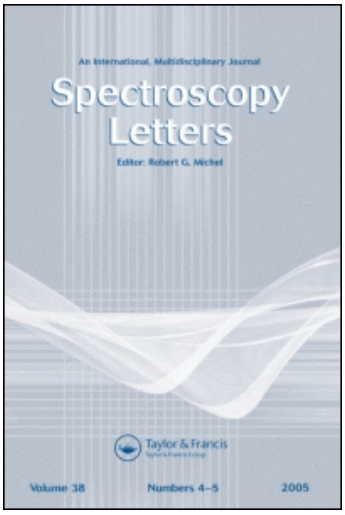

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CHEMILUMINESCENT $GeCl_4$ + O_2 + Ar/He/ REACTIONS

KEY WORDS: chemiluminescence spectra, populations, plasma temperature, GeO, GeCl

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ABSTRACT

A chemiluminescent flame was produced in the reaction between $GeCl_4$ and an excited mixture of argon or helium with oxygen. Spectra of the reaction products were recorded and studied. Relative populations of the products in analyzed electronic, vibrational and rotational states corresponded to different temperatures.

INTRODUCTION

Numerous papers have concerned chemiluminescent reactions occuring with group IVA elements. Chemiluminescence arising from reactions of Ge atomic vapor with several oxidizers was studied and rate coefficients and photon yields were measured.[1-7] The Ge atoms were produced by flowing GeH_4 through a hollow cathode discharge,[1,2] by photolysis of $GeCl_4$[3] or $GeBr_4$[4,5] and vaporizing molten Ge in a flow reactor.[6,7]

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This study presents results of investigations of the chemiluminescent $GeCl_4 + [O_2 + Ar]^*$ and $GeCl_4 + [O_2 + He]^*$ reactions. Internal /electronic, vibrational, rotational/ energy distributions of some products of the chemiluminescent reactions have been determined and discussed.

EXPERIMENTAL

Plasma was produced by the chemiluminescence of $GeCl_4$ vapor mixed with stream of argon /or helium/ containing a small amount of oxygen. Before the reaction with $GeCl_4$ the mixture of noble gas and oxygen was excited by passing through a high frequency discharge[8] /at 2 - 25 torr argon pressure and 5 - 30 torr helium pressure/ or a hollow cathode discharge with open-ended cathodes made of copper /at 2 - 10 torr argon pressure and 5 - 10 torr helium pressure/. The $GeCl_4$ flow rates ranged from 1.5×10^{-8} to 5×10^{-8} mole/sec. The emission spectra were recorded at right angle to the flowing streams in the first order of a plane grating spectrograph PGS-2 on Agfa-Gevaert and Kodak plates.

The method of reducing of the plates and other details of the experiment have been the same as those reported previously.[8]

RESULTS AND DISCUSSION

A white-aquamarine flame was produced in the reaction between $GeCl_4$ and the mixture of argon /helium/ and oxygen excited in the high frequency discharge. The $GeCl_4$ vapor mixed with the stream of argon and oxygen passed through the hollow cathode discharge formed a light blue flame. Substitution of argon by helium resulted in a pink-blue flame changing to white-violet at higher flow rates of

$GeCl_4$. The chemiluminescent flame was distinctly stronger in the presence of argon.

Chemiluminescent spectra observed in the first method /high frequency discharge/ contained strong molecular bands of GeO and GeCl and atomic lines. The spectra excited in the second method /hollow cathode discharge/ were rich in ionic and atomic lines. Molecular bands of GeO, GeCl and CuCl were weak.

It was observed that experimental conditions /pressure, flow rate of $GeCl_4$, discharge power/ influence on intensity ratios of the GeO bands related to the GeCl bands and the Ge I lines /Fig. 1/. Substitution of Ar by He decreased the absolute spectrum intensity.

