

Theoretical Predictions and Experimental Detection of the SiC Molecule

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 (Received 26 October 1987)

The 0-0 band of the $d^1\Sigma^+ - b^1\Pi$ electronic transition of SiC was detected near 6100 cm^{-1} . The SiC molecule was observed by high-resolution Fourier-transform emission spectroscopy from a composite-wall hollow cathode. *Ab initio* quantum chemical calculations confirm the identity of the carrier of the spectrum as SiC and the $d^1\Sigma^+ - b^1\Pi$ assignment. Combination of the observed r_0 for SiC $b^1\Pi$ with theoretical shifts in bond lengths from $b^1\Pi$ to $X^3\Pi$ gives the astrophysically important bond lengths $r_0 = 1.723\text{ \AA}$ and $r_e = 1.719\text{ \AA}$ for $X^3\Pi$ to an estimated accuracy of 0.001 \AA .

PACS numbers: 33.20.Ea, 35.20.Pa

SiC is a very elusive molecule. Although the homonuclear molecules C_2 and Si_2 are well-known species,¹ SiC has escaped spectroscopic identification. Many efforts have been made to detect SiC but, until now, without success. We report here the observation of the 0-0 band of the $d^1\Sigma^+ - b^1\Pi$ system of SiC near 6100 cm^{-1} .

The SiC molecule is predicted by various chemical models to be abundant in dense interstellar clouds² and stellar atmospheres.^{3,4} For example, Suzuki² predicts that under steady-state conditions, SiC is more abundant than SO, which is widely observed. The SiC_2 molecule occurs widely in stellar atmospheres⁵⁻⁷ and has recently been detected in the interstellar medium.⁸ For many years SiC_2 was thought to be linear, like C_3 , but Michalopoulos *et al.* proved that SiC_2 had a triangular structure.⁹ Si_2C has been detected in matrix isolation experiments.¹⁰

When carborundum (crystalline SiC) is heated, the major constituents of the vapor are Si (83%), SiC_2 (9%), Si_2C (8%), and Si_2 (0.2%), with SiC present only in trace amounts.¹¹⁻¹³ The detection of SiC in a high-temperature experiment in thermodynamic equilibrium is, therefore, an extremely difficult experiment. We circumvented this problem by sputtering SiC in a hollow-cathode discharge lamp.

In our experiment, a 1:3 mixture of SiC powder (600 grit carborundum from a local gem store) and copper powder (100 mesh) was pressed and drilled through to form a hollow cathode. The composite-wall hollow cathode was operated at 200 mA with a flow of 1.5 Torr of Ne gas. The emission from the hollow cathode was observed with the McMath Fourier-transform spectrometer of the National Solar Observatory at Kitt Peak. Sixty-nine scans were coadded in 8.3 h of integration with an unapodized resolution of 0.02 cm^{-1} . InSb detectors and a silicon filter limited the spectrometer band pass to approximately $1800\text{--}9000\text{ cm}^{-1}$.

The main molecular species observed was C_2 (Si_2 was not found). A previously recorded comparison spectrum of C_2 was used to eliminate the dominant C_2 lines from consideration. The remaining molecular features could be picked out and were attributed to two different electronic transitions of SiC.

Near 6100 cm^{-1} (Fig. 1) lines belonging to a *P*, a *Q*, and an *R* branch could be assigned (Table I). Unfortunately, the signal-to-noise ratio was low (about 10 for the strongest lines), and so the first lines were not observed. However, the intensity of the *Q* branch and the Λ doubling of the $^1\Pi$ state determine this transition to be $^1\Pi - ^1\Sigma$ or $^1\Sigma - ^1\Pi$.

The lines of Table I were rotationally assigned by the method of combination differences¹¹ and fitted with the customary energy-level expression¹⁴

$$F(J) = BJ(J+1) - D[J(J+1)]^2 + H[J(J+1)]^3 \\ \pm \delta_{\Lambda,1}[J(J+1)/2][q + q_D J(J+1)].$$

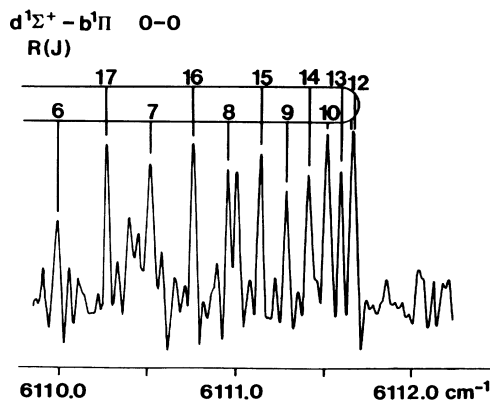


FIG. 1. A portion of the 0-0 band of the $d^1\Sigma^+ - b^1\Pi$ spectrum of SiC near the *R* band head.

