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Electronic Absorption Spectra of SiC^- and SiC in Neon Matrices

M. Grutter, P. Freivogel, and J. P. Maier*

Institute of Physical Chemistry, University of Basel, Klingelbergstrasse 80, CH-4056 Basel, Switzerland

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The A $^2\Pi \leftarrow X\ ^2\Sigma^+$ and B $^2\Sigma^+ \leftarrow X\ ^2\Sigma^+$ electronic transitions of SiC^-, with origin bands at 3538 cm^{-1} and 21 683 cm^{-1}, have been identified in 5 K neon matrices using mass-selected deposition. Neutralization of the anions leads to the observation of two known systems of SiC, as well as of a new system, B $^3\Sigma^+ \leftarrow X\ ^3\Pi$, with origin at 11 749 cm^{-1}.

I. Introduction

Silicon−carbon molecules are of interest in astrophysical and terrestrial environments. The SiC molecule has been identified by radioastronomy in dense interstellar clouds and stellar atmospheres,[1] and SiC_4 in the circumstellar shell of a carbon star.[2] The absorption bands of some carbon-rich stars have been proven to belong to the SiC_2 electronic system.[3]

The first experimental observation for SiC in the gas phase was a weak band of the $d^1\Sigma^+ \rightarrow b^1\Pi$ electronic transition.[4] Detection of the rotational spectrum of SiC produced in a dc glow discharge followed.[1] The A $^3\Sigma^- \rightarrow X\ ^3\Pi$ electronic transition was identified in emission,[5] with a 0−0 band at 4578 cm^{-1}. Subsequent theoretical studies reassigned this to the 1−0 transition.[6,7] The C $^3\Pi \rightarrow X\ ^3\Pi$ transition of SiC was found by laser-induced fluorescence using a laser vaporization source.[8] An electronic spectrum of SiC_2 has also been observed, and the rotational structure analyzed.[9] A number of infrared transitions of up to penta atomic silicon−carbon clusters have been identified in argon matrices,[10] as well as Si_2C_3[11] and SiC_4[12] in the gas phase.

The electron affinity of SiC has been calculated to be in the 1.98[13]− 2.25 eV[14] range. The *ab initio* calculations on SiC^- predict a $^2\Sigma^+$ ground and a bound $^2\Pi$ excited state,[13,14] but no experimental data are available. In this contribution absorption spectra from the ground to two electronic excited states of SiC^-, as well as a further transition of SiC, measured in 5 K neon matrices are presented.

II. Experimental Section

The experimental technique for the production of anions from a cesium sputter source was described previously.[15,16] A silicon carbide rod was used as target from which carbon, silicon, and carbon−silicon anionic clusters were extracted upon bombarding its surface with a 1 keV Cs^+ beam. The mass-selected SiC^- ions were condensed together with excess of neon on a rhodium-coated sapphire plate cooled to 5 K. An ion current of around 250 nA was maintained during the growth of a ~200 μm thick matrix. The trapped ions were neutralized by photodetaching the electrons with a 80 W medium-pressure mercury lamp during or after the 2 h deposition. Visible and near infrared absorption spectra were measured with 0.1 nm resolution in a waveguide configuration.[17] A Fourier-transform spectrometer was used for reflection measurements below 10 000 cm^{-1}.

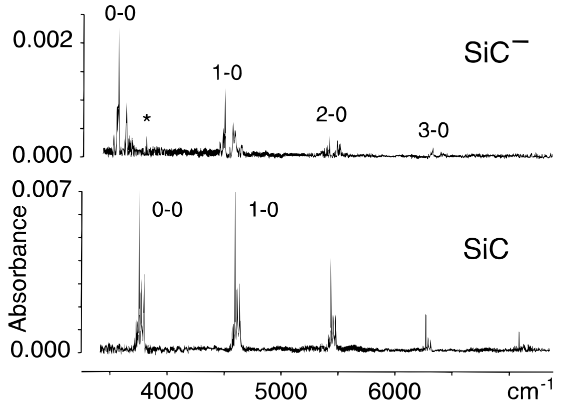

Figure 1. Absorption spectrum of the A $^2\Pi \leftarrow X\ ^2\Sigma^+$ electronic transition of SiC^- in a 5 K neon matrix (top). The spectrum was measured after codeposition of mass-selected SiC^- with excess of neon. The bottom spectrum is the A $^3\Sigma^- \leftarrow X\ ^3\Pi$ transition of SiC observed when the matrix is irradiated by UV photons during deposition to neutralize the anions. The asterisk marks the absorption peak of water trapped in neon, and the noise below 4000 cm^{-1} is caused by the background subtraction (bands of water in air).

