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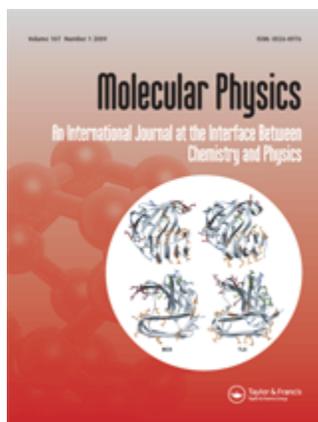
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9 **The $A^2\Sigma^+ - X^2\Pi$ transition of SiCl revisited in the near ultraviolet**

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21 High-resolution emission spectra were obtained from a hollow cathode discharge in
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23 SiCl₄ /Ar mixtures. In the 360-450 nm region the **emission** of the $\tilde{C}-\tilde{X}$ transition of SiCl₄⁺
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25 was detected and also the $A^2\Sigma^+ - X^2\Pi$ transition of SiCl, previously analyzed by Bredohl et
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27 al. Some new bands of the A-X system of SiCl were identified and their rotational structure
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29 analyzed. Improved molecular constants for the $A^2\Sigma^+$ state of SiCl have been obtained
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31 from the new data and those of Bredohl et al. For the **emission** of the $\tilde{C}-\tilde{X}$ transition of
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33 SiCl₄⁺ no vibrational **or** rotational structure could be resolved with a resolution of 10⁻³ nm.
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1. Introduction

Emission from highly excited electronic states of polyatomic molecules is a rare phenomena. Exceptions are found in the group of tetrafluoro molecular ions, such as CF_4^+ [1], and tetrachloro molecular ions, such as SiCl_4^+ [2]. The $\tilde{\text{C}}$ state of SiCl_4^+ has been found to fluoresce in a photoion-fluorescence coincidence measurements following photoionization of SiCl_4 and the fluorescence was assigned to the $\tilde{\text{C}}^2\text{T}_2-\tilde{\text{X}}^2\text{T}_1$ and $\tilde{\text{C}}^2\text{T}_2-\tilde{\text{A}}^2\text{T}_2$ transitions of SiCl_4^+ on the basis of electron and ion impact ionization of SiCl_4 studied via emission[3]. This assignment was confirmed by dispersion of the fluorescence recorded with a resolution of 4 nm following photoexcitation with monochromatised synchrotron radiation[4], showing two broad bands with a maximum around 410 and 570 nm for the $\tilde{\text{C}}-\tilde{\text{X}}$ and $\tilde{\text{C}}-\tilde{\text{A}}$ transitions, **respectively**. Because the ground state of the parent ion $\tilde{\text{X}}$ as well as the $\tilde{\text{C}}$ state are bound in contrast tot the repulsive $\tilde{\text{A}}$ state, a continuum is anticipated for the $\tilde{\text{C}}-\tilde{\text{A}}$ transition and at least some discrete part of emission for the $\tilde{\text{C}}-\tilde{\text{X}}$ transition .

The present high-resolution study of the **emission** from the $\tilde{\text{C}}$ state of SiCl_4^+ obtained from a much less defined excitation source of a discharge in Ar/ SiCl_4 shows a continuum in the spectral range between 450 and 600 nm and in the 360-450 nm region another continuum together with a lot of structure. However, in the violet wavelength region also several transitions of the SiCl radical are known, in particular the $\text{A}^2\Sigma^+-\text{X}^2\Pi$ transition[5].

Detailed inspection of the 360-450 nm region with a resolution of $\approx 10^{-3}$ nm shows besides structureless emission also extensive radiation from overlapping bands of the A-X system of SiCl. This band system was studied by Bredohl et al.[5] and previously by Verma et al.[6]. Bredohl et al. analyzed transitions with ν' values of 0 and from 5 up to 13, but for the **11-0 and 13-1 transitions** only one sub-band. In the present examination of the 360-450 nm wavelength region we identify and analyze a few new bands of the A-X system of the SiCl radical, which together with a previous analysis of Bredohl et al.[5], yield more precise equilibrium constants for the $\text{A}^2\Sigma^+$ state of SiCl.

2. Experimental

Emission spectra were obtained from a hollow cathode of a dc discharge in a flowing mixture of Ar/SiCl₄ with experimental conditions similar to those described in a earlier study on CF₄⁺ emission[1]. Spectra were photographed in 15th or 16th orders of the 4m Czerny-Turner spectrograph at University College London with a resolution better than 10⁻³ nm. Spectral line positions were obtained by means of Adobe Illustrator from digital recordings of the spectra with calibration lines.