TABLE I. Measured wave numbers for the 0-0 band of the $d^1\Sigma^+ - b^1\Pi$ transition of SiC. (Numbers in parentheses refer to observed minus calculated values calculated with the constants of Table II.)

| J | P(J) | Q(J) | R(J) |
|----|-----------------|-----------------|----------------|
| 2 | - | 6103.1493(-3) | - |
| 3 | - | - | - |
| 4 | - | 6102.4448(22) | - |
| 5 | - | 6101.9367(-10) | 6109.3688(8) |
| 6 | - | 6101.3338(19) | 6110.0086(89) |
| 7 | - | 6100.6266(13) | 6110.5258(-45) |
| 8 | 6089.8936(-101) | 6099.8208(29) | 6110.9581(-17) |
| 9 | - | 6098.9139(41) | 6111.2863(-19) |
| 10 | 6085.5080(-3) | 6097.9001(-10) | 6111.5155(-1) |
| 11 | 6083.1615(17) | 6096.7868(-50) | 6111.6480(60) |
| 12 | 6080.7100(-10) | 6095.5826(4) | 6111.6671(-4) |
| 13 | 6078.1607(-13) | 6094.2805(83) | 6111.5903(-19) |
| 14 | 6075.5125(-4) | 6092.8637(17) | 6111.4131(-31) |
| 15 | 6072.7619(-19) | 6091.3535(18) | 6111.1398(2) |
| 16 | 6069.9152(3) | 6089.7434(19) | 6110.7643(19) |
| 17 | 6066.9679(15) | 6088.0286(-29) | 6110.2858(10) |
| 18 | 6063.9172(-13) | 6086.2217(-2) | 6109.7059(-11) |
| 19 | 6060.7713(1) | 6084.3115(-13) | 6109.0317(28) |
| 20 | 6057.5265(16) | 6082.3077(34) | 6108.2476(-32) |
| 21 | 6054.1801(5) | 6080.1967(-1) | 6107.3711(-18) |
| 22 | 6050.7365(9) | 6077.9893(-10) | 6106.3960(8) |
| 23 | 6047.1903(-28) | 6075.6875(25) | 6105.3177(-2) |
| 24 | 6043.5521(-3) | 6073.2824(12) | 6104.1404(-9) |
| 25 | 6039.8119(-17) | 6070.7783(-8) | 6102.8601(-53) |
| 26 | 6035.9757(-12) | - | 6101.4891(-14) |
| 27 | 6032.0406(-21) | 6065.4811(1) | 6100.0162(-6) |
| 28 | 6028.0117(5) | 6062.6861(7) | 6098.4457(12) |
| 29 | 6023.8795(-32) | 6059.7916(-8) | - |
| 30 | 6019.6427(-147) | 6056.8025(1) | 6095.0062(13) |
| 31 | 6015.3319(-37) | 6053.7160(4) | 6093.1409(28) |
| 32 | 6010.9159(-17) | 6050.5335(12) | 6091.1727(-9) |
| 33 | 6006.4027(-10) | 6047.2485(-43) | 6089.1143(26) |
| 34 | 6001.7961(19) | 6043.8774(1) | 6086.9491(-35) |
| 35 | 5997.0886(-9) | 6040.4081(18) | 6084.6954(-12) |
| 36 | 5992.2872(-27) | 6036.8416(16) | 6082.3488(48) |
| 37 | 5987.3981(25) | 6033.1769(-20) | 6079.8982(31) |
| 38 | 5982.4132(61) | 6029.4241(10) | - |
| 39 | 5977.3310(62) | - | 6074.7152(56) |
| 40 | 5972.1588(98) | - | 6071.9749(12) |
| 41 | 5966.8789(-11) | 6017.5910(-10) | - |
| 42 | 5961.5118(-65) | 6013.4609(-7) | 6066.2125(-44) |
| 43 | 5956.0688(45) | 6009.2394(8) | 6063.1931(-38) |
| 44 | 5950.5161(-22) | - | - |
| 45 | 5944.8819(10) | 6000.5149(-12) | - |
| 46 | 5939.1458(-65) | 5996.0153(-23) | - |
| 47 | 5933.3294(-38) | 5991.4297(17) | - |
| 48 | 5927.4248(9) | 5986.7451(-29) | - |
| 49 | 5921.4271(23) | 5981.9755(-24) | - |
| 50 | - | 5977.1180(-3) | - |
| 51 | - | 5972.1588(-108) | - |
| 52 | - | 5967.1380(57) | - |

