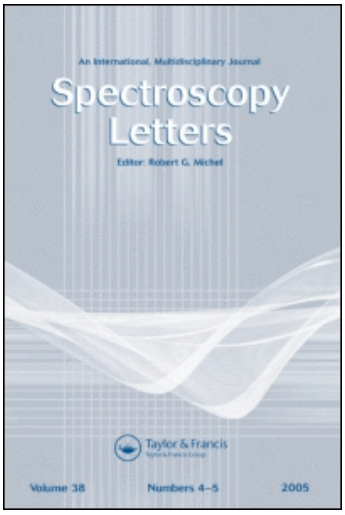

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CHEMILUMINESCENT $SiCl_4 + O_2 + Ar/He/$ REACTIONS

KEY WORDS : chemiluminescence spectra, populations, the SiO molecule, plasma temperature

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ABSTRACT

A chemiluminescent flame was formed in the reaction between $SiCl_4$ and oxygen in an atmosphere of argon or helium. Internal state distributions of some reaction products were studied. Inverted vibrational populations in the $A^1\Pi$ and $f^3\Pi_1$ states of SiO were observed. The relative electronic populations of atomic silicon and relative rotational populations in the SiO $A^1\Pi$ state corresponded to temperatures of about 3400 K and 400 K, respectively.

INTRODUCTION

In recent years many papers have been devoted to chemiluminescence studies. Chemiluminescence spectra often show electronic or vibrational transitions which are not observed under other experimental conditions. Often the chemiexcitation is very selective and permits spectroscopic observation of chosen electronic transitions. Numerous papers have reported investigations concerning the prospect of applying the chemiluminescence processes /involving electronic transitions/ for developing visible chemical lasers. Monoxides of carbon group elements have been predicted to be good chemical laser candidate systems[1]. Chemiluminescence spectra of SiO were studied by Hager et al.[2,3] and Linton et al.[4,5] .

The aim of this study is to investigate the population distribution of the internal states /electronic, vibrational, rotational/ of some products /the SiO molecule and atomic silicon/ of the chemiluminescence reactions of $SiCl_4$ with oxygen in the presence of argon or helium.

EXPERIMENTAL

A flow systems very similar to that used in

Ref. 4 was applied here. A mixture of argon or helium and a trace of oxygen was passed through a high frequency discharge /27.4 MHz/ and discharge products were mixed with $SiCl_4$ vapor, forming a compact flame. The chemiluminescence was observed at 5 - 25 torr argon pressure and 10 - 25 torr helium pressure. The $SiCl_4$ flow rates ranged from 1.5×10^{-8} to 5.5×10^{-8} mole/sec.

The emission spectra were recorded in the first order of a plane grating spectrograph PGS-2, at a reciprocal dispersion of 7 Å/mm. The slit width was 0.080 mm. Exposure times from 10 min to 1 hour were sufficient to record the spectra on Kodak III-F plates.

Two standard lamps, a deuterium lamp in the region from 2200 Å to 3500 Å and a tungstem lamp in the region 3500 - 5000 Å, were used as reference sources of known intensity. The lamps were calibrated by comparision with standard lamps of the National Bureau of Standards /Washington D. C./. The spectra were reduced with the aid of a recording microphotometer MD-100. The density curves /one curve for range of about 80 Å/ were constructed using a three - step filter of the spectrograph taking into account the variation of the photographic emulsion sensivity with the wavelength.

RESULTS

Spectra

A close, white, bright flame was produced during the reaction between $SiCl_4$ vapor and oxygen in the presence of an argon atmosphere. In the present study substitution of argon by helium has resulted in a flame similar to that which was produced with argon but of considerably less intensity. Shanker, Linton and Verma[4] did not observe the chemiluminescence flame with $SiCl_4$ and mixture of oxygen and helium. It was stated that the chemiluminescent flame brightness was very sensitive to changes of ratio of $SiCl_4$ to argon /or helium/.

All reported[4] bands of the $A^1\Pi - X^1\Sigma^+$ system of SiO have been observed here, except a few very weak bands. All known triple-headed bands of the $c^3\Sigma^+ - b^3\Pi_r$ and $f^3\Pi_i - b^3\Pi_r$ systems[4,6] have been identified. It is surprising that bands of intercombination systems, which were previously[2-5] observed, have not been recorded here. Low population of the $a^3\Sigma^+$ and $b^3\Pi_r$ states produced during our experiment may be responsible for this. The SiO spectrum was partially overlapped by bands of the $C^2\Pi - X^2\Pi_r$, $B'^2\Delta - X^2\Pi_r$ and $B^2\Sigma^+ - X^2\Pi_r$ systems of the SiCl molecule. In addition to these a few bands of

O_2 /3357 and 4071 Å/, O_2^+ /3972 and 4050 Å/ and OH /3064 and 2811 Å/ and a number of unidentified, previously reported[4] bands in the region 3900 - 4400 Å were observed.

