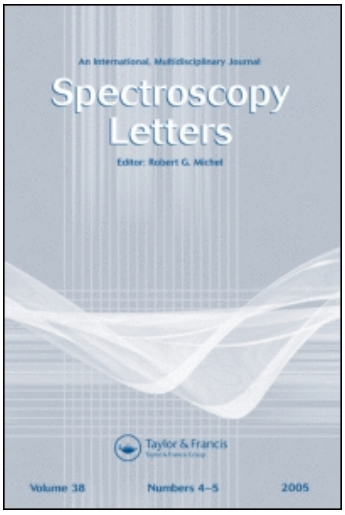

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

On the Ultra-Violet Spectra of GeCl

W. Zyrnicki[a]
[a] Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wroclaw, Wroclaw, Poland

To cite this Article Zyrnicki, W.(1978) 'On the Ultra-Violet Spectra of GeCl', Spectroscopy Letters, 11: 12, 913 — 919
To link to this Article: DOI: 10.1080/00387017808063463
URL: http://dx.doi.org/10.1080/00387017808063463

SPECTROSCOPY LETTERS, 11(12), 913-919 (1978)

ON THE ULTRA-VIOLET SPECTRA OF GeCl

KEY WORDS : rotational analysis, the GeCl molecule

W. Zyrnicki
Institute of Inorganic Chemistry and Metallurgy of Rare Elements, Technical University of Wrocław
50-370 Wrocław, Poland

ABSTRACT

Bands of GeCl in the region 335 - 370 nm have been attributed to the $^4\Sigma^- - X^2\Pi$ transition on the basis of high resolution studies of the bands at 339.2 and 350.1 nm. The rotational analysis of the (0,0) band of the $^4\Sigma^-_{3/2} - X^2\Pi_{3/2}$ subsystem has been carried out.

INTRODUCTION

A few band systems of the GeCl molecule have been reported[1-5]. A vibrational analysis of the band systems, all of which involve the ground state, has been performed but vibrational constants have been

obtained from band head measurements. Up to now a rotational analysis has been carried out for only two bands of GeCl (the $B^2\Sigma^+ - X^2\Pi_{3/2}$ transition)[6]. The rotational structure of the analyzed bands was not well resolved and rotational constants were obtained graphically[6].

The band system of GeCl in the region 335 - 370 nm was first observed by Barrow and Lagerqvist[2]. The general appearance was of two subsystems and the $^2\Delta - ^2\Pi$ transition was suggested[2]. Spectra of the GeCl and SnCl molecules show remarkable similarities. The corresponding system of the SnCl molecule, which was previously assigned to the $^2\Delta - ^2\Pi$ transition, was shown to be the $^4\Sigma^- - ^2\Pi$ system and the same change was suggested for the GeCl molecule[7]. Thus high resolution studies of the GeCl bands at 339.2 and 350.1 nm have been undertaken to establish the nature of the upper state and to determine rotational constants.

EXPERIMENTAL DETAILS

The spectrum was excited in an electrodeless discharge through a mixture of argon and germanium tetrachloride which was kept flowing at a pressure of 15 Torr. The r.f. power (300 W) was supplied from a 27.4 MHz oscillator. High resolution spectra were photographed in the eighth order of a plane

grating spectrograph at a reciprocal dispersion of 0.04 nm/mm. Exposure times of approximately one hour were necessary to record the spectra on Agfa-Gevaert plates. Spectral lines of argon and iron were used as reference standards and the plates were measured on a Hilger comparator.

RESULTS AND DISCUSSION

The analyzed band system consists of two strong subsystems with well marked sequences and a weak subsystem. All observed bands are degraded to the red. The (0,0) bands (at 339.2 and 350.1 nm) of the strong subsystems have been recorded at a high resolution.

In the band at 350.1 nm two series of strong sharp lines and a weak line-like branch could be easily picked out. Combination differences have shown that the two series of lines form an R and a P branch; R_{ff} and P_{ff} or R_{ee} and P_{ee} according to the notation of Kopp and Hougen[8]. The first lines of these branches are R(1.5) and P(2.5). The line-like branch has been identified as the Q branch and this has been confirmed by a comparison of the calculated and observed isotopic shifts. Lines of another P branch have also been found. Some irregularities have been observed in the analyzed spectrum.

Four branches have been recognized in the 339.2 nm band and have been assigned as the R_{ee}, Q_{fe}, Q_{ef} and P_{ee} branches. The Q_{fe} lines, going from ν_o towards shorter wavelengths, and the Q_{ef} lines, going from ν_o towards longer wavelengths, are prominent.

