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Rapid Note

The optical spectrum of HCSi

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Abstract. A new emission band system has been observed in the gas phase at around 850 nm. This system correlates with absorption bands previously measured in a neon matrix and assigned to a triplet electronic transition of SiC. However, the gas phase bands display a clear doublet structure. Preliminary molecular parameters resulting from the rotational analysis of the (000) - (000) band coincide with the expected values obtained by a recently published *ab initio* calculation carried out on the HCSi radical. We conclude that both the gas phase and the neon matrix spectra originate from the HCSi radical which is here identified for the first time.

PACS. 33.20.Kf Visible spectra – 3.15.Mt Rotation, vibration, and vibration-rotation constants

1 Introduction

Optical spectra of di- or triatomic molecular species involving the C-Si bond were scarce until recently, although these species are of great interest in astrophysics, since carbon and silicon belong to the most abundant elements in the universe.

While the first laboratory spectrum of SiC_2 was recorded in 1957 [1], one must wait until the 1980's to find a thorough spectroscopic study of SiC_2 [2], a rare gas matrix spectrum of Si_2C [3,4], and the first optical spectrum of SiC [5] followed by the first microwave spectrum of the same species [6]. Finally, Grutter *et al.* [7] presented electronic absorption spectra of SiC^- and SiC in neon matrices, but until the present work, no experimental spectroscopic data were available on HCSi nor on HSiC hydrogenated compounds.

We present here a preliminary analysis of the $A\,^2\Sigma^+ - X^2\Pi_i$ band system of HCSi observed in the 10700−13000 cm^{-1} spectral region.

2 Experimental

The emission source was a Schüler type tube similar to that used previously to produce, for example, spectra of the benzyl and xylyl radicals [8]. A DC discharge (2000 V, 100 mA) was established through a flowing mixture of helium (p = 5 mb) and hexamethyl disilane ($(CH_3)_3{-}Si{-}Si{-}(CH_3)_3$) at a low pressure (just sufficient to obtain a grey-pink positive column). Very recently, Deo and Kawaguchi [9] showed that this technique allowed them to obtain Fourier Transform spectra of new vibrational bands of the $A^3\Sigma^- - X^3\Pi$ system of SiC, *i.e* that it provides larger excited SiC concentration than the hollow cathode (made of a SiC/Cu composite) sputtering technique previously developed by Bernath *et al.* [5].

The spectrum was recorded by means of a Bruker IFS 120 HR Fourier Transform spectrometer. The detector was an avalanche silicon photodiode associated with a long-pass wavelength coloured glass filter. The spectrum was obtained after Fourier transformation of 200 coadded interferograms recorded at an apodized resolution of 0.05 cm^{-1}.

3 Results and discussion

Three double double-headed bands are observed in the 10700−13000 cm^{-1} spectral interval. All of them are degraded towards short wavelength. Table 1 gives the wavenumbers of 12 observed subband heads of 3 bands that we assigned to (000)−(100), (000)−(000), and (100)−(000) of a $^2\Sigma^+ - ^2\Pi$ electronic transition of the linear HCSi radical. Figure 1 shows part of the $^2\Sigma^+ - ^2\Pi_{3/2}$ subband of the (000)−(000) band with two prominent heads, at 11788.9 and 11801.1 cm^{-1}. The spectrum is interspersed by lines of molecular hydrogen which are easily identifiable by their broader line width of about 0.25 cm^{-1}.

The rotational analysis of the 12 branches of the band that we assign to (000)−(000) was straightforward.