Relative intensities of the $A^2\Sigma^+ - X^2\Pi$, $a^4\Sigma^- - X^2\Pi$ and $B^2\Sigma^+ - X^2\Pi$ band systems of GeCl varied very slightly with conditions of forming of the chemiluminescent flame.

Relative vibrational populations of the GeO and GeCl molecules were determined unter the assumption that their electronic transition moments were constant. These relative populations have been derived from the expression $I_{v',v''}(\nu)/\nu^4_{v',v''}q_{v',v''}$. The intensity area measurement method[9] with consideration of the estimated contribution of neighbouring bands was used to determine the band intensities.
Only bands of the $A^1\Pi - X^1\Sigma^+$ system of GeO could be measured on our plates. The bands with $v' \leqslant 11$ were observed but the bands with $v' > 8$ were too weak for accurate measurements. Franck-Condon factors reported by Capelle and Brom[6] were taken here for the GeO bands. The $a^4\Sigma^- - X^2\Pi$ and $B^2\Sigma^+ - X^2\Pi$ band systems of GeCl were used for vibrational population investigations. The Franck-Condon factors for these systems have been computed[10] using molecular constants of

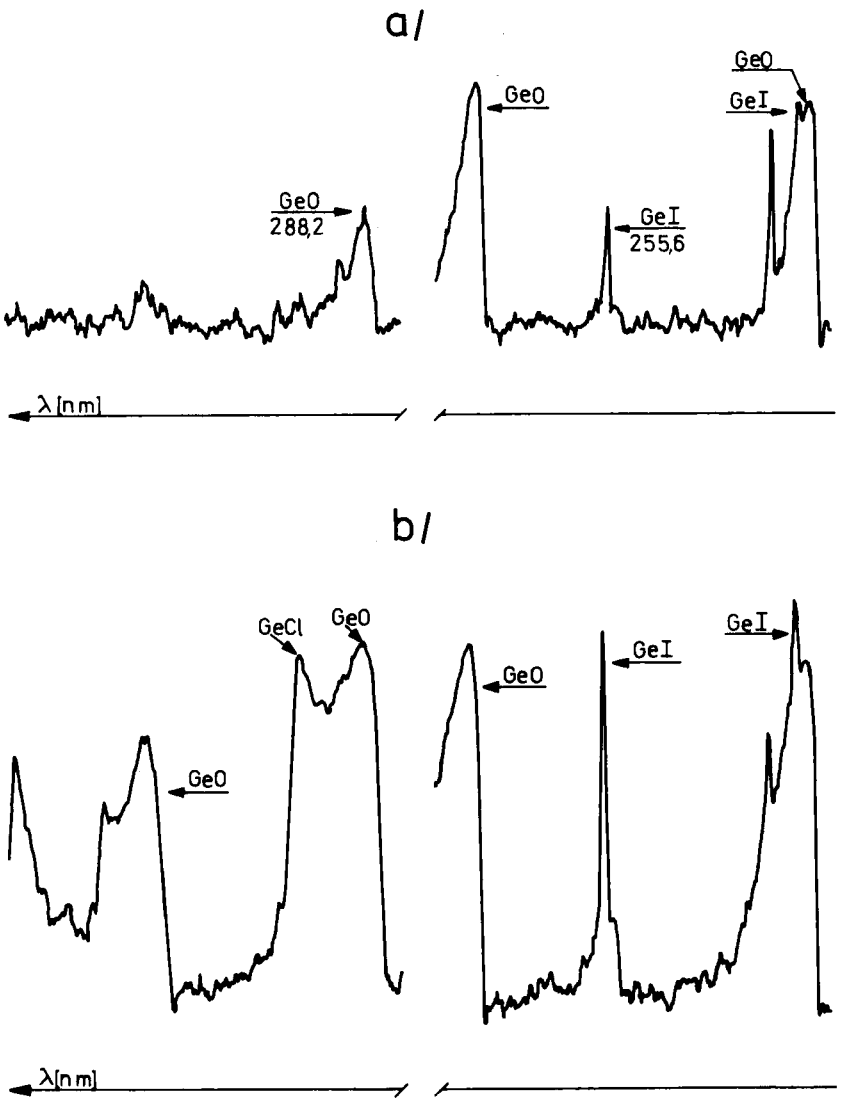

Fig. 1. Chemiluminescent spectra excited in high frequency /200 W, flow rate of $GeCl_4$ - $3x10^{-8}$ mole/sec/, a/ p_{Ar} = 3.5 torr, b/ p_{Ar} = 7 torr