Since the lower state of the 339.2 and 350.1 nm bands is the well established $^2\Pi_{(a)}$ state, the rotational structure of these bands indicates that the upper state must be $^4\Sigma^-$ and not $^2\Delta$. The subbands at 339.2 and 350.1 nm should arise from the $^4\Sigma^-_{1/2} - {}^2\Pi_{1/2}$ and $^4\Sigma^-_{3/2} - {}^2\Pi_{3/2}$ transitions, respectively. The weak subsystem should belong to the $^4\Sigma^-_{1/2} - {}^2\Pi_{3/2}$ transition. The $^4\Sigma^- - {}^2\Pi$ transition of GeCl, analyzed here, looks very similar to this transition for SnCl[7] and differs from that observed for the GeF molecule[9].

Approximate rotational numbering in the each resolved branch (R_{ee}, Q_{fe}, Q_{ef} and P_{ee}) of the 339.2 nm band showed that it was not possible to obtain rotational constants of the upper and lower states using combination differences. Many overlapping lines due to isotopes of GeCl have made the rotational analysis complicated and have involved an uncertainty in it. Since rotational constants of the $X^2\Pi_{1/2}$ substate are unknown, rotational constants for the $^4\Sigma^-_{1/2}$ substate could not be derived from this analysis of the 339.2 nm band.

The effective rotational constants have been determined for the $^4\Sigma^-_{3/2}$ and $X^2\Pi_{3/2}$ substates from which the 350.1 nm band arises. The rotational term values for the $^4\Sigma^-_{3/2}$ substate were represented by the following formulae[7] :

$$F(J) = B_{eff}J(J+1) \pm a(J+b) - D_{eff}J^2(J+1)^2$$

The well known expression[10] was applied for the $^2\Pi_{3/2}$ substate. The least squares procedure was employed to determine rotational constants. The results are given in Table 1 along with their standard deviations. The value of B_o, obtained here, for the $X^2\Pi_{3/2}$ substate is considerably different than that derived by Mishra and Khanna[6] from a rotational analysis of the (0,0) band of the $B^2\Sigma^+ - X^2\Pi_{3/2}$ subsystem. New rotational constants for the $B^2\Sigma^+$ and $X^2\Pi_{3/2}$ states have been calculated by the author using wave numbers of rotational lines reported by Mishra and Khanna[6] and varying slightly their J numbering. The value of B_o, so recalculated from the $B^2\Sigma^+ - X^2\Pi_{3/2}$ (0,0) subband agrees quite well with this value derived from the $^4\Sigma^-_{3/2} - X^2\Pi_{3/2}$ (0,0) subband.

Results of the present analysis suggest that the rotational constants given by Mishra and Khanna[6] are incorrect. Studies of the $A^2\Sigma^+ - X^2\Pi$, $B^2\Sigma^+ - X^2\Pi$ and $^4\Sigma^- - X^2\Pi$ transitions are in progress.

TABLE 1

Rotational Constants of the GeCl Molecule in cm^{-1}

State	Constant	$B^2\Sigma^+ - X^2\Pi_{3/2}$			$^4\Sigma^-_{3/2} - X^2\Pi_{3/2}$
		Mishra and Khanna[6] (graphical method)	The author's recalculations (a least squares procedure) the previous[6] J assignment	a revised J assignment	The present experiment
$X^2\Pi_{3/2}$	B_o	0.1625	0.1620(7)	0.1511(6)	0.1517(2)
	$D_o x 10^6$		-0.44(11)	-0.095(88)	0.29(10)
$B^2\Sigma^+$	B_o	0.1775	0.1739(7)	0.1643(7)	
	$D_o x 10^6$		-0.73(11)	-0.32(11)	
	γ_o	0.0160	~0	~0	
$^4\Sigma^-_{3/2}$	B_o				0.1515(2)
	$D_o x 10^6$				0.38(12)

Numbers in parentheses represent standard deviation uncertainties in the last digits.

REFERENCES

1. W. Jevons, L.A. Bashford and H.V.A. Briscoe, Proc. Phys. Soc., 49, 532 (1937)
2. R.F. Barrow and A. Lagerqvist, Ark. Fys., 1, 221 (1949)
3. P. Deschamps, A.F. Robert and G. Pannetier, J. Chim. Phys., 65, 1084 (1968)
4. A.B. Caller and R.J. Oldman, Spectrosc. Lett., 1, 149 (1968)
5. G.A. Oldershaw and K. Robinson, Trans. Faraday Soc., 66, 532 (1970)
6. R.K. Mishra and B. N. Khanna, Ind. J. Pure Appl. Phys., 8, 825 (1970)
7. A. Chatalic, D. Iacocca and G. Pannetier, J. Chim. Phys., 70, 481 (1973)
8. I. Kopp and J.T. Hougen, Can. J. Phys., 45, 2581 (1967)
9. G. Herzberg, Spectra of Diatomic Molecules. (D. Van Nostrand Co., Princeton, New Jersey) 2nd Ed., 1950
10. R.W. Martin and A.J. Merer, Can. J. Phys., 51, 125 (1973)

Received 4-28-78
Accepted 10-19-78