

# The $A^3\Sigma^- - X^3\Pi$ transition of the SiC radical

C. R. Brazier

*Astronautics Laboratory/LSX, Edwards Air Force Base, California 93523*

L. C. O'Brien<sup>a)</sup> and P. F. Bernath<sup>b)</sup>

*Department of Chemistry, University of Arizona, Tucson, Arizona 85721*

(Received 14 August 1989; accepted 8 September 1989)

The 0-0 band of the  $A^3\Sigma^- - X^3\Pi$  system of SiC, analogous to the Ballik-Ramsay system of  $C_2$ , has been observed in emission near  $4500\text{ cm}^{-1}$ . The internuclear separations ( $r_0$ ) were found to be 1.813 56 and 1.721 87 Å for the  $A^3\Sigma^-$  and  $X^3\Pi$  states, respectively.

## INTRODUCTION

Last year we reported the first experimental observations of the SiC radical, by detection of the  $d^1\Sigma^+ - b^1\Pi$  electronic transition.<sup>1</sup> The ground state of this elusive radical now has been well-characterized following the laboratory and astrophysical observation of microwave transitions by Cernicharo, *et al.*<sup>2</sup> In our earlier paper,<sup>1</sup> we reported the observation of two  $Q$  branches near the theoretically predicted position of the  $A^3\Sigma^- - X^3\Pi$  transition. The two branches were assigned as  $Q_1$  and  $Q_3$ , but due to the low signal-to-noise ratio of the spectrum and high line density, no other branches could be found. A complete set of experimental and theoretical references to previous work on SiC is provided in our previous paper.<sup>1</sup>

Since our last report, we have tried to obtain spectra of SiC with better signal to noise, but without success. SiC is a difficult species to produce. The microwave transitions tied down the ground state constants and using this information, it was possible to obtain absolute  $J$  quantum number assignments for the two previously identified branches. Using this information, many other branches were found and a full rotational analysis of the  $A^3\Sigma^- - X^3\Pi$  system obtained.

## EXPERIMENTAL

The  $A^3\Sigma^- - X^3\Pi$  system of SiC was observed in the same Fourier transform spectrum as the  $d^1\Sigma^+ - b^1\Pi$  system.<sup>1</sup> The spectrum was observed in emission from a composite wall hollow cathode (1:3 SiC powder to copper powder) and recorded with the McMath Fourier transform spectrometer at the National Solar Observatory at Kitt Peak. A total of 69 scans were co-added in 8.3 h at a resolution of  $0.02\text{ cm}^{-1}$  using InSb detectors and a silicon filter. This gave a bandpass of  $1800\text{--}9000\text{ cm}^{-1}$ .

The spectrum consisted primarily of  $C_2$  lines, but two bands with a rotational spacing characteristic of SiC were observed. Absolute calibration of the spectrum was obtained from the Ne atomic lines, which have been calibrated against  $OH^3$  in an  $OH\text{--}Ne$  spectrum. The absolute accuracy of the line positions is about  $\pm 0.002\text{ cm}^{-1}$ .

<sup>a)</sup> Current address: Food and Drug Administration, Division of Drug Analysis, 1114 Market Street, St. Louis, MO 63101.

<sup>b)</sup> Alfred P. Sloan Fellow, Camille and Henry Dreyfus Teacher-Scholar.

## RESULTS AND ANALYSIS

Figure 1 shows a section of the spectrum near the strongest lines of the two previously identified branches  $Q_1$  and  $Q_3$ . It is immediately apparent why this system was un-analyzable without the help of microwave constants. The spectrum is very congested and the signal-to-noise ratio is quite low, about 5 to 1 for the  $Q_1$  and  $Q_3$  lines. The  $Q_1$  and  $Q_3$  branch lines were fitted to a  $^3\Sigma^- - ^3\Pi$  Hamiltonian with the ground state constants held fixed to those of Cernicharo *et al.*<sup>2</sup> By varying the excited state constants  $T$ ,  $B$ ,  $D$ , and  $\gamma$ , it was possible to fit either branch with any reasonable  $J$  assignment; however, only for one assignment could both branches be described using the same set of constants.