GeCl recently determined. Rotational constants for the $A^2\Sigma^+$ state of GeCl are not available, thus the Franck-Condon factors could not be calculated and the $A^2\Sigma^+ - X^2\Pi$ system was not taken into account.

The relative vibrational populations of the $A^1\Pi$ state of GeO observed at different experimental conditions are presented in Fig. 2. Employing the least squares procedure for the levels $v' \geqslant 2$ it was found that these populations /high frequency discharge/ correspond to the following temperatures : 3950 $\pm$ 350 K /4 torr of Ar/, 4100 $\pm$ 560 K /7 torr of Ar/, 3100 $\pm$ 300 K /12 torr of Ar/ and 3200 $\pm$ 350 K /7 torr of He/.
Comparison of the observed and calculated intensity distributions in the $A^1\Pi - X^1\Sigma^+$ 0-1, 1-1 and 2-3 bands leads to the Boltzmann temperature of about 300 K.

The relative vibrational populations of the $B^2\Sigma^+$ and $a^4\Sigma^-$ states of the GeCl molecule are plotted in Fig. 3. Only the low vibrational levels were observed. Nevertheless temperatures corresponded to vibrational Boltzmann plots could be determined quite accurately. The vibrational temperatures of GeCl listed in Table 1 along with their standard deviation uncertainties are considerably lower than those derived from the GeO bands. These temperatures differ for the analyzed systems and depend on the excitation method of the Ar/He/ + O_2 mixture.

The excitation temperatures of some atoms and ions /Ge I, He I, Cu I, Ar II/ observed in the chemiluminescent spectra were measured under the assumption of the Boltzmann distribution, plotting $\ln(I\lambda/gA)$ against E, where the symbols have common known meanings. The transition probabilities for Ge I taken here from Ref. 11 are not accurate but only for