3. Results and discussion

The bands of the A-X system of the SiCl radical consist of two sub-bands in which two branches have most of the intensity: R₁₁ and Q₁₁ of the ²Σ⁺-²Π_{1/2} and Q₂₂ and P₂₂ of the ²Σ⁺-²Π_{3/2} sub-band. Rotational constants were determined by fitting the lines to the Hill-Van Vleck formula[7] and by taking Λ-doubling in the Π_{1/2} multiplet component into account by a term ±½ *p* (*J*+½), where the plus and minus signs refer to the e and f levels. For the new bands and the previously analyzed 7-0 band we used a non-linear least-squares procedure in order to determine the molecular constants. The molecular constants obtained are given in table 1 in which some of the ground-state constants were fixed to values from a previous analysis of the 0-0 and 0-1 bands of the B²Σ-X²Π system[5]. Table 2 presents the equilibrium constants of the A²Σ⁺ state by combining the *B_v* values of the previously determined values for *v*= 0, 5-10 and the present values for *v*=11 and 13, omitting in the fit the less accurate value for *v*= 12.

In the present analysis we did not calculate the *J* independent term 'o' as in [5] and we did not include a small *J*-dependent multiplet-splitting parameter *A_J*, which was also disregarded in the analysis of the B-X transition[8]. The electronic perturbation term 'o' can be calculated from the value of the Λ-doubling constant *p*, the spin-orbit coupling constant *A_v*, and the rotational constant *B_v*, of the Π state in the single perturber approximation. By omitting the 'o' term, the present value for the band-origin *ν₀* and *A_v* contain a small contribution of the 'o' term. The previous determined values for 'ν₀',

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' A_v ' and ' o ' are related to the present determination of molecular constants by $\nu_0 = ' \nu_0 ' - \frac{1}{2} ' o '$ and $A_v = 'A_v' - 'o'$. Taking these relations into account, the present values obtained for the molecular constants of the 7-0 band compare well with the previous determination[5].

The ν_0 and A_v values presently obtained for the 13-1 band are more accurate than those previously obtained[5], because both sub-bands could be used in the analysis. For the molecular constants of the $\nu'=11$ level of the A state, also both sub-bands of the 11-1 band were used instead of one sub-band for the previously reported 11-0 band[5]. In the present study also only one 11-0 sub-band was accessible for analysis due to spectral congestion, while the 11-1 band was a relatively less overlapped. Considerable overlapping of sub-bands occurred in almost all cases, while emission of the Si ^{37}Cl isotope produced supplementary congestion.

Close inspection of the spectra yielded also other bands **terminating on $\nu''=1$** : the 9-1 and 12-1 bands. While the 9-1 band did not provide new information due to the known 9-0 band[5], the 12-1 band does. However only a part of the rotational structure of the latter band could be analyzed, because lines with J' values lower than 20.5 could not be detected, probably due to perturbations.

It is noted that the molecular constants given in table 1 yield a standard deviation of the $\nu_{obs} - \nu_{cal}$ differences of about 0.05 cm^{-1} except for the 12-1 band, considerably better than about 0.1 cm^{-1} as obtained in the previous analysis for bands with $\nu' \geq 7$ [5].

The currently observed bands provided revised values for the B_v rotational constants with $\nu=11$ and 13 levels of the A state and a new estimate for the $\nu=12$ level. The improved B_v values with $\nu=11$ and 13 together with the previously determined for the levels $\nu=0$ and 5-10 provided the equilibrium molecular constants of the A state given in table 2.

In the spectrum recorded with a resolution of $\approx 10^{-3} \text{ nm}$, an intense continuum was **also** observed in the investigated wavelength region. This continuum was undoubtedly resulting from the $\tilde{C}-\tilde{X}$ transition of SiCl_4^+ due to the composition of the mixtures used: a small concentration of SiCl_4 and an excess of Ar. This ensured an excess of Ar^+ ions, which in the case of collisions with SiCl_4 produce with a high probability SiCl_4^+ ions in the \tilde{C} state via a near resonant charge exchange process. Due to the nonselective nature of the

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excitation processes in the discharge, also other and higher electronic states of SiCl_4 and SiCl_4^+ are produced of which one or more dissociative states yield excited fragments such as the A state of SiCl . Upon using a discharge in He instead of Ar together with traces of SiCl_4 [5], certainly yields a somewhat different distribution of excited states of SiCl_4 and SiCl_4^+ and related fragments in comparison with the **present** study.