A spectrum prediction program, using the intensity formulas of Budo,<sup>4</sup> was used to predict the positions of the connecting  $P_1$ ,  $R_1$ ,  $P_3$ , and  $R_3$  branches. Lines for all four branches were found in the predicted positions confirming the  $J$  assignment of the  $Q_1$  and  $Q_3$  branches. These lines were all very weak, having a signal-to-noise of 3 to 1 or less as was predicted by the intensity formulas.

The  $Q_2$  lines were predicted with a signal-to-noise ratio of about 3 to 1. The  $F_2$  energy levels are quite sensitive to the value of  $\lambda$  in the  $^3\Sigma^-$  state, but the spacing between the  $Q_2$  lines could be predicted accurately and by matching the predicted spacings with the spectrum, an assignment was obtained. The  $P_2$  and  $R_2$  lines were also observed and added to the data set.

The  $A^3\Sigma^- - X^3\Pi$  system of SiC is a Hund's case (b)—case (a) transition<sup>5</sup> and, in principle, all 27 possible branches have reasonable intensities. The calculated intensities for the four  $Q$ -type satellite branches are comparable to those for the other newly assigned lines, and using the prediction these branches were picked out and assigned. The remaining satellite branches are predicted to have an intensity about of at least a factor of 2 less than the weakest of the ones previously assigned and, while some lines could be seen in the spectrum, the signal-to-noise ratio was poor and they were not measured.

A total of 393 lines from 13 branches were assigned and fitted to a  $^3\Sigma^- - ^3\Pi$  Hamiltonian. The line positions and residuals are available through PAPS<sup>6</sup> or directly from the authors. The effective Hamiltonian for a  $^3\Sigma^-$  state is given

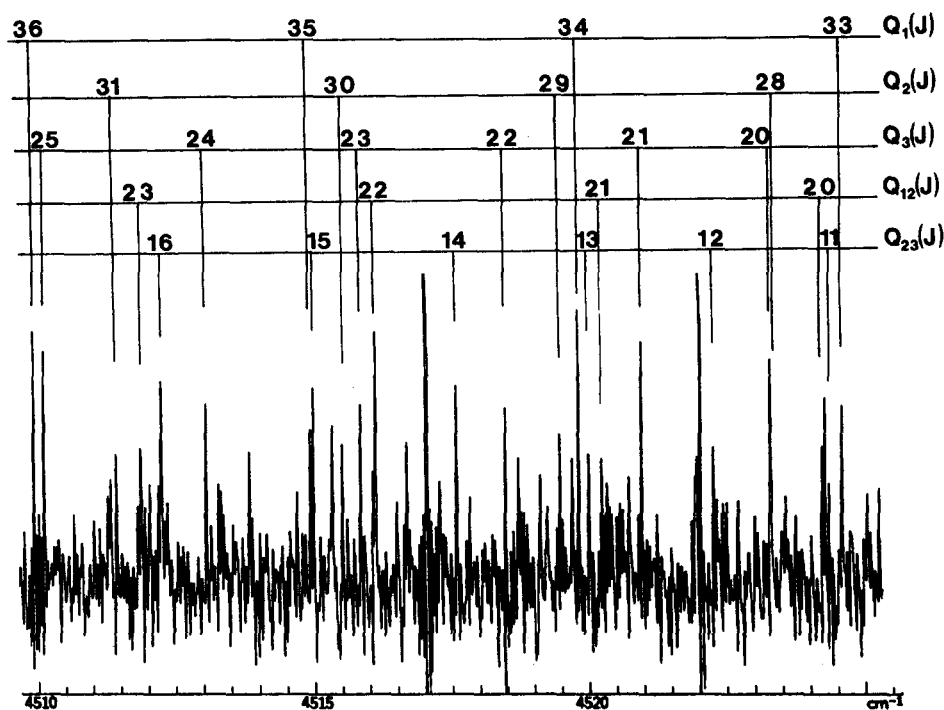


FIG. 1. Part of the 0-0 band of the  $A^3\Sigma^- - X^3\Pi$  system of SiC showing the dense rotational structure due to the many overlapping branches. In addition to the Q lines indicated, many P and R branch lines are also present in this region.

