 = 3$ B-type constant will likely fall in the 12 680 MHz range with similar expectations of roughly 56 250 MHz for A and 9 810 MHz for C. The combination bands' constants typically fall close to the average of the first overtones for the two composing modes indicating that the rotational constants' predictions for these vibrational states are also viable. As such, all of the reported rotational constants are behaving as expected and should correlate with laboratory experiment with an eye toward radioastronomical observation. Additionally, further analyses using these computed results also provides more insight into the rovibrational nature of SiC_2.

3.3. Estimation of Rotational Transition Frequencies of SiC_2 with $v_3 \geq 3$

One motivation for the present investigation is estimating frequencies of SiC_2 for the rotational transitions in excited vibrational states with $v_3 \geq 3$ for which no accurate predictions are available. Even the current CcCR results degrade quickly for this mode and its overtones due to the non-linearity of the anharmonicity in more highly excited vibrational states. Extrapolation from the known $v_3 \leq 2$ data is one possible solution to provide the rotational data for these states.

$$P_v = P_{ne} + \sum_i (v_i + 1/2)\, D_i^1(P) + \sum_{i,j} (v_i + 1/2)(v_j + 1/2)\, D_{ij}^2(P) + ... \qquad (5)$$

with P_v being a parameter in an excited state v, P_{ne} the corresponding (near-) equilibrium parameter, $D_i^1(P)$, $D_{ij}^2(P)$, etc. are first, second, etc. order vibrational corrections to the parameter, and the v_i, v_j etc. with $1 \leq i \leq J \leq 3$ are the excitations of the vibrational quanta. Ideally, P_{ne} would be the equilibrium parameter and $D_i^1(P) \equiv -\alpha_i(P)$, $D_{ij}^2(P) \equiv \gamma_{ij}(P)$, etc. With vibrational corrections for most of the parameters only available for $v_3 = 1$ and 2, the P_{ne} may only be near equilibrium values. If the vibrational

corrections for the ν_3 mode only are larger in magnitude than all other vibrational corrections and if Eq. 5 is a reasonable approximation, the P_{ne} are better approximations to the equilibrium values than the ground state parameters P_0. It should be pointed out that even if Eq. 5 is a good approximation for lower vibrational states, it will fail as the excitation in ν_3 gets closer to the barrier to linearity.

Ground state rotational transitions and parameters are from Ref. [5]. The $v_3 = 1$ rotational transitions are from Ref. [16] as reported. Additional $v_3 = 1$ and 2 data are taken from Ref. [17] with estimated uncertainties of 30 and 50 kHz, respectively. The ν_1 and ν_2 vibrational corrections to the rotational parameters are the CcCR values from Table 3. Vibrational corrections $D_3^1(P)$ and $D_{33}^2(P)$ are based on previous fits [17]. Because of the floppiness of the SiC$_2$ molecule, rather large sets of distortion parameters are needed to to obtain a satisfactory fit [3, 16, 17, 12, 18, 5], and the changes from the ground state parameters to those of $v_3 = 1$ and 2 are known to be rather large [16, 17]. The final spectroscopic parameters are given in Table 5 together with the ground state values [5].

The near equilibrium rotational parameters should be very close to the equilibrium values because of the use of the *ab initio* α_1 and α_2 values even though some higher order contributions may not be negligible. Similarly, the D_3^1 corrections to the rotational parameters should be close to $-\alpha_3$ values. Contributions from γ_{13} and γ_{23} as well as even higher order contributions may again be not negligible. Possibly the largest contributions arise from the neglect of D_{333}^3. It is likely positive, and its magnitude may well be several MHz. Assuming $D_{333}^3(A) = 14$ MHz in a trial fit, $D_{33}^2(A)$ is reduced to $\sim$121 MHz, $D_3^1(A)$ is increased to $\sim$507 MHz, and A_{ne} is decreased to $\sim$52206 MHz.