III. Results and Discussion

1. SiC^-. A. A $^2\Pi \leftarrow X\ ^2\Sigma^+$ Transition. When mass-selected SiC^- anions are codeposited with neon to form a matrix at 5 K, an absorption system with origin band at 3538 cm^{-1} (~0.44 eV) is observed (Figure 1, top trace). It shows a complex site structure, which repeats for the vibrationally excited bands. Irradiation of the matrix with UV light results in the disappearance of these bands, and a stronger absorption system due to the known A $^3\Sigma^- \leftarrow X\ ^3\Pi$ transition of SiC with origin at 3738 cm^{-1} emerges (Figure 1, bottom trace). This band was estimated to lie near 3753 cm^{-1} according to the reassignment[7] of the reported spectrum.[5] It is worthwhile to note that the absorption spectrum shown in Figure 1 confirms this assignment directly, because at 5 K only the lowest vibrational level of the ground state is populated. Thus the first intense band observed on the lower energy side is the 0−0 transition. Also, a better T_e in the gas phase can now be determined using only experimental data. Taking the matrix ω_e and $\omega_e x_e$ values for the A $^3\Sigma^-$ state, together with the X $^3\Pi$ constants[18] and the 1−0 band position[5] from the gas-phase studies, yields $T_e = 3774$ cm^{-1} for SiC.

Ab initio calculations on SiC^- predict two bound electronic states: the ground X $^2\Sigma^+$ state and an excited A $^2\Pi$ state lying 0.4 eV above.[13,14] The excited state vibrational frequency has been calculated as 951 cm^{-1},[14] and values of 949 and 5.5 cm^{-1} have been reported for ω_e and $\omega_e x_e$, respectively.[13] From the position of the three members of the vibrational progression in the matrix spectrum (Table 1) one infers the constants $\omega_e = 941(3)$ cm^{-1} and $\omega_e x_e = 6(1)$ cm^{-1}. On the basis of the conversion of the spectrum of mass-selected SiC^- to that of

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TABLE 1: Observed Absorption Bands in the Electronic Transitions of SiC^- and SiC in 5 K Neon Matrices; The Most Intense Site Is Given for the A ← X Transitions of SiC^- and SiC, the Band Maximum for the B ← X Transition of SiC^- and the C ← X One of SiC, and the Zero-Phonon Line for the B ← X Transition of SiC

λ (nm)[a]	ν (cm^{-1})[b]	$\Delta\nu$ (cm^{-1})	assignment
			SiC^- $A\,^2\Pi \leftarrow X\,^2\Sigma^+$
	3538.4	0	0−0
	4468.0	929.6	1−0
	5387.2	919.2	2−0
	6294.6	907.4	3−0
			SiC^- $B\,^2\Sigma^+ \leftarrow X\,^2\Sigma^+$
461.2	21 683	0	0−0
446.9	22 376	693	1−0
433.6	23 064	688	2−0
420.9	23 757	693	3−0
409.7	24 408	651	4−0
			SiC $A\,^3\Sigma^- \leftarrow X\,^3\Pi$
	3738.0	0	0−0
	4592.2	854.2	1−0
	5436.4	844.2	2−0
	6270.1	833.7	3−0
	7094.0	823.9	4−0
			SiC $B\,^3\Sigma^+ \leftarrow X\,^3\Pi$
851.1	11 749	0	0−0
774.1	12 919	1170	1−0
710.5	14 076	1157	2−0
656.7	15 227	1151	3−0
			SiC $C\,^3\Pi \leftarrow X\,^3\Pi$
440.7	22 692	0	0−0
429.3	23 292	600	1−0
418.9	23 875	583	2−0
409.2	24 438	563	3−0
400.1	24 993	555	4−0
391.5	25 542	549	5−0
393.5	26 076	534	6−0
376.0	26 596	520	7−0
368.7	27 122	526	8−0

[a] Wavelength measurement (±0.2 nm). [b] The uncertainty can be determined from the first column. The A ← X transitions of SiC^- and SiC were measured in wavenumbers with an FTIR instrument (±1 cm^{-1}).