by Zare *et al.*,<sup>7</sup> while Brown and Merer<sup>8</sup> give the  $^3\Pi$  Hamiltonian. Explicit matrix elements for both states are given by Brazier *et al.*<sup>9</sup> The microwave data of Cernicharo *et al.*<sup>2</sup> were included in the fit and weighted according to their estimated precision. The Fourier transform data were weighted according to the signal to noise of the lines. The  $Q_1$  and  $Q_3$  branches are estimated to have a precision of  $0.003 \text{ cm}^{-1}$ , the  $P_1$ ,  $R_1$ ,  $P_3$ ,  $R_3$ ,  $Q_2$ ,  $Q_{12}$ ,  $Q_{23}$ ,  $Q_{32}$ , and  $Q_{21}$  branches  $0.005 \text{ cm}^{-1}$  and the  $P_2$  and  $R_2$  branches  $0.007 \text{ cm}^{-1}$ . Some low and high  $J$  rotational lines were deweighted slightly and 32 lines were deweighted because of blending. The constants from our final fit are reported in Table I.

## DISCUSSION

We have analyzed a single vibrational band of the  $A^3\Sigma^- - X^3\Pi$  system of SiC. The ground vibrational level is clearly  $v = 0$  from the microwave observations,<sup>2</sup> but the excited state vibrational assignment is not immediately obvious. The Franck-Condon factors for this transition were calculated from the constants obtained, assuming assignment to the 0-0 band. The vibrational frequencies determined from the Kratzer relation<sup>5</sup>  $D = 4B^3/\omega^2$  are  $\omega_e = 965 \text{ cm}^{-1}$  for  $X^3\Pi$  and  $\omega_e = 861 \text{ cm}^{-1}$  for  $A^3\Sigma^-$ . By looking at similar molecules, values for  $\omega_e x_e$  of 5 and  $4 \text{ cm}^{-1}$  for the  $X$

TABLE I. Molecular constants for the 0-0 band of the  $A^3\Sigma^- - X^3\Pi$  transition of SiC in  $\text{cm}^{-1}$ . The numbers in parentheses correspond to one standard deviation in the last digit.

Constant	$X^3\Pi^a$	$X^3\Pi^b$	$A^3\Sigma^-^a$
$T_0$	...	...	4 577.819 51(63)
$B_0$	0.677 054 474(25)	0.677 054 457(33)	0.610 325 9(24)
$D_0 \times 10^6$	1.351 34(38)	1.351 27(33)	1.258 8(24)
$H_0 \times 10^{12}$	...	...	- 2.68(22)
$\lambda_0$	- 0.037 28(30)	- 0.038 660(33)	0.342 95(85)
$\lambda_{D0} \times 10^5$	0.201(46)	...	- 2.401(83)
$\gamma_0 \times 10^3$	6.290 0(70)	6.204(67)	- 2.515(27)
$\gamma_{D0} \times 10^7$	...	...	- 3.43(12)
$A_0$	- 41.630 31(44)	- 41.635 5(43)	...
$a_0$	0.896 41(34)	0.890 8(20)	...
$o_{D0} \times 10^6$	- 1.85(29)	...	...
$p_0 \times 10^3$	4.538 0(78)	4.403(33)	...
$q_0 \times 10^5$	- 3.572(60)	3.952 7(33)	...

<sup>a</sup> This work.

<sup>b</sup> Reference 2.

and  $A$  states, respectively, were estimated. From these  $\omega_e x_e$  values,  $\alpha_e$ 's of 0.0049 and 0.0041  $\text{cm}^{-1}$  were calculated from the Pekeris relation<sup>5</sup>  $\alpha_e = 6\sqrt{\omega_e x_e B_e^3}/\omega_e - 6B_e^2/\omega_e$ . The Franck-Condon factors for the 0-1, 0-0, and 1-0 bands were found to be 0.4, 0.5, and 0.4, respectively. This implies that more than one band should be seen. An additional weak band showing dense structure characteristic of SiC was found about 900  $\text{cm}^{-1}$  to the red, but no significant structure could be seen to the blue. If the analyzed band is 0-0, then this adjacent band is 0-1. The intensity of the adjacent band is a factor of 2 to 3 less than the 0-0 band as predicted by the  $\nu^3$  dependence of the emission intensity. The very poor signal-to-noise ratio of the spectrum (less than 2), together with interference from extensive atmospheric  $\text{CO}_2$  absorption, makes it impossible to pick out any structure in this band. The 1-0 band would be expected to have 1.5 times the intensity of the origin system if the vibrational populations in  $v = 0$  and  $v = 1$  were equal. However, no sign of emission from  $v = 1$  was seen in the  $d^1\Sigma^+ - b^1\Pi$  system,<sup>1</sup> implying a fairly low vibrational temperature. A vibrational temperature of  $\sim 1000$  K compared to the  $\sim 600$  K rotational-temperature would be required to see the 1-0 band. The only alternative assignment of the observed spectrum to the 1-0 band would imply a 2-1 band of at least comparable intensity to the blue where none is seen. From this evidence, we are reasonably confident that we have observed the 0-0 band of the  $A^3\Sigma^- - X^3\Pi$  system of SiC.

