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High-resolution OPO spectroscopy of Si₂C₃ at 5 μm: Observation of hot band transitions associated with ν₃S. Thorwirth^{a,*}, J. Krieg^a, V. Lutter^a, I. Keppeler^a, S. Schlemmer^a, M.E. Harding^b, J. Vázquez^b, T.F. Giesen^a^a I. Physikalisches Institut, Universität zu Köln, Zùlpicher Str. 77, 50937 Köln, Germany^b Center for Theoretical Chemistry, Department of Chemistry and Biochemistry, University of Texas at Austin, Austin, TX 78712, USA

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ABSTRACT

Close inspection of the ν₃ fundamental vibrational mode of Si₂C₃ observed recently (Krieg et al., Rev. Sci. Instrum. 82 (2011) 063105) reveals the presence of another weak mode of which more than 40 rovibrational transitions have now been analyzed. Based on comparison against molecular parameters from high-level quantum chemical calculations this new series of lines is identified as the (ν₃+ν₇)-ν₇ hot band.

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1. Introduction

Silicon–carbon clusters are of considerable scientific interest owing to their significance in fundamental and structural chemistry, material science, molecular spectroscopy, and astronomy (e.g. Refs. [1–4] and references therein). In the gas phase, the number of experimental studies of the monosila-variants SiC_m outweighs those of any other form because of the presence of a permanent electric dipole moment, making the molecules amenable to pure rotational spectroscopy. Consequently, clusters as large as SiC₈ have been characterized by Fourier transform microwave spectroscopy [2]. While several molecules of the form Si_nC_m with *n* = 2 and 3 have been observed by matrix isolation infrared spectroscopy [5–9] the only molecule studied to date at high spectral resolution in the gas phase remains linear Si₂C₃, Si=C=C=Si, which is non-polar and hence does not exhibit any pure rotational spectrum. Its first high-resolution investigation was performed using diode-laser spectroscopy of a free jet [10]. In a recent first characterization of the new Cologne OPO spectrometer operating at 5 μm, we have reinvestigated the ν₃ fundamental vibrational mode located at 1968 cm⁻¹ and obtained an improved parameter set for the associated vibrational modes ν₃ = 0,1 [11]. Close inspection of this mode (Fig. 1) reveals the presence of a weaker series of lines on whose analysis will be reported in the following.

Si₂C₃ was observed through laser ablation from a commercial silicon–carbide rod using a recently updated version of the Cologne Carbon Cluster Experiment [12] now also featuring an optical

parametric oscillator (OPO) operating at 5 μm. The new setup, the OPO, the production of Si₂C₃ via laser ablation and the data reduction procedure have been described in detail elsewhere [11].

The ν₃ fundamental vibrational band is shown in Fig. 1 which also displays close-up views of the *P*- and *R*-branches of the new band. In these, the much stronger lines of the ν₃ fundamental were blanked to enhance the visibility of the much weaker new band of which a total of 44 rovibrational transitions were recorded (Table 1). Spectral analysis and line fitting of data presented here was performed using the programs PGOPHER [13] and SPFIT [14]. It is found that the spacing between adjacent lines in the band is regular with about half the spacing observed in the ν₃ fundamental and an intensity ratio of roughly 10%. This is a strong indication of the relationship of the band to the Si₂C₃ molecule. Owing to D_{∞h}-symmetry and Bose–Einstein statistics, the line-spacing in a σ-vibrational band of Si₂C₃ (such as the ν₃ mode) is 4*B*. Consequently, the spacing observed in the new series may be rationalized as being due to an isotopic species in which the D_{∞h}-symmetry is broken or from the involvement of a vibrational state of π-symmetry, i.e. a bending vibrational mode.

As shown already in a previous investigation [7], only the mono-substituted ²⁹Si and ³⁰Si species exhibit a small isotopic shift (<0.5 cm⁻¹) relative to the parent species, with the isotopic shift of any ¹³C species being much larger. At the CCSD(T)/cc-pV(T+d)Z level of theory, the fundamental frequencies of ν₃ in Si₂C₃, ²⁹SiC₃Si and ³⁰SiC₃Si coincide within 0.1 cm⁻¹ (see Table 2). However, the natural isotopic abundances of ²⁹Si (4.7%) and ³⁰Si (3.1%) are similar and the rotational constants sufficiently different (Table 3) such that one would expect the presence of two (at least partly resolved) vibrational bands with an intensity ratio of about 3:2.