Even though $A_3 - A_0 = 1293$ MHz is much larger than the calculated value of $-\alpha_3^A = 1054$ MHz, $D_3^1(A) = 926$ MHz is actually considerably smaller. This is in line with the ν_3 fundamental being calculated somewhat too low. In addition, $D_3^1(B)$ and $D_3^1(C)$ are closer to the calculated values of $-\alpha_3^B$ and $-\alpha_3^C$, respectively, rather than $B_3 - B_0$ and $C_3 - C_0$. It is remarkable that, with the exception of Δ_J, none of the near equilibrium centrifugal distortion parameters in Table 5 is closer to the *ab initio* equilibrium values than the ground state values. However, the good agreement between *ab initio* equilibrium distortion parameters and experimental ground state values is possibly a consequence of the fortuitous agreement between the *ab initio* value for ω_3 and the experimental ν_3 value.

In fact, Izuha et al. use a simplified model to show that the large vibrational changes in Δ_K, Δ_{JK}, and δ_K are caused at least to a great extent by the anharmonicity of the low-lying ν_3 mode [17]. Therefore, we are quite confident that the near equilibrium quartic distortion parameters are a much better approximation to the equilibrium values than the ground state values. It is quite possible that the sextic and higher distortion parameters behave in a similar fashion, in particular those dependent most strongly on K. However, the rather large magnitudes of some of the D_3^1 and D_{33}^2 could be a consequence of the small data sets of $v_3 = 1$ and even more so $v_3 = 2$. Furthermore, it is possible that Eq. 5 is not a good approximation for deriving vibrational contributions to the sextic and higher distortion parameters even though this appears to be the case for the rotational and quartic distortion parameters. It should be noted that Ross et al. employed a model that is able to account for states highly excited in v_3 [21]. Their model reproduced the vibrational data quite well, but performed poorly for the pure rotational data.

We use the parameters in Table 5 with their uncertainties and correlations to cal-

culate low-J rotational transition frequencies of SiC_2 in its $v_3 = 3$ excited vibrational state because these transitions have intrinsically the smallest uncertainties. Moreover, low-J transition frequencies are probably not as much affected by the missing higher order corrections than higher-J transition frequencies are. Finally, molecular beam Fourier transform microwave or millimeter wave spectroscopy combined with electric discharge is a powerful tool to generate molecules in higher excited vibrational states [51–54]. For convenience, we have also calculated two low-J transitions of $v_3 = 2$ and 4. The transitions are gathered in Table 6. More extensive calculations are or will be available in the Cologne Database for Molecular Spectroscopy, CDMS[1] [55]. Data for $v_3 \leq 2$ are in the catalog section[2] while the $v_3 = 3$ and 4 predictions as well as the associated line, parameter, and fit files are in the catalog archive section[3]. The $v_2 = 2$ data are extrapolations to lower quantum numbers and should thus be very reliable. The calculated uncertainties for $v_3 = 3$ and 4 transition frequencies should be taken with considerable caution. The true uncertainties may well be larger than a factor of 10 or more. However, a value of $D^3_{333}(A)$ as discussed above has a negligible effect on the transition frequencies in Table 6. More lines for most of the vibrational levels, especially $v_3 = 3$ and 4, will be provided in the CDMS.

4. Conclusions

In order to find new molecules in CSM, fainter lines associated with known, more populous species, such as SiC_2 must be identified. Additionally, since the antisymmetric stretching mode and its overtones are so low-lying, thermal populations detected through rovibrational spectra can provide a probe for physical conditions in which this abundant circumstellar molecule is found. In this work, the two-quanta vibrational frequencies (and $v_3 = 3$) of SiC_2, $^{29}SiC_2$, and $SiC^{13}C$ are determined as well as their associated rotational constants. Comparison to experiment for the known ground vibrational state values and those from the ν_3 fundamental give good agreement showing a range for the aforementioned predicted values of the vibrationally-excited frequencies. The anharmonicity of the ν_3 mode is over corrected within VPT2, but the higher frequency ν_1 and ν_2 modes exhibit differences between theory and experiment of less than 5 cm^{-1}. As such, the higher vibrationally excited states should be well-described here. The rotational constants associated with all of the vibrational states for which data are experimentally known are consistent across isotopologues and do not appear to be greatly affected by other inaccuracies in the associated frequencies themselves. Hence, the ν_1, ν_2, $2\nu_1$, $2\nu_2$, and $\nu_1 + \nu_2$ vibrational frequencies will certainly assist in infrared spectroscopic analyses from instruments such as those on the Stratospheric Observatory for Infrared Astronomy (SOFIA). Furthermore, the rotational spectroscopic constants computed for these modes as well as the newly determined rotational data for the $v_3 \leq 3$ states provided give fresh spectral predictions for more of the vibrationally-excited modes present in this abundant molecule. Such insights will help to resolve the spectra of ALMA and other, modern radioastronomical tools so that other species may be found or the astrophysical conditions of certain environments may be probed.