The bond lengths obtained  $r_0 = 1.72187 \text{ \AA}$  and  $r_0 = 1.81356 \text{ \AA}$  for the  $X^3\Pi$  and  $A^3\Sigma^-$  states are in very good agreement with the theoretical  $r_0$  values<sup>1</sup> of 1.726 and 1.810  $\text{\AA}$ , respectively. The theoretical  $T_{00}$  value<sup>1</sup> of 3600  $\text{cm}^{-1}$  compares reasonably well with the experimental value of 4578  $\text{cm}^{-1}$ . The *ab initio*  $T_{00}$  value of Bauschlicher and Langhoff<sup>10</sup> is 3700  $\text{cm}^{-1}$ .

The ground molecular constants (Table I) which we derived from our analysis are in good agreement with the values of Cernicharo *et al.*<sup>2</sup> This is not surprising since the microwave data was included in our final fit. The optical data allows the determination of some additional higher order constants such as  $\lambda_D$  and  $o_D$ . The optical data also directly determine the spin-orbit constant  $A_0$ , which is only indirectly determined from spin uncoupling effects in the pure

rotational microwave data. In summary, the  $X^3\Pi$  constants of Table I should be slightly better than those reported by Cernicharo *et al.*<sup>2</sup> The constants for the  $A^3\Sigma^-$  state are determined for the first time.

## CONCLUSION

We have analyzed the origin band of the  $A^3\Sigma^- - X^3\Pi$  system of SiC. The band is very weak, presumably due to the difficulty in making SiC and was only analyzable with the aid of ground state microwave constants.

## ACKNOWLEDGMENTS

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. Acknowledgment is made to the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work. Support was also provided by the Air Force Astronautics Laboratory, Grant No. F04611-87-0020. We thank C. Gottlieb for a copy of Ref. 2 in advance of publication. These microwave data were the key to our analysis.

<sup>1</sup>P. F. Bernath, S. A. Rogers, L. C. O'Brien, C. R. Brazier, and A. D. McLean, *Phys. Rev. Lett.* **60**, 197 (1988).

<sup>2</sup>J. Cernicharo, C. A. Gottlieb, M. Guélin, P. Thaddeus and J. M. Vrtilik, *Astrophys. J. Lett.* **341**, L25 (1989).

<sup>3</sup>T. Amano, *J. Mol. Spectrosc.* **103**, 436 (1984).

<sup>4</sup>A. Budo, *Z. Phys.* **105**, 579 (1937).

<sup>5</sup>G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed. (Van Nostrand Reinhold, New York, 1950).

<sup>6</sup>See AIP document no. PAPS JCPA-91-7384-4 for 4 pages of measured line positions of the 0-0 band of the  $A^3\Sigma^- - X^3\Pi$  transition of SiC. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The price is \$1.50 for each microfiche (98 pages) or \$5.00 for photocopies of up to 30 pages, and \$0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.

<sup>7</sup>R. N. Zare, A. L. Schmeltekopf, W. J. Harrop, and D. L. Albritton, *J. Mol. Spectrosc.* **46**, 37 (1973).

<sup>8</sup>J. M. Brown and A. J. Merer, *J. Mol. Spectrosc.* **74**, 488 (1979).

<sup>9</sup>C. R. Brazier, R. S. Ram, and P. F. Bernath, *J. Mol. Spectrosc.* **120**, 381 (1986).

<sup>10</sup>C. W. Bauschlicher and S. R. Langhoff, *J. Chem. Phys.* **87**, 2919 (1987).