A very rich spectrum of Si I was recorded. Lines of Ar I /or He I/, Cl I and relatively weak hydrogen lines were identified. No ionic lines were observed.

It was observed that the addition of more $SiCl_4$ greatly enhanced the intensity of the SiCl bands relative to the SiO bands. Increasing intensities of the Si I lines was associated with decreasing intensities of the SiO bands.

Population distribution

Two procedures are applied to determine the relative band intensities. The band intensity is determined both from the intensity peak height of the band head and from the intensity area integrating intensities versus wavelength with the estimated contribution of neighbouring bands substracted out /see e.g. Refs. 7 - 9/. It was stated that these methods led to very close results. When the intensity area of the band was measured, the contribution of the unobserved part of the band was found using the method reported by Robinson and Nicholls[10], which is more accurate than a graphical estimation.

The relative intensities within the SiO spectrum /$A^1\Pi - X^1\Sigma^+$, $c^3\Sigma^+ - b^3\Pi_r$, $f^3\Pi_i - b^3\Pi_r$/ have shown a weak dependence on pressure. The intensity ratio of the (0,0) bands of the A - X, c - b and f - b systems in argon plasma has been found to be approximately 1.0 : 2.5 : 0.1. The intensity ratio of the (0,0) bands of the A - X and c - b systems in helium plasma was 1.0 : 0.5. Since relative transition probabilities for the triple states of SiO were not available we can not determine the relative populations in the here analyzed electronic states of SiO.

Assuming a constant electronic transition moment the relative populations of the vibrational levels v' of the analyzed electronic state may be derived from the expression $I_{v',v''}/\nu^4_{v',v''}q_{v',v''}$ i.e. from a knowledge of the emission intensity, the frequency of the band and the Franck-Condon factor. The Franck-Condon factors for the $A^1\Pi - X^1\Sigma^+$ system have been taken according to Suchard[11] and for the $c^3\Sigma^+ - b^3\Pi_r$ and $f^3\Pi_i - b^3\Pi_r$ transitions have been calculated using the method reported in Ref. 12. The relative vibrational populations for the excited states of SiO in the reactions of $SiCl_4$ with oxygen at 12 and 22 torr argon pressure and 12 torr helium pressure are presented in Figs. 1 and 2,