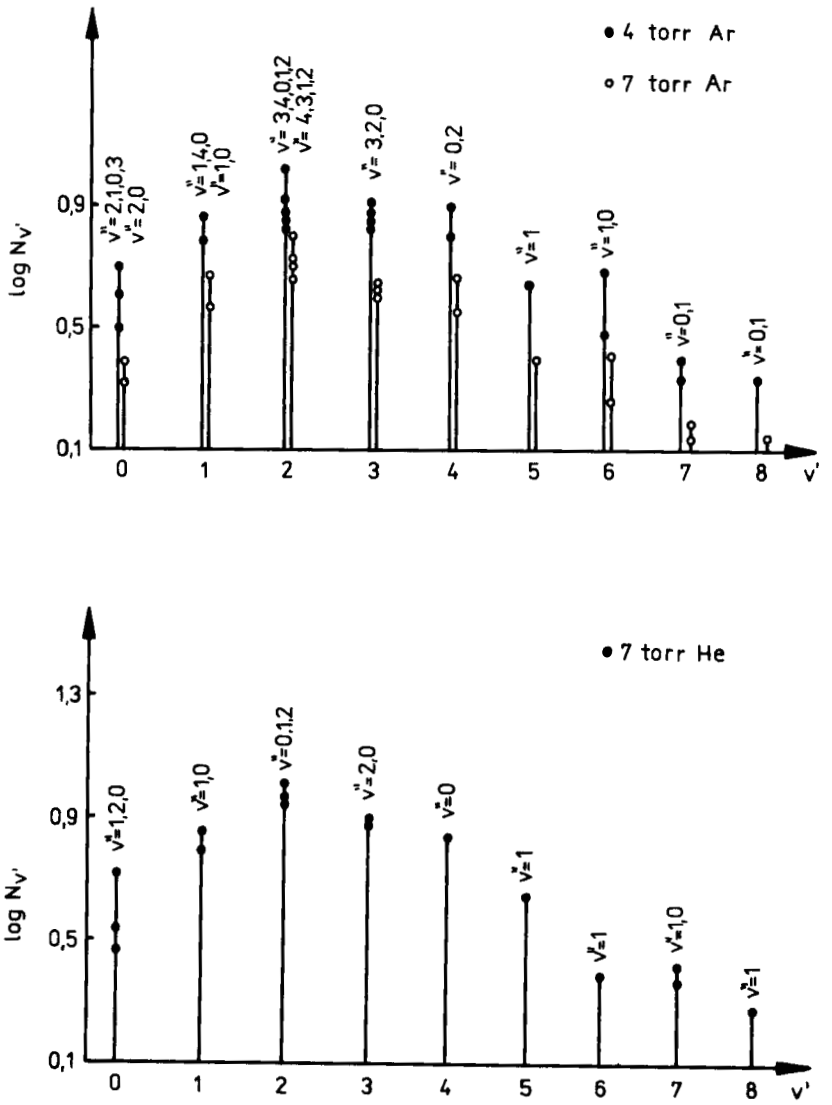

Fig. 2. Relative vibrational populations of the GeO $A^1\Pi$ state, arbitrary units