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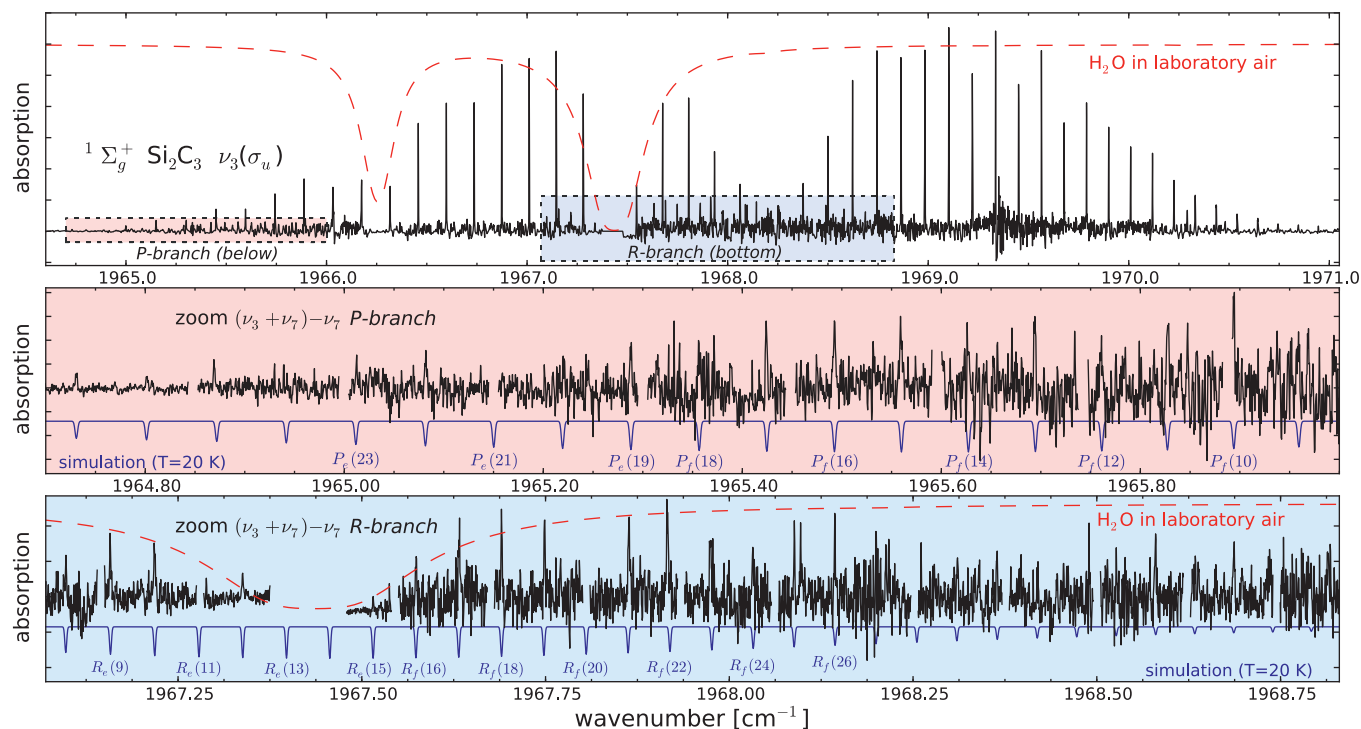


Fig. 1. The ν_3 vibrational band as observed in Ref. [11] (top spectrum) and P - and R -branches (center and bottom spectra) of the weaker $(\nu_3 + \nu_7) - \nu_7$ hot band analyzed here. The two bands were covered almost completely except for a small region around 1967.4 cm^{-1} which was found heavily perturbed by the presence of water in laboratory air.

However, only one band is observed. In addition, the isotopic shift calculated here is much smaller than the displacement of the new band ($\approx -2 \text{ cm}^{-1}$) relative to ν_3 as seen in Fig. 1.