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[1] http://www.astro.uni-koeln.de/cdms/
[2] http://www.astro.uni-koeln.de/cdms/entries
[3] http://www.astro.uni-koeln.de/site/vorhersagen/catalog/archive/SiC2/

5. Acknowledgements

[1] Thaddeus, P.; Cummins, S. E.; Linke, R. A. *Astrophys. J.* **1984**, *283*, L45–L48.

[2] Cernicharo, J.; Kahane, C.; Gomez-Gonzalez, J.; Guélin, M. *Astron. Astrophys.* **1986**, *267*, L9–L12.

[3] Cernicharo, J.; Guélin, M.; Kahane, C.; Bogey, M.; Demuynck, C. *Astron. Astrophys.* **1991**, *246*, 213–220.

[4] McCarthy, M. C.; Thaddeus, P. *Chem. Soc. Rev.* **2001**, *30*, 177–185.

[5] Müller, H. S. P.; Cernicharo, J.; Agúndez, M.; Decin, L.; Encrenaz, P.; Pearson, J. C.; Teyssier, D.; Waters, L. B. F. M. *J. Mol. Spectrosc.* **2012**, *271*, 50–55.

[6] Nyman, L.-Å.; Olofsson, H.; Johansson, L. E. B.; Booth, R. S.; Carlström, U.; Wolstencroft, R. *Astron. Astrophys.* **1993**, *269*, 377–389.

[7] Gensheimer, P. D.; Snyder, L. E. *Astrophys. J.* **1997**, *490*, 819–822.

[8] Patel, N. A.; Young, K. H.; Gottlieb, C. A.; Thaddeus, P.; Wilson, R. W.; Menten, K. M.; Reid, M. J.; McCarthy, M. C.; Cernicharo, J.; He, J. H.; Brünken, S.; Trung, D.-V.; Keto, E. *Astrophys. J. Suppl. Ser.* **2011**, *193*, 17.

[9] Cernicharo, J.; Daniel, F.; Castro-Carrizo, A.; Agundez, M.; Marcelino, N.; Joblin, C.; Goicoechea, J. R.; Guélin, M. *Astrophys. J.* **2013**, *778*, L25.

[10] Cernicharo, J.; Agúndez, M.; Kahane, C.; Guélin, M.; Goicoechea, J. R.; Marcelino, N.; De Beck, E.; Decin, L. *Astron. Astrophys.* **2011**, *529*, L3.

[11] Belloche, A.; Müller, H. S. P.; Menten, K. M.; Schilke, P.; Comito, C. *Astron. Astrophys.* **2013**, *559*, 47.

[12] He, J. H.; Dinh-V-Trung,; Kwok, S.; Müller, H. S. P.; Zhang, Y.; Hasegawa, T.; Peng, T. C.; Huang, Y. C. *Astrophys. J.* **2008**, *177*, 275–325.

[13] Michalopoulos, D. L.; Geusic, M. E.; Langridge-Smith, P. R. R.; Smalley, R. E. *J. Chem. Phys.* **1984**, *80*, 3556–3560.

[14] Nielsen, I. M. B.; Allen, W. D.; Császár, A. G.; Schaefer, III, H. F. *J. Chem. Phys.* **1997**, *107*, 1195–1211.

[15] Gottlieb, C. A.; Vrtilek, J. M.; Thaddeus, P. *Astrophys. J.* **1989**, *349*, L29–L32.