Despite the high intensity of the radiation from the \tilde{C} state of SiCl_4^+ in the current study, no discrete structure from the \tilde{C} state of SiCl_4^+ could be found besides the continuum.

Although not all discrete structure could be identified in the 360-450 nm range, it is believed that most if not all may be attributed to the A-X system of SiCl . **The principal rotational constant B for the \tilde{C} and \tilde{X} states of SiCl_4^+ will differ considerably from those obtained for the diatomic radical SiCl . Those for the SiCl_4^+ parent ion can be estimated when one disregards the difference in equilibrium bond length Si-Cl of SiCl_4 and SiCl_4^+ . Using $r_e = 2.019 \text{ \AA}$ [9] for SiCl_4 yields then an estimate of $\approx 0.044 \text{ cm}^{-1}$ for the B value of the SiCl_4^+ ion states. In view of this small value only a partly resolved rotational structure for the \tilde{C} - \tilde{X} transition might be expected at the resolution presently available.**

It is noted that in the photoelectron spectrum of SiCl_4 [2] only vibrational structure could be resolved for the \tilde{D}^2A_1 state but not for **either** the \tilde{C}^2T_2 state **or** \tilde{X}^2T_1 states of SiCl_4^+ **at a resolution of 48 cm^{-1} and 24 cm^{-1} for the \tilde{C} respectively \tilde{X} state**, or considerably smaller than the fundamental frequencies anticipated for the parent ion. The lack of structure of the \tilde{C} and \tilde{X} bands in the photoelectron spectrum as well as in the \tilde{C} - \tilde{X} **emission** presently studied with a resolution of $\approx 0.06 \text{ cm}^{-1}$ might indicate the presence of spectral congestion by several vibrational modes, spin-orbit coupling and/or Jahn-Teller distortion of the tetrahedral symmetry in the \tilde{C} as well as the \tilde{X} state of SiCl_4^+ . For the \tilde{C} **triply-degenerate** state a spin splitting of $+285 \text{ cm}^{-1}$ has been calculated[10]. This calculated splitting, however, might well be reduced by the Ham effect, as in the case of the \tilde{C} state of CF_4^+ [11].

For a detailed study of the \tilde{C} state as well as the \tilde{X} state of SiCl_4^+ , a higher resolution study **of the \tilde{C} - \tilde{X} emission** would be of interest.

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Table 1. Molecular constants(cm^{-1}) from band fits of the A $^2\Sigma^+$ -X $^2\Pi$ transition of Si ^{35}Cl .

v'	v''	ν_0	B'	$D' \times 10^7$	B''	$D'' \times 10^7$	A''	$p \times 10^3$	J_{\max} obs	N^0 lines	σ fit
9	1	24956.75(2)	0.19237(8)	3.0(7)	0.25375 ^a	2.5 ^a	206.82(11)	4.8(14)	34.5	89	0.051
11	1	25515.90(1)	0.19090(2)	3.8(1)	0.25375 ^a	2.5 ^a	206.77(5)	2.0(8)	44.5	144	0.039
12 ^b	1	25792.06(7)	0.19077(11)	5.9(4)	0.25375 ^a	2.5 ^a			50.5	72	0.15
13	1	26068.44(1)	0.18912(4)	3.3(2)	0.25375 ^a	2.5 ^a	206.82(6)	3(2)	41.5	129	0.058
		24921.89(1)	0.19396(1)	3.74(4)	0.25544 ^a	2.4 ^a	207.14(2)	3.7(5)	54.5	164	0.045
7	0	24921.91(1) ^c	0.19396(2) ^c	3.9(1) ^c	0.25544 ^{a,c}	2.4 ^{a,c}	207.18 ^c	4.6 ^c	69.5 ^c	224 ^c	0.123 ^c

Values in parenthesis are one standard deviation in units of the last digits.

^aConstants fixed and obtained from the 0-0 and 0-1 B-X bands [5]

^bOnly rotational levels with $J' \geq 20.5$ observed

^cFrom [5]; the values of the band origin ν_0 and the spin-orbit coupling constant A'' have been corrected for omitting the term ' o '(see text); a term A_J has been disregarded[8]

Table 2. Equilibrium constants(cm^{-1}) for the A $^2\Sigma^+$ state of Si ^{35}Cl .

B_e	0.19861(15)
α_e	$0.50(4) \times 10^{-3}$
γ_e	$-0.14(3) \times 10^{-5}$
$r_e(\text{\AA})$	2.3343(9)

Values in parenthesis are one standard deviation in units of the last digits.