A conclusive assignment is obtained by assuming that the vibrational band is a hot band $(\nu_3 + \nu_i) - \nu_i$, with i being the vibrational index of a low-lying bending mode, most plausibly from the mode of lowest vibrational energy ν_7 . Such hot-bands have been observed previously for a number of pure carbon clusters produced under similar conditions (see e.g., Refs. [15–18] and references therein). Since the weak nature of the vibrational band did not permit observation of low- J - and/or Q -branch transitions (see Table 1) and hence the location of the band center was not determinable in a straightforward fashion, the assignment of transitions was performed under consideration of the data from high-level quantum-chemical calculations. In addition to a previous quantum-chemical study by Botschwina [19] we have performed complementary calculations of the anharmonic force field at the CCSD(T) level of theory yielding anharmonic vibrational frequencies ν_i , rotation–vibration interaction constants α_i and ℓ -type doubling constants q_i (Table 4). Under the assumption that the newly observed series is the $(\nu_3 + \nu_7) - \nu_7$ hot band and using the experimental ground state rotational constant B_0 and B_3 [11] and the calculated rotation–vibration interaction constant α_7 (Table 4), we estimate the rotational constants $B_7 \approx 949.11 \text{ MHz}$ and $B_{3+7} \approx 944.87 \text{ MHz}$.¹ Subsequent trial fits resulted in the final assignment of experimental transition frequencies to the rotational quantum numbers J as given in Table 1. The resulting fit yields rotational constants that differ only by 0.5 MHz from the prediction (Table 5). Changing the present J assignment by ± 1 leads to significant changes in the rotational constants of $\pm 4.2 \text{ MHz}$ that cannot

be approximated by any other reasonable combination of the rotational and rotation–vibration interaction constants.

Table 1

Transition frequencies of the $\nu_3 + \nu_7 - \nu_7$ hot band and residuals ($o - c$) of the fit (in cm^{-1}).

| J | ℓ | $R(J)$ | $(o - c) \times 10^4$ | $P(J)$ | $(o - c) \times 10^4$ |
|-----|--------|-----------|-----------------------|-----------|-----------------------|
| 3 | 1e | 1966.7907 | 3 | ... | ... |
| 4 | 1f | 1966.8526 | 2 | ... | ... |
| 5 | 1e | 1966.9139 | -2 | ... | ... |
| 6 | 1f | 1966.9751 | -4 | ... | ... |
| 7 | 1e | 1967.0368 | 2 | 1966.0903 | -1 |
| 8 | 1f | 1967.0974 | 0 | ... | ... |
| 9 | 1e | 1967.1578 | -1 | ... | ... |
| 10 | 1f | 1967.2181 | -1 | 1965.8938 | 2 |
| 11 | 1e | ... | ... | 1965.8275 | 0 |
| 12 | 1f | 1967.3378 | -1 | 1965.7607 | -3 |
| 13 | 1e | ... | ... | 1965.6939 | -4 |
| 14 | 1f | ... | ... | 1965.6266 | -7 |
| 15 | 1e | 1967.5155 | 2 | 1965.5593 | -7 |
| 16 | 1f | 1967.5738 | -1 | 1965.4926 | 2 |
| 17 | 1e | 1967.6325 | 3 | 1965.4242 | -4 |
| 18 | 1f | 1967.6902 | 0 | 1965.3567 | 3 |
| 19 | 1e | 1967.7486 | 7 | 1965.2879 | -1 |
| 20 | 1f | ... | ... | 1965.2206 | 13 |
| 21 | 1e | 1967.8635 | 9 | ... | ... |
| 22 | 1f | ... | ... | 1965.0818 | 7 |
| 23 | 1e | ... | ... | 1965.0123 | 7 |
| 24 | 1f | 1968.0321 | -3 | ... | ... |
| 25 | 1e | 1968.0884 | -1 | 1964.8693 | -23 |
| 26 | 1f | 1968.1435 | -7 | 1964.8017 | 4 |
| 27 | 1e | 1968.1999 | 2 | 1964.7307 | 1 |
| 28 | 1f | ... | ... | 1964.6596 | -1 |
| 29 | 1e | 1968.3104 | 6 | 1964.5885 | 1 |
| 30 | 1f | 1968.3641 | -4 | 1964.5170 | 1 |
| 31 | 1e | ... | ... | 1964.4457 | 5 |
| 34 | 1f | 1968.5798 | -5 | ... | ... |
| 36 | 1f | 1968.6864 | -1 | ... | ... |

¹ It should be noted that the rotation–vibration constant α_5 yields very similar results for a corresponding hot band under participation of the ν_5 bending mode. However, this mode is calculated to lie significantly higher in energy than the ν_7 mode (187 cm^{-1} vs. 77 cm^{-1} , see Table 4).