SiC, as well as the good agreement with *ab initio* predictions,[13,14] the top spectrum in Figure 1 is assigned to the $A\,^2\Pi \leftarrow X\,^2\Sigma^+$ transition of SiC^-.

B. $B\,^2\Sigma^+ \leftarrow X\,^2\Sigma^+$ Transition. A second absorption system with origin at 21 683 cm^{-1} (Figure 2, top) is observed before photobleaching. This electronic transition is located at an energy 0.4−0.7 eV larger than the calculated electron affinity of SiC (1.98−2.25 eV[13,14]). Detachment of electrons from the SiC^- ions embedded in the neon matrix was established to take place between 3.5 and 4.0 eV by means of wavelength-selected irradiation. As has been reported for matrix studies of other anionic species,[15,19] stabilization in the neon environment leads to an increase in electron detachment threshold of about 1 eV relative to the gas phase. Thus the observed electronic excited state of the anion lies above the electron detachment threshold in the gas phase. The band system discernible partially overlaps with the known $C\,^3\Pi \leftarrow X\,^3\Pi$ transition of SiC.[8,18] The latter grows significantly after electron detachment is induced by UV illumination of the matrix (Figure 2 middle).

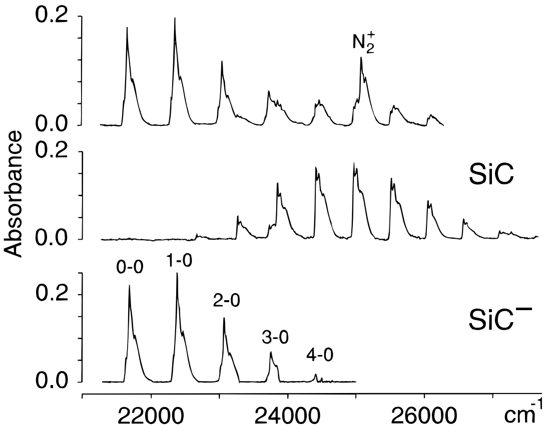

Figure 2. The $B\,^2\Sigma^+ \leftarrow X\,^2\Sigma^+$ electronic transition of SiC^- (bottom). It was obtained by subtracting the spectrum observed after a neon matrix with mass-selected SiC^- had been grown and UV-irradiated (middle) from that before the irradiation was performed (top). The absorption spectrum in the middle is the $C\,^3\Pi \leftarrow X\,^3\Pi$ transition of SiC, which is, although weak, already present before irradiation.

First-row isovalent diatomics, C_2^-, CN, or N_2^+ have a second $^2\Sigma^+$ state characterized by a ...$\sigma\pi^4\sigma^2$ electron configuration. For those containing a second-row element the $B\,^2\Sigma^+$ state arises from the electron configuration ...$\sigma^2\pi^3\sigma\pi^*$.[13] The second $^2\Sigma^+$ state of SiC^-, corresponding to the $B\,^2\Sigma^+$ state of C_2^-, has been calculated to lie at energies exceeding the electron affinity of SiC.[13]

The bottom spectrum in Figure 2 is a subtraction of the trace in the middle (neutral SiC) from the actual spectrum (top) with scaling. It is assigned to the $B\,^2\Sigma^+ \leftarrow X\,^2\Sigma^+$ electronic transition of SiC^-. In Table 1 are given the wavelengths of the observed bands together with the vibrational assignment.