The resulting molecular constants are displayed in Table II. The standard deviation of the fit is about 0.003 cm^{-1} , consistent with the signal-to-noise ratio of the data. The absolute calibration of the wave-number scale of the spectrum is about $\pm 0.002 \text{ cm}^{-1}$. This calibra-

tion was carried out with the Ne atomic lines present in the spectrum, which in turn were calibrated with OH¹⁵ in a previously recorded OH-Ne spectrum.

The SiC molecule has six low-lying electronic states which arise from the configurations $\pi^4 (a^1\Sigma^+)$, $\pi^3\sigma^1 (b^1\Pi, X^3\Pi)$, and $\pi^2\sigma^2 (A^2\Sigma^-, c^1\Delta, \text{ and } d^1\Sigma^+)$. The predicted energies of these electronic states and some spectroscopic constants are presented in Table III.

Calculations were performed at several different levels, appropriate for the specific states or excitation energies. For example, the $X^3\Pi$, $A^3\Sigma^-$, and $a^1\Sigma^+$, involving three different electronic configurations, were calculated with the multireference second-order configuration-interaction (MR SOC1) method parallel to earlier calculations on Si₂.¹⁶ For the $X^3\Pi - b^1\Pi$ and $A^3\Sigma^- - c^1\Delta$ energy separations, calculations were done at the single-configuration self-consistent field (SCF) level plus single and double excitations [Hartree-Fock (HF)+SD] CI. For the $a^1\Sigma^+ - d^1\Sigma^+$ separation, the calculations were two-configuration (π^4 and $\pi^2\sigma^2$) self-consistent field plus singles and doubles (2MC-SCF+SD) MR-CI. The sources of the entries in Table III are indicated in footnotes. Davidson-corrected potential curves are used for internuclear separations and ω_e values since this correction almost universally improves the shape of the curves. Energy separations have not been corrected. A large Slater basis (6s, 4p, 3d, and 2f type functions for carbon, and 8s, 6p, 3d, and 2f type functions for silicon) was used for all orbital expansions and for constructing the configuration spaces of the calculations.

Our initial electronic assignment of the observed singlet system was $b^1\Pi - a^1\Sigma^+$, the SiC analog of the Phillips system of C₂. However, the *ab initio* calculations (Table III) rule out this assignment. The energy separation is too small and one of the observed r_0 values (1,800 Å) cannot possibly belong to the b or the a state. Instead, we assign the singlet system to the $d^1\Sigma^+ - b^1\Pi$ transition. This transition has not been observed for C₂, but was recently analyzed by Davis and Brault for Si₂.¹⁷ The theoretical excitation energy of 5079 cm^{-1} is in agreement with the experimental T_{00} value of 6103 cm^{-1} , at least to the accuracy that can be expected from the calculations. In addition, the experimental r_0 values of 1,800 Å for $d^1\Sigma^+$ and 1,731 Å for $b^1\Pi$ agree well with computed values of 1,796 Å and 1,734 Å, respectively, so that we can be quite confident of our assignment. The Franck-Condon factors calculated from the theoretical potential curves are consistent ($q_{0-0} = 0.831$, $q_{1-1} = 0.575$,

TABLE II. Molecular constants (in inverse centimeters) for $v=0$ of the $d^1\Sigma^+$ and $b^1\Pi$ states of SiC.