Table 2
Vibrational frequencies of Si₂C₃ and rare Si-isotopologues (fc-CCSD(T)/cc-pV(T+d)Z, in cm⁻¹).

| | SiCCCSi | | ²⁹ SiCCCSi ^a | | ³⁰ SiCCCSi ^a | |
|---------------------|----------|-------------|------------------------------------|-------------|------------------------------------|-------------|
| | Harmonic | Fundamental | Harmonic | Fundamental | Harmonic | Fundamental |
| $\nu_1(\sigma_g)$ | 1558 | 1532 | 1557 | 1532 | 1556 | 1531 |
| $\nu_2(\sigma_g)^b$ | 459 | 480 | 455 | 478 | 452 | 475 |
| $\nu_3(\sigma_u)^c$ | 2020 | 1981 | 2020 | 1981 | 2020 | 1981 |
| $\nu_4(\sigma_u)$ | 903 | 898 | 900 | 895 | 897 | 893 |
| $\nu_5(\pi_g)$ | 193 | 193 | 193 | 192 | 193 | 192 |
| $\nu_6(\pi_u)^b$ | 548 | 544 | 548 | 543 | 548 | 543 |
| $\nu_7(\pi_u)$ | 80 | 79 | 79 | 79 | 79 | 79 |

^a For the sake of comparability, the denotation of the vibrational modes of the rare Si species follows that of the parent molecule.

^b Values after deperturbation and diagonalization: SiCCCSi: $\nu_2 = 476$ cm⁻¹, $\nu_6 = 539$ cm⁻¹; ²⁹SiCCCSi: $\nu_2 = 473$ cm⁻¹, $\nu_6 = 539$ cm⁻¹; ³⁰SiCCCSi: $\nu_2 = 470$ cm⁻¹, $\nu_6 = 539$ cm⁻¹. See text for details.

^c Consideration of one decimal place for this mode yields for the harmonic/anharmonic pairs values of 2019.8/1981.0 cm⁻¹ (SiCCCSi), 2019.8/1980.9 cm⁻¹ (²⁹SiCCCSi), and 2019.7/1980.9 cm⁻¹ (³⁰SiCCCSi).

Table 3
Predicted rotational constants of Si₂C₃ and rare Si-isotopologues (in MHz).^a

| Isotopolog | B_e^b | ΔB_0^c | B_0^d | $B_{0,exp}$ | $B_{0,scaled}^e$ |
|-----------------------|---------|----------------|---------|-------------|------------------|
| SiCCCSi | 945.903 | -1.679 | 947.582 | 946.4 | ... |
| ²⁹ SiCCCSi | 930.684 | -1.655 | 932.339 | ... | 931.2 |
| ³⁰ SiCCCSi | 916.288 | -1.633 | 917.921 | ... | 916.8 |

^a The structural parameters at the fc-CCSD(T)/cc-pV(Q+d)Z and ae-CCSD(T)/cc-pwCVQZ levels of theory are $r_{Si-C} = 1.6903$ Å, $r_{C-C} = 1.2927$ Å, and $r_{Si-C} = 1.6829$ Å, $r_{C-C} = 1.2895$ Å, respectively.

^b CCSD(T)/cc-pwCVQZ.

^c fc-CCSD(T)/cc-pV(Q+d)Z.

^d $B_0 = B_e - \Delta B_0$.

^e $B_{0,scaled} = (B_{0,exp}/B_0)_{SiCCCSi} \times B_0$.

Table 4
CCSD(T) calculations of selected spectroscopic constants of Si₂C₃ (vibrational modes given in cm⁻¹, α_i and q_i in MHz).

| Vib. mode | Ref. [19] ^a | This work ^b | | Exp. |
|-------------------|------------------------|------------------------|------------------|---------------------|
| | | Harmonic | Fundamental | |
| $\nu_1(\sigma_g)$ | 1558 | 1565 | 1540 | ... |
| $\nu_2(\sigma_g)$ | 458 | 462 | 482 ^c | ... |
| $\nu_3(\sigma_u)$ | 2020 | 2016 | 1979 | 1968.2 ^d |
| $\nu_4(\sigma_u)$ | 901 | 910 | 905 | 898.9 ^e |
| $\nu_5(\pi_g)$ | 192 | 189 | 187 | ... |
| $\nu_6(\pi_u)$ | 547 | 547 | 547 ^c | ... |
| $\nu_7(\pi_u)$ | 79 | 78 | 77 | ... |
| Parameter | Ref. [19] ^a | This work ^c | | |
| α_1 | 3.11 | ... | 3.25 | ... |
| α_2 | 0.69 | ... | 0.69 | ... |
| α_3 | 4.07 | ... | 4.24 | 4.1 ^d |
| α_4 | 2.10 | ... | 2.10 | ... |
| α_5 | -2.86 | ... | -2.99 | ... |
| α_6 | -1.21 | ... | -1.10 | ... |
| α_7 | -2.61 | ... | -2.73 | -3.3 ^f |
| q_5 | 0.32 | ... | 0.33 | ... |
| q_6 | 0.14 | ... | 0.14 | ... |
| q_7 | 0.76 | ... | 0.78 | ... |

^a fc-CCSD(T)/cc-pVTZ.