[16] Bogey, M.; Demuynck, C.; Destombes, J. L.; Walters, A. D. *Astron. Astrophys.* **1991**, *247*, L13–L16.

[17] Izuha, M.; Yamamoto, S.; Saito, S. *J. Mol. Spectrosc.* **1994**, *50*, 1371–1378.

[18] Kokkin, D. L.; Brünken, S.; Young, K. H.; Patel, N. A.; Gottlieb, C. A.; Thaddeus, P.; McCarthy, M. C. *Astrophys. J. Suppl. Ser.* **2011**, *196*, 17.

[19] Shepherd, R. A.; Graham, W. R. M. *J. Chem. Phys.* **1988**, *88*, 3399–3401.

[20] Butenhoff, T. J.; Rohlfing, E. A. *J. Chem. Phys.* **1991**, *95*, 1–8.

[21] Ross, S. C.; Butenhoff, T. J.; Rohlfing, E. A.; Rohlfing, C. M. *J. Chem. Phys.* **1994**, *100*, 4110–4126.

[22] Guélin, M.; Green, S.; Thaddeus, P. *Astrophys. J.* **1978**, *224*, L27–L30.

[23] Cernicharo, J.; Guèlin, M.; Agundez, M.; McCarthy, M. C.; Thaddeus, P. *Astrophys. J.* **2008**, *688*, L83–L86.

[24] Huang, X.; Lee, T. J. *J. Chem. Phys.* **2008**, *129*, 044312.

[25] Huang, X.; Lee, T. J. *J. Chem. Phys.* **2009**, *131*, 104301.

[26] Huang, X.; Taylor, P. R.; Lee, T. J. *J. Phys. Chem. A* **2011**, *115*, 5005–5016.

[27] Fortenberry, R. C.; Huang, X.; Francisco, J. S.; Crawford, T. D.; Lee, T. J. *J. Chem. Phys.* **2011**, *135*, 134301.

[28] Fortenberry, R. C.; Huang, X.; Francisco, J. S.; Crawford, T. D.; Lee, T. J. *J. Chem. Phys.* **2012**, *136*, 234309.

[29] Fortenberry, R. C.; Huang, X.; Francisco, J. S.; Crawford, T. D.; Lee, T. J. *J. Phys. Chem. A.* **2012**, *116*, 9582–9590.

[30] Huang, X.; Fortenberry, R. C.; Lee, T. J. *J. Chem. Phys.* **2013**, *139*, 084313.

[31] Zhao, D.; Doney, K. D.; Linnartz, H. *Astrophys. J. Lett.* **2014**, *791*, L28.

[32] Fortenberry, R. C.; Huang, X.; Francisco, J. S.; Crawford, T. D.; Lee, T. J. *J. Chem. Phys.* **2011**, *135*, 214303.

[33] Fortenberry, R. C.; Huang, X.; Crawford, T. D.; Lee, T. J. *Astrophys. J.* **2013**, *772*, 39.

[34] Botschwina, P.; Stein, C.; Sebald, P.; Schröder, B.; Oswald, R. *Astrophys. J.* **2014**, *787*, 72.

[35] Raghavachari, K.; Trucks., G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479–483.

[36] Scheiner, A. C.; Scuseria, G. E.; Rice, J. E.; Lee, T. J.; Schaefer III, H. F. *J. Chem. Phys.* **1987**, *87*, 5361–5373.

[37] Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007–1023.

[38] Peterson, K. A.; Dunning, T. H. *J. Chem. Phys.* **1995**, *102*, 2032–2041.

[39] Kendall, R. A.; Dunning, T. H.; Harrison, R. J. *J. Chem. Phys.* **1992**, *96*, 6796–6806.

[40] Martin, J. M. L.; Taylor, P. R. *Chem. Phys. Lett.* **1994**, *225*, 473–479.

[41] Martin, J. M. L.; Lee, T. J. *Chem. Phys. Lett.* **1996**, *258*, 136–143.

[42] Douglas, M.; Kroll, N. *Ann. Phys.* **1974**, *82*, 89–155.