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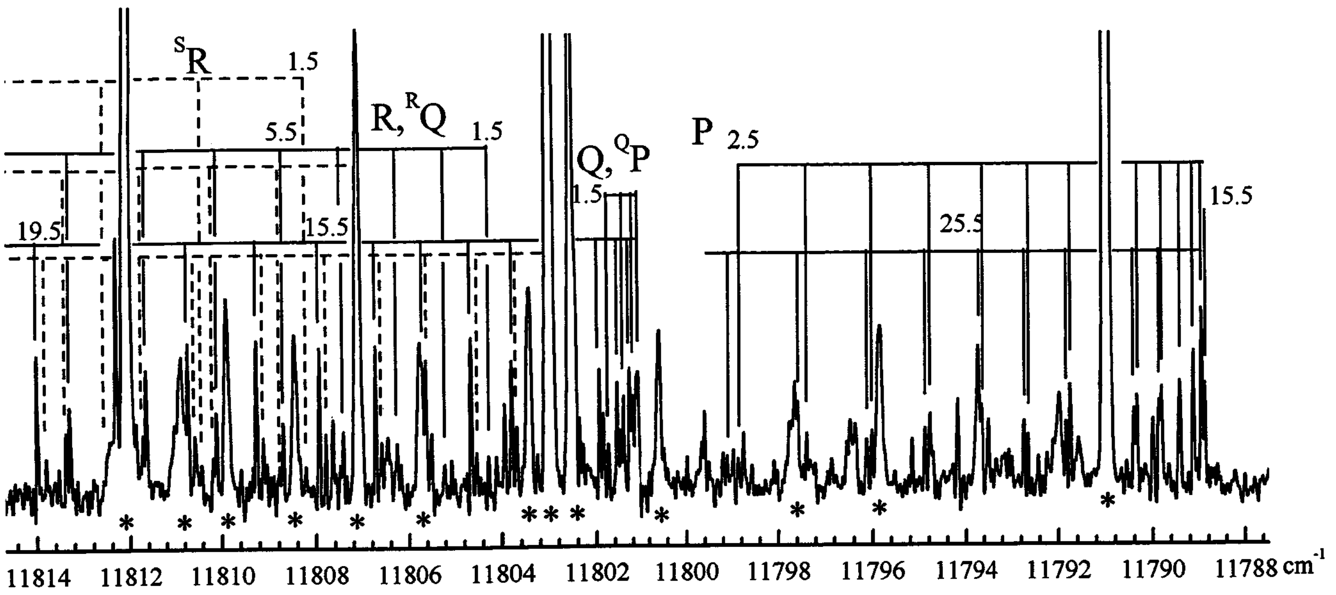

Fig. 1. Fourier transform emission spectrum of the (000)−(000) $A^2\Sigma^+$–$X^2\Pi_{3/2}$ of HCSi. Asterisks indicate molecular hydrogen lines.

Table 1. Subband heads (in cm^{-1}) of the $A^2\Sigma^+$–$X^2\Pi_i$ transition of HCSi.

(000)−(100)	(000)−(000)	(100)−(000)	Branch
10702.6	11715.2	12882.0	P_2
10716.1	11729.8	12897.4	Q_2
10775.1	11788.9	12955.6	P_1
10786.5	11801.1	12968.7	Q_1

A least-squares fit was performed on 211 lines of this band, using the rotational energy formulae given in a study of the electronic transition $A^2\Sigma^+ - X^2\Pi_i$ of NCO [10]. The standard deviation of the fit was 0.0058 cm^{-1}.

We make the further arguments as follows in support of our assignments:

(*i*) A recent *ab initio* calculation performed by Robbe *et al.* [11] showed that HCSi is linear in both its $^2\Pi$ ground state and $^2\Sigma^+$ first excited state. The equilibrium energy of the first excited state is calculated to be 12200 cm^{-1} above the ground state, whereas the predicted rotational constant for the ground state is 0.5737 cm^{-1}. These values are in very good agreement with those reported in Table 2 ($\nu_0 = 11766.72$ cm^{-1} and $B_0'' = 0.5804$ cm^{-1}). Note that the rotational constant was not calculated for the excited state in reference [11], but as the calculated r(C-Si) internuclear distance [11] is larger in the ground state (1.702) than in the excited state (1.587), one can reasonably assume that the latter is more bound than the $X^2\Pi$ state. As a consequence, the electronic transition bands are degraded towards short wavelength.

Concerning the spin-orbit constant A of $X^2\Pi_i$, Robbe *et al.* [11] calculated a value of −41.63 cm^{-1}, whereas the experimental one is −69.82 for the (000) level. Although the theoretical result is correct in predicting an inverted $^2\Pi$ state, the agreement of the experimental and theoretical absolute values of A is less satisfactory. However, the theoretical value was calculated only at the CASSCF level, as pointed out by Robbe *et al.* [11], so that the uncertainty might exceed the 10% claimed by the authors.