^b fc-CCSD(T)/cc-pV(Q+d)Z.

^c Values after deperturbation and diagonalization: $\nu_2 = 478$ cm⁻¹ and $\nu_6 = 541$ cm⁻¹. See text for details.

^d Gas phase value [11,10].

^e Ar matrix value [7].

^f This work.

The data obtained for the new vibrational band unfortunately lack the accuracy to determine one other important diagnostic, the ℓ -doubling constant q_7 . With only three parameters released

Table 5
Spectroscopic parameters of the $\nu_3 + \nu_7 - \nu_7$ hotband as determined in the present study (B_i and q_i given in MHz, ΔE in cm⁻¹).

| Parameter | Experimental | QCC ^a |
|--------------------------------|----------------|------------------|
| B_7 | 949.68(11) | 949.11 |
| q_7 | ... | 0.78 |
| B_{3+7} | 945.46(11) | 944.99 |
| q_{3+7} | ... | ... |
| $\Delta E_{\nu_3+\nu_7-\nu_7}$ | 1966.53984(24) | ... |

^a Rotational constants estimated from B_0 and B_3 given in Ref. [11] and the calculated vibration rotation interaction parameter α_7 .

in the fit, B_7 , B_{3+7} and the energy difference ΔE , the rms is 5.4×10^{-4} cm⁻¹ and hence roughly half of the experimental uncertainty of 10^{-3} cm⁻¹, resulting in a dimensionless weighted rms (wrms) of 0.54. Introduction of the calculated $q_7^e = 0.78$ MHz into the fit as a fixed parameter results in a wrms of 0.91 whereas releasing q_7 yields a wrms of 0.49 and an unphysical negative value of $q_7 = -0.36(22)$ MHz. From this it is inferred that q_7 should be (significantly) smaller than what is expected from the quantum-chemical calculations. The calculated anharmonic force field does not yield any evidence for q_7^e being influenced by a perturbation.

The fundamental frequencies of Si₂C₃ and its mono-²⁹Si and ³⁰Si species in Tables 4 and 2 were calculated by second order vibrational perturbation theory (VPT2) [20]. The presence of Fermi resonances was investigated and it was found that ν_2 and ν_6 are slightly perturbed in the three isotopic species. ν_2 is mainly perturbed by the overtone $2\nu_5$ and slightly by the combination band $\nu_6 + \nu_7$. ν_6 is in resonance with the combination $\nu_2 + \nu_7$. The straightforward VPT2 frequencies were corrected by removing the term involving the resonance denominators, and next by building and diagonalizing the corresponding resonance matrix.

The present study suggests that other linear silicon-carbon chains of the form SiC_nSi may be detectable with our instrument. While the ν_4 mode of SiC₄Si (³Σ_g⁻) is comparably weak and located around 1859 cm⁻¹ [9] and hence below the current lower frequency limit of our infrared spectrometer, a harmonic force field calculation predicts the strongest σ_u mode of SiC₅Si at 2098.5 cm⁻¹ [21] which hence is a promising target for future investigation.

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Appendix A. Quantum-chemical calculations

Quantum-chemical calculations of Si_2C_3 were performed using coupled-cluster theory [22], in particular the singles and doubles model augmented by a perturbative treatment for triple excitations, CCSD(T) [23]. All calculations were performed using the CFOUR program package [24,25]. Dunning's hierarchies of correlation-consistent polarized valence and polarized core valence basis sets were used throughout: in the frozen core (fc) approximation, the basis sets cc-pV(X + d)Z (X = T and Q) [26] were used for silicon atoms and the cc-pVXZ basis sets [27] for carbon. The cc-pwCVXZ (X = T and Q) basis sets [28] were used when considering all electrons (ae) in the correlation treatment. The equilibrium geometry of Si_2C_3 was obtained using analytic gradient techniques [29]. Harmonic and anharmonic force fields were calculated at the CCSD(T)/cc-pV(X + d)Z level of theory (X = T, Q) using analytic second-derivative techniques [30,31] followed by additional numerical differentiation to calculate the third and fourth derivatives needed for the anharmonic force field [31,32].

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