2. SiC: $B\,^3\Sigma^+ \leftarrow X\,^3\Pi$ Transition. When the matrix was irradiated either during or after codeposition of SiC^- and neon, three band systems appeared. Two of these are the already known $A\,^3\Sigma^- \leftarrow X\,^3\Pi$ and $C\,^3\Pi \leftarrow X\,^3\Pi$ transitions of SiC, which are been found near 3738 and 22 692 cm^{-1} in neon. The

TABLE 2: Comparison of the Spectroscopic Constants for SiC and SiC^- Observed in Neon Matrices with Gas Phase or Calculated Values

	T_e (cm^{-1})		ω_e (cm^{-1})		$\omega_e x_e$ (cm^{-1})	
SiC	gas	neon[a]	gas	neon[a]	gas	neon[a]
$X\,^3\Pi$	0	0	965.16(24)[b]		5.910(36)[b]	
$A\,^3\Sigma^-$	3774[c]	3788(2)	862[d]	864(3)	4.89[d]	5(1)
$B\,^3\Sigma^+$		11 642(2)		1178(3)		5(1)
$C\,^3\Pi$	22 829.46(16)[e]	22 876(20)	618.85(21)[e]	600(25)	11.01(8)[e]	−

	T_e (cm^{-1})		ω_e (cm^{-1})		$\omega_e x_e$ (cm^{-1})	
SiC^-	calc	neon[a]	calc	neon[a]	calc	neon[a]
$X\,^2\Sigma^+$	0	0	976[g]		4.5[g]	
$A\,^2\Pi$	~3200[f]	3556(2)	949[g]	941(3)	5.5[g]	6(1)
$B\,^2\Sigma^+$		21 813(20)		717(25)		

[a] This work. [b] Reference 18. [c] Estimated from the experimental 1−0 band[5] and the vibrational constants obtained in ref 18 for the ground state and in a neon matrix for the excited state. [d] Calculated in reference 7. [e] Reference 8. [f] Calculated in reference 14 at 0.4 eV and in reference 13 at 0.39 eV. [g] Reference 13.

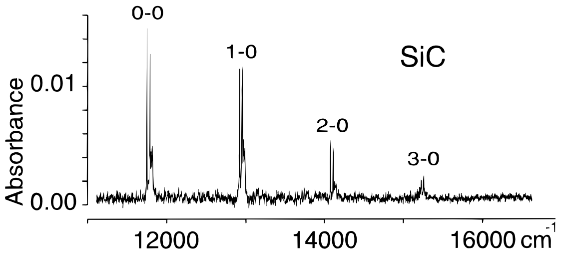

Figure 3. Absorption spectrum of the B $^3\Sigma^+ \leftarrow$ X $^3\Pi$ electronic transition of SiC in a 5 K neon matrix. The spectrum was recorded after a mass-selected beam of SiC$^-$ was codeposited with excess of neon while irradiating with a medium-pressure mercury lamp.

third, shown in Figure 3, has its origin band at 11 749 cm^{-1} (zero phonon line, Table 1) and is a factor 10 less intense than the C $^3\Pi \leftarrow$ X $^3\Pi$ transition. The intensity of this new band system correlates with the other two of SiC and grows as the band systems of SiC$^-$ diminish. Thus it is an electronic transition of SiC. The spectrum shows three members of a vibrational progression with similar site structure. The inferred vibrational constants are $\omega_e = 1178(3)$ cm^{-1} and $\omega_e x_e = 5(1)$ cm^{-1}.

Several high-quality calculations on SiC have been published, but only one of them treats excited triplet electronic states lying above A $^3\Sigma^-$. In this, a B $^3\Sigma^+$ state is located in between the A $^3\Sigma^-$ and C $^3\Pi$ ones, at around 18 900 cm^{-1}.[20] Though there is a discrepancy (0.9 eV) between the calculation and experiment, the observed band system is attributed to the B $^3\Sigma^+ \leftarrow$ X $^3\Pi$ transition of SiC, because no other absorption system is discernible between this and the C $^3\Pi \leftarrow$ X $^3\Pi$ transition. In Table 2 the experimentally determined spectroscopic constants for SiC and SiC$^-$ are summarized.

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