[43] Werner, H.-J. et al. MOLPRO, version 2010.1, a Package of *Ab Initio* Programs. 2010; see http://www.molpro.net.

[44] Fortenberry, R. C.; Huang, X.; Yachmenev, A.; Thiel, W.; Lee, T. J. *Chem. Phys. Lett.* **2013**, *574*, 1–12.

[45] Allen, W. D.; coworkers, 2005; *INTDER* 2005 is a General Program Written by W. D. Allen and Coworkers, which Performs Vibrational Analysis and Higher-Order Non-Linear Transformations.

[46] Watson, J. K. G. In *Vibrational Spectra and Structure*; During, J. R., Ed.; Elsevier: Amsterdam, 1977; pp 1–89.

[47] Papousek, D.; Aliev, M. R. *Molecular Vibration-Rotation Spectra*; Elsevier: Amsterdam, 1982.

[48] Mills, I. M. In *Molecular Spectroscopy - Modern Research*; Rao, K. N., Mathews, C. W., Eds.; Academic Press: New York, 1972; pp 115–140.

[49] Gaw, J. F.; Willets, A.; Green, W. H.; Handy, N. C. In *Advances in Molecular Vibrations and Collision Dynamics*; Bowman, J. M., Ratner, M. A., Eds.; JAI Press, Inc.: Greenwich, Connecticut, 1991; pp 170–185.

[50] Fortenberry, R. C.; Crawford, T. D. *J. Phys. Chem. A* **2011**, *115*, 8119–8124.

[51] Sanz, M. E.; McCarthy, M. C.; Thaddeus, P. *J. Chem. Phys.* **2005**, *122*, 194319.

[52] Thorwirth, S.; Theulé, P.; Gottlieb, C. A.; Müller, H. S. P.; McCarthy, M. C.; Thaddeus, P. *J. Mol. Struct.* **2006**, *795*, 219–229.

[53] Müller, H. S. P.; Spezzano, S.; Bizzocchi, L.; Gottlieb, C. A.; Degli Esposti, C.; McCarthy, M. C. *J. Phys. Chem. A* **2013**, *117*, 13843–13854.

[54] Nakajima, M.; Yue, Q.; Li, J.; Guo, H.; Endo, Y. *Chem. Phys. Lett.* **2015**, *621*, 129–133.

[55] Müller, H. S.; Schlöder, F.; Stutzki, J.; Winnewisser, G. *J. Mol. Struct.* **2005**, *742*, 215227.

Table 1: The CcCR SiC$_2$ Quadratic, Cubic, and Quartic Force Constants (in mdyn/Å^n·rad^m)^a

F_{11}	4.934 546	F_{222}	−373.7634	F_{2221}	500.18
F_{21}	8.403 810	F_{331}	−3.5127	F_{2222}	3389.16
F_{22}	33.591 149	F_{332}	24.2760	F_{3311}	5.03
F_{33}	0.260 039	F_{1111}	40.86	F_{3321}	−89.82
F_{111}	−15.8590	F_{2111}	31.96	F_{3322}	−377.71
F_{211}	−19.3025	F_{2211}	105.59	F_{3333}	126.57
F_{221}	−74.6250				

^{a}Defined in terms of the coordinate system given in the Computational Details.

Table 2: The CcCR QFF Harmonic and Anharmonic (VPT2) Vibrational Frequencies (in cm^{-1}) for SiC$_2$, ^{29}SiC$_2$, and SiC^{13}C.