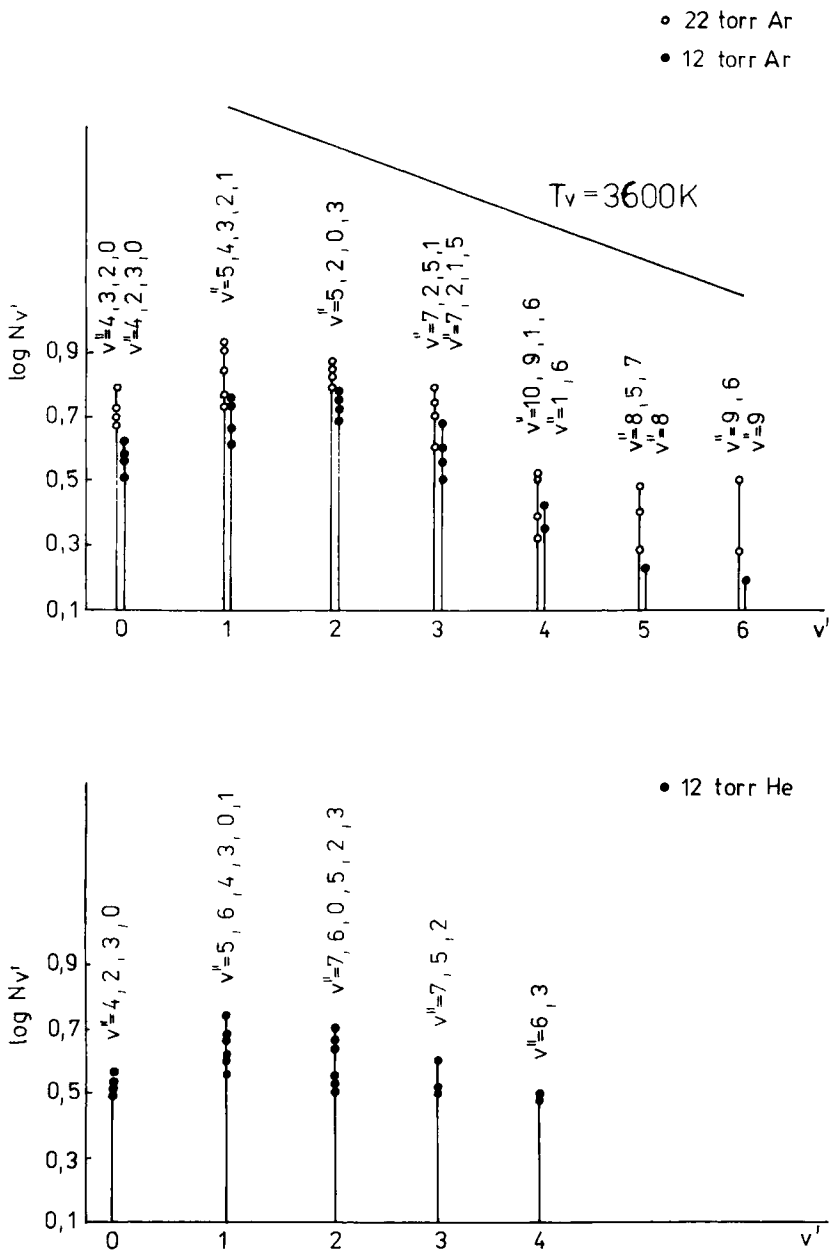

Fig.1 Relative vibrational populations of the SiO $A^1\Pi$ state, arbitrary units.