| | T_0 | B_0 | $10^7 D_0$ | $10^{12} H_0$ | $10^5 q_0$ | $10^8 q_{D0}$ |
|---------------|----------------|----------------|------------|---------------|------------|---------------|
| $d^1\Sigma^+$ | 6103.45265(73) | 0.6194496(147) | 9.972(59) | 3.00(86) | ... | ... |
| $b^1\Pi$ | 0.0 | 0.6699942(146) | 13.570(55) | 0.0 | 6.997(167) | 2.335(98) |

TABLE III. Molecular constants for SiC predicted by *ab initio* quantum chemical calculation.

| State | T_e (cm^{-1}) | r_e (\AA) | r_0 (\AA) | ω_e (cm^{-1}) |
|---------------|-------------------------------|---------------------------|---------------------------|------------------------------------|
| $d^1\Sigma^+$ | 12338 ^a | 1.794 ^b | 1.796 ^b | |
| $c^1\Delta$ | 9094 ^c | 1.821 ^d | 1.829 ^d | |
| $b^1\Pi$ | 7259 ^e | 1.728 ^d | 1.734 ^d | 963 ^d |
| $a^1\Sigma^+$ | 5079 ^f | 1.677 ^g | 1.684 ^g | 955 ^g |
| $A^3\Sigma^-$ | 3619 ^f | 1.802 ^d | 1.810 ^d | 835 ^g |
| $X^3\Pi$ | 0 | 1.722 ^d | 1.726 ^d | 927 ^g |

^a $d^1\Sigma^+$ - $a^1\Sigma^+$ separation from 2MC-SCF+SD calculation.

^bDavidson-corrected 2MC-SCF+SD.

^c Δ - $A^3\Sigma^-$ separation from HF+SD calculation.

^dDavidson-corrected HF+SD.

^e $b^1\Pi$ - $X^3\Pi$ separation from HF+SD calculation.

^fSeparation from $X^3\Pi$ calculated from MR-SOCI wave functions in unpublished calculations of H. P. Lüthi and A. D. McLean.

^gDavidson-corrected MR-SOCI.

and $q_{2-2}=0.406$) with our assignment of the observed band to the 0-0 vibrational band. Since we observed only one vibrational band and the Franck-Condon factor is predicted to be the largest for the 0-0 band, our vibrational assignment is reasonably secure.

The discovery of the SiC molecule illustrates the important role that *ab initio* quantum chemical calculations can play in the discovery of unknown molecular species. We have found two Q branches near the predicted *ab initio* T_0 value of the $A^3\Sigma^-$ - $X^3\Pi$ transition, but the signal-to-noise ratio is too small to permit analysis. The $d^1\Sigma^+$ - $a^1\Sigma^+$ transition (predicted to occur near 7300 cm^{-1}) was not found in our spectrum, presumably because the transition is too weak. Experiments are under way to improve the quality of our spectra and confirm the observation of the $A^3\Sigma^-$ - $X^3\Pi$ transition.

Identification of SiC in the interstellar clouds has long been a goal of astrophysicists. This goal has been frustrated by lack of knowledge of the spectroscopic constants of the $X^3\Pi$ ground state. As a result of our spectroscopic determination of $r_0=1.731$ \AA for the $b^1\Pi$ state and our computational determination of the shift in bond lengths from $^1\Pi$ to $^3\Pi$, we can finally report values of $r_e=1.719$ \AA and $r_0=1.723$ \AA for $x^3\Pi$, probably accurate to within 0.001 \AA . The r_e value is in precise agreement with the computational prediction of Bauschlicher and Langhoff,¹⁸ although their prediction, which relied on an empirical correction for core-valence correlation effects, must be assigned a larger error bar. There have been many previous *ab initio* calculations on SiC, but at lower levels of theory.¹⁹⁻²⁴

The National Solar Observatory is operated by the Association of Universities for Research in Astronomy,

Inc., under contract with the National Science Foundation. We thank J. Wagner and G. Ladd for assistance in acquiring the SiC spectrum. Acknowledgement is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this work. Some partial support was provided by the Air Force Astronautics Laboratory Grant No. F 04611-87-K-0020. We thank John Black for his comments on the astrophysical importance of SiC. One of us (P.F.B.) acknowledges receipt of an Alfred P. Sloan Fellowship.

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