(*ii*) The doublet structure of the observed bands allowed us to rule out the hypothesis of SiC as the emitter. An important remark should be made on this subject: Grutter *et al.* [7] observed in their neon matrix spectra a progression of four absorption bands in the same spectral region as that considered here. They were assigned to a $B^3\Sigma^+$–$X^3\Pi$ transition of SiC, despite of the great discrepancy between the experimental (11642 cm^{-1}) and theoretical [13] (18900 cm^{-1}) transition energies. Among those bands, two bands at 11749 and 12919 cm^{-1}, assigned as the (0,0) and (1,0) bands clearly coincide, taking into account the same solid-gas shift (35 cm^{-1}), with those given in Table 1 for the HCSi, $A^2\Sigma^+$–$X^2\Pi$ (000)−(000) and (100)−(000) gas phase emission bands. In addition to the doublet structure being incompatible with an assignment to neutral SiC, one can also verify that the vibrational frequency ($\Delta G_{1/2} = 1012.6$ cm^{-1}) of the lower state (inaccessible in the solid phase spectrum) does not correspond to that of the SiC ground state ($\Delta G_{1/2} =$ 953.2 cm^{-1}) given in reference [12]. On the contrary, the experimental vibrational spacing ($\Delta G_{1/2} = 1012.6$ cm^{-1}) deduced from Table 1 in the lower state agrees nicely with the calculated stretching frequency ($\omega_1 = 1011.9$ cm^{-1}) of reference [11]. The species responsible for the 11749 cm^{-1} progression bands observed in neon matrix [7] should therefore be re-identified as belonging to HCSi rather than SiC. The unavoidable presence of hydrogen (an absorption peak of water trapped in neon was indicated in Fig. 1 of Ref. [7]) surely accounts for the formation of HCSi in the experiment of Grutter *et al.* [7]. Note that the inevitable presence of hydrogen is also responsible for the appearance of the two weak unidentified emission band heads at 772 and 848 nm (respectively 12953 and 11792 cm^{-1}) reported

Table 2. Molecular constants (in cm^{-1}) obtained from the rotational analysis of the (000)−(000) $A^2\Sigma^+ - X^2\Pi_i$ of HCSi compared to the *ab initio* calculated values of reference [11].

	This work		From Ref. [11]	
	X (000) $^2\Pi_i$	A (000) $^2\Sigma^+$	X (000) $^2\Pi_i$	A (000) $^2\Sigma^+$
B	0.58044 (3) [a]	0.63539 (3)	0.5737	
$10^6 D$	0.66 (3)	0.69 (4)		
A	−69.816 (2)		−41.0	
$10^2\gamma$	0.026 (26)	0.902 (6)		
$10^2 p$	0.23 (1)			
$10^3 q$	−0.128 (9)			
ν_0	11766.7205 (9)		12200 [b]	
S.D.	0.0058			

[a] Error limit are one σ.

[b] This value is given relative to the minimum energy of the $^2\Pi$ state potential.

in reference [14] and recorded on photographic plate from an electric discharge with a SiC/Cu composite cathode in a transverse magnetic field. Due to the poor quality of the photographic plate spectra, these bands were not rotationally analysed. However, they can now be identified with some of the subband heads given in Table 1 of the present work.

(*iii*) Finally, the hypothesis of SiC^+ or SiC^- as possible emitters must be rejected in view of calculated potential energies [15,16] and because SiC^+ could not have been formed in the Grutter *et al.* [7] experiment, whereas, in the same experiment, the intensity of the band system considered does not correlate with those already known to belong to SiC^-.

4 Conclusion

We observed three emission bands in the 10700 − 13000 cm^{-1} near infrared region, and assigned them to the $A^2\Sigma^+ - X^2\Pi_i$ transition of HCSi. The identification of the emitter is based on results from rotational analysis which coincide with a recent *ab initio* calculation [11]. Correlation of several of these bands with several bands previously observed in a neon matrix [7] allowed us, on the one hand, to reassign the latter to HCSi rather than to SiC, and, on the other hand, to determine the vibrational numbering, *i.e.* the 11715 cm^{-1} band is actually the (000)−(000) band. As can be seen in Figure 1, all of the observed lines are not yet assigned. This situation is even more pronounced for the (000)−(100) band, whereas several not yet assigned features appear in the 10500−11700 cm^{-1} spectral range. Previous analyses of discharge emission spectra have been carried out on the same type of molecules, such as C_2H [17] and NCO [18]. They contributed to a better knowledge of their Renner-Teller electronic ground states. An extensive analysis of the present spectrum is in progress. It will be interesting to compare the forthcoming results on HCSi with those of the isoconfigurational radical C_2H detected 16 years ago, in the infrared region, by means of color center laser spectroscopy [19].

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