Molecule	Description	Mode	Harmonic	Anharmonic	Experiment[a]
SiC$_2$	a_1 C$-$C stretch	ν_1	1781.9	1750.5	1746.0[b]
	a_1 Si$-$C stretch	ν_2	815.1	844.7	840.6[b]
	b_1 antisymm. stretch	ν_3	201.4	175.4	196.37[b]
	Zero-point Energy	ν_0	1399.2	1391.2	
		$2\nu_1$	3563.8	3476.2	3465.8[b]
		$2\nu_2$	1630.2	1683.5	1667.8[b]
		$2\nu_3$	402.8	296.9	352.85[c]
		$3\nu_3$	604.2	364.6	487.2[b]
		$\nu_1 + \nu_2$	2597.0	2591.9	2579.2[b]
		$\nu_1 + \nu_3$	1983.3	1908.9	1925[b]
		$\nu_2 + \nu_3$	1016.5	1091.9	1072.2[b]
^{29}SiC$_2$	a_1 C$-$C stretch	ν_1	1782.0	1750.4	1745.9
	a_1 Si$-$C stretch	ν_2	808.6	838.6	834.5
	b_1 antisymm. stretch	ν_3	201.1	175.2	196.2
	Zero-point Energy	ν_0	1395.8	1387.9	
		$2\nu_1$	3563.9	3476.3	3465.9
		$2\nu_2$	1617.2	1671.5	1655.8
		$2\nu_3$	402.2	296.5	352.5
		$3\nu_3$	603.3	363.8	486.4
		$\nu_1 + \nu_2$	2590.6	2585.8	2573.1
		$\nu_1 + \nu_3$	1983.0	1908.8	1924.9
		$\nu_2 + \nu_3$	1009.7	1086.2	1066.5
SiC^{13}C	a_1 C$-$C stretch	ν_1	1747.2	1717.1	1712.7
	a_1 Si$-$C stretch	ν_2	806.6	834.3	830.2
	b_1 antisymm. stretch	ν_3	197.8	172.6	193.6
	Zero-point Energy	ν_0	1375.8	1368.0	
		$2\nu_1$	3594.5	3410.1	3399.7
		$2\nu_2$	1613.3	1662.3	1646.6
		$2\nu_3$	395.5	293.7	349.7
		$3\nu_3$	593.3	363.2	485.8
		$\nu_1 + \nu_2$	2553.9	2548.0	2535.3
		$\nu_1 + \nu_3$	1945.0	1873.3	1889.4
		$\nu_2 + \nu_3$	1004.4	1075.2	1055.5

[a] SiC$_2$ Experimental results are marked ([b], [c]). Otherwise, the reported value is the expected experimental value for each isotopologue scaled from the theoretical's respective relationship to experiment for the standard isotopologue. [b] Ref. [20]. [c] Ref. [21].

Table 3: The SiC$_2$ and Isotopologue CcCR QFF Minimum Energy Structures, A-Reduced Hamiltonian Spectroscopic Constants (in MHz), and Vibration-Rotation Interaction Constants (in MHz).