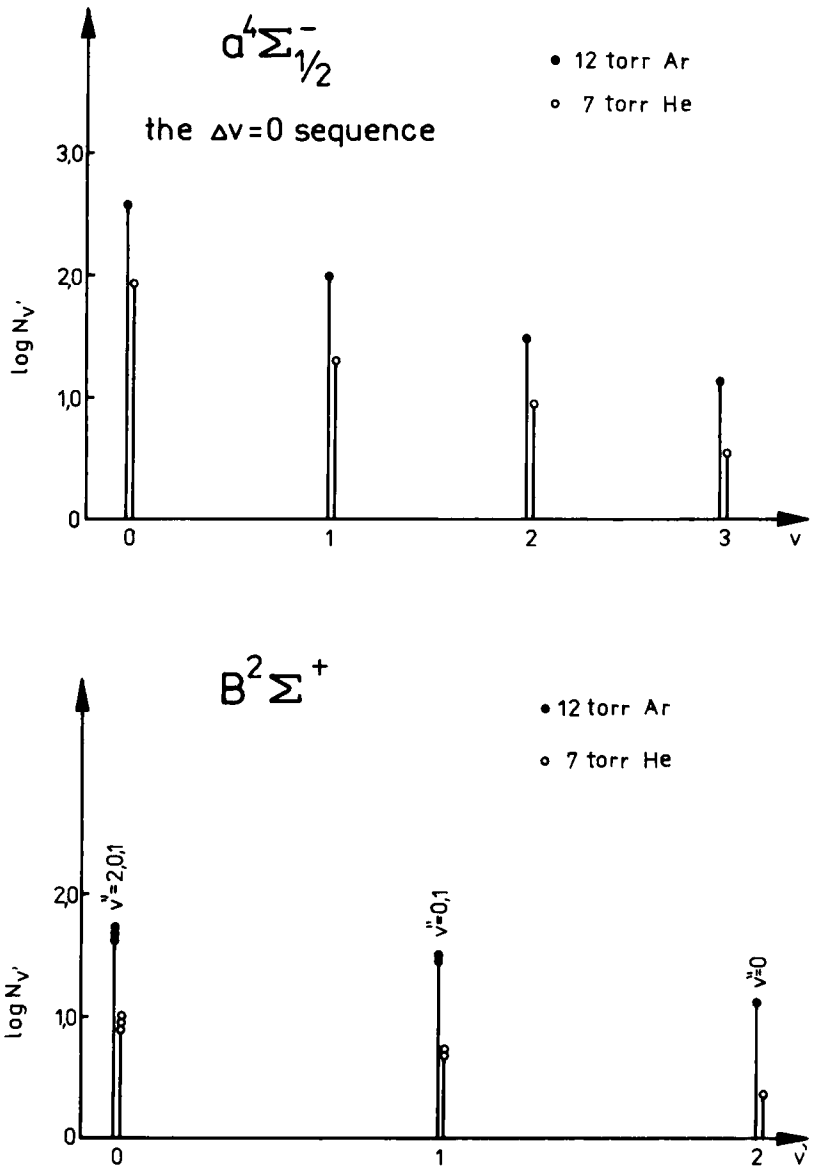

Fig. 3. Relative vibrational populations of the $a^4\Sigma^-$ and $B^2\Sigma^+$ states of GeCl, arbitrary units

TABLE 1

Vibrational Temperatures of GeCl

State	Inert gas	Pressure torr	Flow rate mole/sec	T ± T K
$a^4\Sigma^-_{1/2}$	Ar[a]	12	5×10^{-8}	400± 40
$a^4\Sigma^-_{1/2}$	He[a]	7	3×10^{-8}	440± 40
$a^4\Sigma^-_{1/2}$	He[b]	8	3×10^{-8}	640± 10
$a^4\Sigma^-_{1/2}$	He[b]	10	1.5×10^{-8}	610±100
$B^2\Sigma^+$	Ar[a]	12	5×10^{-8}	1270±130
$B^2\Sigma^+$	He[a]	7	3×10^{-8}	1480±170

a - I method /high frequency discharge/
b - II method /hollow cathode discharge/

a few lines new data are reported.[12] Data for Cu I lines were taken according to Bielski.[13] The transition probabilities given by Wiese et al.[12,14] were employed for Ar II and He I lines. The calculations were carried out using the least squares method. The temperatures along with their standard deviation uncertainties are given in Table 2. The Cu I, Ar II and He I temperatures derived here are very close to those obtained by us in an ordinary hollow cathode discharge.

The relative vibrational populations in the $A^1\Pi$ state of GeO are remarkably similar to those observed previously for the SiO molecule.[8] The plasma produced by the chemiluminescence has appeared to be strongly nonisothermic. As could be deduced from absolute intensities of the spectra the Boltzmann temperatures

TABLE 2

The Excited Temperatures of Some Chemiluminescence Products

	Pressure torr	Flow rate mole/sec	n	T ± T K
Ge I	12 /Ar[a]/	5×10^{-8}	8	11400±3600
Ge I	7 /He[a]/	3×10^{-8}	13	9200±1400
Ge I	4 /Ar[b]/	1.5×10^{-8}	9	8800±1300
Ge I	10 /He[b]/	1.5×10^{-8}	9	9300±2100
Ge I	8 /He[b]/	3×10^{-8}	9	9700±3000
Cu I	4 /Ar[b]/	1.5×10^{-8}	14	2650± 430
Cu I	10 /He[b]/	1.5×10^{-8}	16	2500± 300
Cu I	8 /He[b]/	3×10^{-8}	16	2700± 400
Ar II	4 /Ar[b]/	1.5×10^{-8}	7	22800±3900
He I	10 /He[b]/	1.5×10^{-8}	8	4200± 900
He I	8 /He[b]/	3×10^{-8}	10	3300± 800
He I	7 /He[a]/	3×10^{-8}	10	4100±1300

a - I method /high frequency discharge/
b - II method /hollow cathode discharge/
n - number of lines taken into account

corresponding to relative populations of the excited states of some analyzed chemiluminescence products differ considerably from the temperatures corresponding to absolute populations of these states.

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