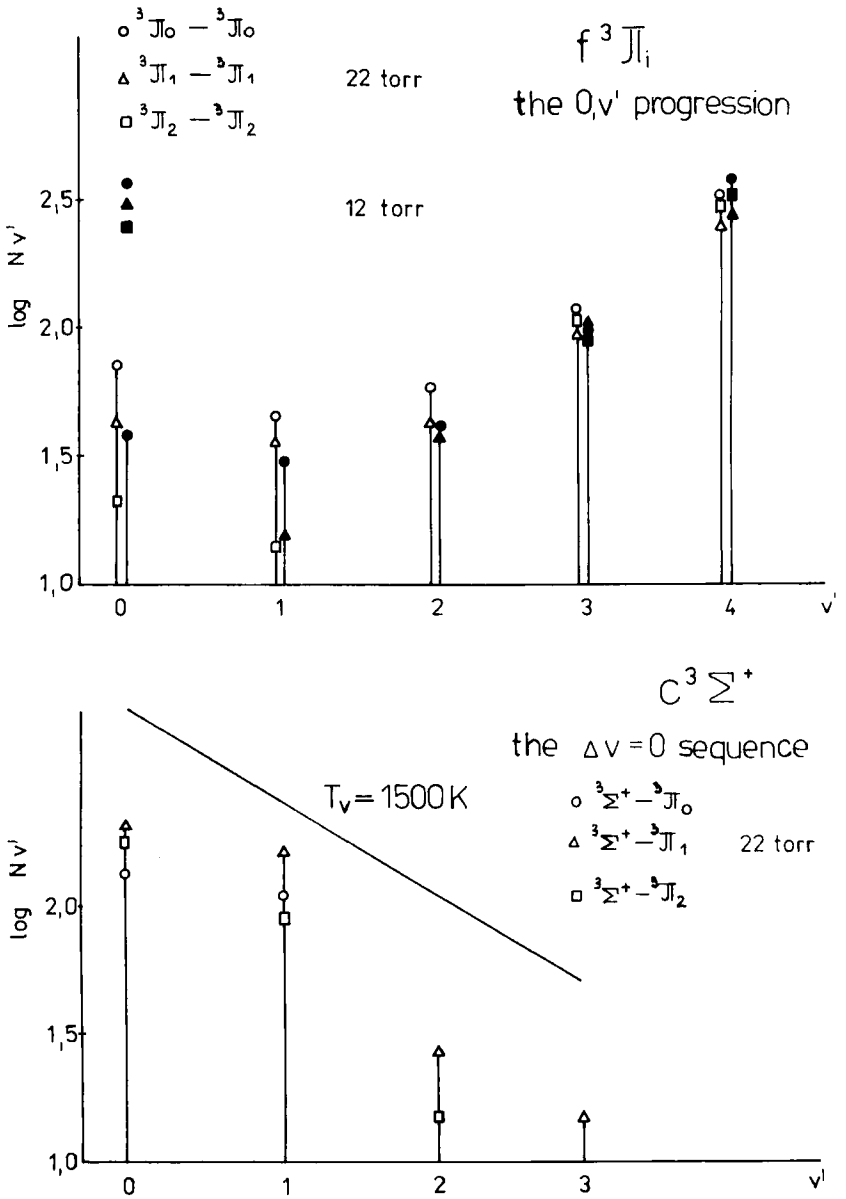

Fig.2 Relative vibrational populations of the $f^3\Pi_i$ and $c^3\Sigma^+$ states of SiO in the presence of argon, arbitrary units.

respectively. The relative populations have been plotted logarithmically. As can be seen from Figs. 1 and 2 the vibrational population distributions within the analyzed electronic states weakly depend on carrier gas pressure. No significant changes in the vibrational population distribution are observed if argon is substituted by helium.

Only the vibrational distribution in the SiO $A^1\Pi$ state could be studied in helium plasma. The f - b and c - b band systems were too weak for exact measurements.

The relative vibrational populations in the $A^1\Pi$, $c^3\Sigma^+$ and $f^3\Pi_i$ states are quite different. For comparison, the vibrational temperatures calculated under the assumption of the Boltzmann distributions for chosen levels v' have been marked in Figs. 1 and 2. The inverted vibrational population of some levels appears strongly in the $f^3\Pi_i$ state and weakly in the $A^1\Pi$ state.

Usually chemiluminescence spectra are too weak to record them at resolved rotational structure. In such a case the band intensity shape can be analyzed /see e.g. Refs. 13,14/. Comparision of the observed and calculated emission shapes of the analyzed $A^1\Pi - X^1\Sigma^+$ (0,1), (0,2), (0,3), (0,4) and (1,4)

bands implies that the relative rotational distributions are the Boltzmann distributions and correspond to the rotational temperature of about 400 K.

In addition to studying relative populations of the excited states of SiO it was interesting to investigate relative populations of the excited electronic states of atomic silicon. The following relationship, derived from the expression for the integrated radiance of an atomic emission line under the assumption of a Boltzmann distribution[15], was investigated:

$$\ln I_n\lambda_n/g_nA_n = \text{constant} - E_n/kT_{ex}$$

where I_n is the line intensity, λ_n is the line wavelength, g_n and E_n denote statistical weight and energy of the upper electronic state, A_n is transition probability, k is the Boltzmann constant, T_{ex} is the excitation temperature, n is the line number. The following lines of Si I were taken into account: 2207.9, 2210.9, 2211.7, 2435.1, 2438.8, 2443.4, 2452.1, 2506.9, 2519.2, 2524.1, 2528.5, 2532.4, 2631.3, 3006.7 and 3020.0 Å. The transition probability values have been taken according to Refs. 16 and 17. Using the least squares method the excitation temperature values with their standard deviation uncertainties have been calculated to be 3200 $\pm$ 500 K

and 3600 $\pm$ 1000 K for argon and helium plasma respectively.

Chemiluminescence processes associated with the reactions $SiCl_4 + O/O_2 + Ar/He/$ are very complex and have not yet been investigated. Thermodynamic considerations have shown that the reaction

$$Me + O = MeO^*$$

is sufficiently exothermic to obtain all levels responsible for the emission spectra of SiO recorded here. Three body reactions

$$Me + O_2 + Ar^* = MeO^* + O + Ar$$

$$MeCl + O + Ar^* = MeO^* + Cl + Ar$$

$$MeCl + OH + Ar^* = MeO^* + HCl + Ar$$

can also lead to high excited levels of SiO. The O_2^+ bands were not observed in the spectrum excited in a mixture of argon and oxygen by the radio frequency discharge. Thus the excited O_2^+ molecule is formed in the chemiluminescence reaction.

The inverted vibrational populations of the SiO states formed here indicate that the chemiluminescence of $SiCl_4$ with oxygen in the presence of an argon atmosphere can be both an excellent source for studying molecular structure of SiO[4] but also is promising for chemically pumped electronic lasers.

More advanced study of the $SiCl_4 + O/O_2 + Ar$ reaction is in progress.

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