	SiC$_2$		^{29}SiC$_2$		SiC^{13}C	
	Theory[a]	Experiment[b]	Theory[a]	Experiment[c]	Theory[a]	Experiment[d]
r_0(Si−C)	184.3761 pm		184.3724 pm		184.1976 pm	
					184.5117 pm	
r_0(C−C)	127.0543 pm		127.0518 pm		127.0537 pm	
$\angle_0$(C−Si−C)	40.309°		40.309°		40.313°	
A_0	52 602.45	52 473.66	52 601.43	52 476.67	50 578.53	50 458.38
B_0	13 145.82	13 158.654	12 936.04	12 948.8024	12 863.80	12 874.290
C_0	10 444.75	10 442.619	10 311.74	10 308.7661	10 182.62	10 180.766
A_1	52 104.63		52 103.61		50 108.43	
B_1	13 154.10		12 944.19		12 870.35	
C_1	10 429.85		10 297.29		10 169.71	
A_2	52 564.66		52 563.94		50 530.71	
B_2	13 083.41		12 875.12		12 804.88	
C_2	10 403.97		10 271.69		10 146.30	
A_3	53 656.39	53 766.72	53 653.04	53 770.58[e]	51 576	51 693.89[e]
B_3	12 966.39	12 992.1312	12 758.17	12 783.66[e]	12 691	12 716.69[e]
C_3	10 221.75	10 212.9217	10 091.42	10 082.71[e]	9 971	9 962.40[e]
$10^3\Delta_J$	11.249	13.1962	10.833	12.8008	10.915	12.609
Δ_{JK}	1.597	1.538195	1.557	1.496222	1.512	1.45396
Δ_K	−1.407	−1.2841	−1.366	−0.7685	−1.329	−0.856
$10^3\delta_J$	2.243	2.41187	2.154	2.354	2.257	2.433
$10^3\delta_K$	818.031	869.88	797.417	845.66	776.320	825.6
$10^6\Phi_J$	0.005	−0.0849	0.005	−0.117	−0.030	−0.218
$10^3\Phi_{JK}$	−0.069	−0.04814	−0.067	−0.10098	−0.062	−0.0753
$10^3\Phi_{KJ}$	0.384	0.381	0.371	0.52960	0.345	0.405
$10^3\Phi_K$	−0.314		−0.303		−0.280	−6.8
$10^6\phi_j$	−0.003		0.003		−0.011	
$10^3\phi_{jk}$	−0.034	−0.03351	−0.035	−0.0366	−0.031	−0.0340
$10^6\phi_k$	0.813	1.084	0.797		0.737	0.67
α^A 1	497.8		497.8		470.2	
α^A 2	37.8		37.5		47.9	
α^A 3	−1053.9	−926.	−1051.6		−997.8	
α^B 1	−8.3		−8.1		−8.1	
α^B 2	62.4		60.9		57.3	
α^B 3	179.4	182.48	177.9		171.0	
α^C 1	14.9		14.4		14.4	
α^C 2	40.8		40.0		37.8	
α^C 3	223.0	220.03	220.3		213.0	
r_e(Si−C)	183.0765 pm	183.058 pm				
r_e(C−C)	126.8536 pm	127.07 pm				
$\angle_e$(C−Si−C)	40.541°	40.618°				
A_e	52 343.22	52 232.6	52 343.22		50 338.68	
B_e	13 264.23	13 274.755	13 052.95		12 973.89	
C_e	10 582.52	10 580.518	10 477.61		10 315.30	

[a]This work.

[b]Experimental ν_0 rotational constants from Refs. [15], experimentally and observationally combined quartic and sextic constants from Ref. [5], and $v_3 = 1$ results from Ref. [17].

[c]From Ref. [18].

[d]From Ref. [3].

[e]Theoretical values scaled by the relationship of the other isotopologue values to experiment. See text for discussion.

Table 4: The Rotational Constants (in MHz) for the Two Quanta Modes as well as $3\nu_3$ for SiC_2 and Its Isotopologues.

		SiC_2	Experiment[a]	$^{29}SiC_2$	$SiC^{13}C$
$2\nu_1$	A	51 606.80		51 605.79	49 638.27
	B	13 162.38		12 952.34	12 878.48
	C	10 414.94		10 282.85	10 155.28
$2\nu_2$	A	52 526.86		52 526.45	50 482.82
	B	13 021.01		12 814.20	12 747.53
	C	10 363.18		10 231.64	10 108.46
$2\nu_3$	A	54 710.33	55 421.6	54 704.64	52 574.10
	B	12 786.96	12 841.411	12 580.30	12 520.17
	C	9 998.75	9 975.554	9 871.10	9 758.09
$3\nu_3$	A	55 764.27		53 571.86	53 571.86
	B	12 607.53		12 349.15	12 349.15
	C	9 775.75		9 545.06	9 545.06
$\nu_1 + \nu_2$	A	52 066.84		52 066.12	50 060.55
	B	13 091.69		12 883.27	12 813.00
	C	10 389.06		10 257.25	10 131.87
$\nu_1 + \nu_3$	A	53 158.57		53 155.21	51 106.18
	B	12 974.67		12 766.32	12 699.33
	C	10 206.84		10 076.97	9 956.68
$\nu_2 + \nu_3$	A	53 618.60		53 615.55	51 528.46
	B	12 903.98		12 697.25	12 633.85
	C	10 180.97		10 051.37	9 933.28

[a]Ref. [17].

Table 5: Ground state (P_0) and near equilibrium spectroscopic parameters (P_{ne}) of SiC_2,[b] and first ($D_3^1(P)$) and second ($D_{33}^2(P)$) vibrational corrections (MHz) with respect to the ν_3 mode.

Parameter	P_0	P_{ne}	$D_3^1(P)$	$D_{33}^2(P)$
A^c	52473.97 (4)	52232.61 (57)	926.36 (155)	183.91 (81)
B^c	13158.7095 (13)	13274.755 (9)	-182.482 (24)	7.961 (12)
C^c	10441.5839 (12)	10580.518 (6)	-220.028 (15)	-4.323 (8)
Δ_K	-1.284 (9)	-1.056 (24)	-0.457 (43)	
Δ_{JK}	1.53820 (7)	0.8366 (7)	1.4484 (18)	-0.0902 (8)
$\Delta_J \times 10^3$	13.1962 (28)	11.611 (8)	2.723 (18)	1.793 (8)
$\delta_K \times 10^3$	869.88 (20)	484.0 (14)	717.9 (33)	107.9 (14)
$\delta_J \times 10^3$	2.4119 (17)	2.469 (6)	-0.384 (15)	0.540 (7)
$\Phi_{KJ} \times 10^6$	381.0 (33)	80. (7)	602. (10)	
$\Phi_{JK} \times 10^6$	-48.14 (81)	90. (6)	$-370.$ (16)	187. (7)
$\Phi_J \times 10^9$	-84.9 (36)	-86.2 (36)		
$\phi_K \times 10^3$	1.084 (16)	2.06 (11)	-3.57 (27)	3.27 (12)
$\phi_{JK} \times 10^6$	-33.5 (4)	4.4 (20)	-89.6 (47)	27.7 (22)
$L_{KKJ} \times 10^9$	320. (23)	10. (29)	607. (41)	
$L_{JK} \times 10^9$	-148.4 (43)	45. (14)	$-391.$ (26)	
$L_{JJK} \times 10^9$	-1.43 (31)	14.8 (11)	-32.2 (21)	
$l_{JK} \times 10^9$	-1.58 (15)	-1.55 (15)		
$P_{KKJ} \times 10^9$	-1.18 (12)	-1.17 (12)		
$P_{KJ} \times 10^{12}$	426. (27)	434. (27)		
$P_{JK} \times 10^{12}$	-49.5 (23)	$-162.$ (13)	224. (27)	

[a] From Ref. [5].

[b] Numbers in parentheses are one standard deviation in units of the least significant figures.

[c] Including calculated vibrational corrections with respect to ν_1 and ν_2 from Table 3.

Table 6: Selected low-J transitions of SiC_2 in its $v_3 = 2$ to 4 excited vibrational states, calculated frequencies (MHz) and uncertainties Unc.[a] (MHz).

$J'_{K'_a K'_c} - J''_{K''_a K''_c}$	Frequency	Unc.
$v_3 = 2$		
$1_{01} - 0_{00}$	22816.990	0.012
$2_{02} - 1_{01}$	45495.692	0.024
$v_3 = 3$		
$1_{10} - 1_{11}$	2959.95	0.11
$2_{11} - 2_{12}$	8879.48	0.32
$3_{12} - 3_{13}$	17753.77	0.63
$4_{13} - 4_{14}$	29565.37	1.05
$5_{14} - 5_{15}$	44272.01	1.55
$2_{12} - 1_{11}$	41892.59	0.09
$2_{11} - 1_{10}$	47812.13	0.15
$3_{13} - 2_{12}$	62753.91	0.13
$3_{12} - 2_{11}$	71628.20	0.23
$4_{14} - 3_{13}$	83518.63	0.16
$4_{32} - 3_{31}$	89653.55	0.20
$4_{31} - 3_{30}$	89678.06	0.20
$4_{13} - 3_{12}$	95330.22	0.30
$5_{15} - 4_{14}$	104163.28	0.19
$5_{33} - 4_{32}$	112177.29	0.23
$5_{32} - 4_{31}$	112262.99	0.24
$5_{14} - 4_{13}$	118869.92	0.37
$v_3 = 4$		
$1_{01} - 0_{00}$	22062.79	0.08
$2_{02} - 1_{01}$	43979.72	0.16

[a] Calculated uncertainties should be quite reliable for $v_3 = 2$ and are only rough values for higher excited states.