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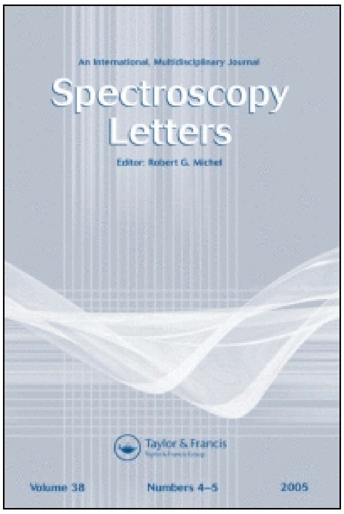

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The Electronic Absorption Spectrum of Hafnium Monochloride

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THE ELECTRONIC ABSORPTION SPECTRUM OF HAFNIUM MONOCHLORIDE.

Key words: hafnium monochloride,
intracavity laser spectroscopy,
vibrational analysis,
rotational analysis,
dissociation energy.

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ABSTRACT

Intracavity laser spectroscopy has been applied for investigation of absorption spectrum of HfCl molecule. In the region 560-700 nm 59 bands have been obtained. Rotational structure analysis of 0-0 band indicated that Hund's case (c) of angular moment coupling applied to this molecule. The molecular constants (cm^{-1}) calculated for upper and ground electronic states are: $\omega' = 353.05\ cm^{-1}$, $\omega'' = 379.65\ cm^{-1}$, $B'=0.21486\ cm^{-1}$ $B'' = 0.21801\ cm^{-1}$.

INTRODUCTION

Intracavity absorption spectroscopic is known to be of extraordinary high sensitivity. The smallest absorption coefficients detected so far are of the order of some 10^{-10} cm^{-1} [1]. Under normal conditions this sensitivity corresponds to a minimum detectable absorption oscillator strength of approximately 10^{-18} in two-level systems.

One of most obvious applications is the analysis of molecular spectra with very small line strengths. Spectroscopy on highly exited states in plasmas by means of intracavity absorption has been demonstrated by Burakov et al. [2]. High sensitivity of intracavity absorption also enables the observation if short-lived intermediate products in chemical reactions.

In this paper an intracavity laser spectroscopy method (ILS) was applied to study the electronic absorption spectrum of hafnium monochloride with the purpose of getting the weak bands of progressions and determining the vibrational and rotational constants for the upper and ground states.

The absorption spectrum of the HfCl molecule has been first obtained in [3]. Molecule HfCl is generated by pulse high voltage discharge through of HfCl vapors. The spectrum of HfCl extending from λ = 550-600 nm consists of three discrete groups of bands degraded to longer wavelengths. Each group is identified as a sequence. From intensity consideration the group at λ = 583.196 nm is indentified as the $\Delta \upsilon$ = Osequence, the groups at λ = 596.322 nm and λ = 571.469 nm identified as the $\Delta \upsilon$ = -1 sequence.

EXPERIMENTAL

The electronic absorption spectrum of hafnium monochloride has been investigated in 560-670 nm region by intracavity laser spectroscopy. The experimental set up was described in detail in Ref. [4]. The quartz cell (of 20 cm pathlength and 2 cm diameter with Brewster angle windows of 2 cm thickness) with $HfCl_4$ powder was placed in the cavity of a flash pumped dye-laser. The cavity is approximately 80 cm long and all mirrors are high reflectors with the back surfaces wedged at 10°.The mirror which transmitted more than 90% while reflecting greater than 99% in the visible region. The dye was tunable in the wavelength range of 550-700 nm. The width of band of the dye laser was about 20 nm. Powdery $HfCl_4$ was introduced into a side arm of a sealed cylindrical quartz cell. Before sealing the cell was thoroughly dried and the substance was distilled several times. During of measurements the temperature of the side arm was adjusted to 200° C resulting in a vapor pressure of $HfCl_4$ of 2 Torr. The HfCl molecules were obtained by pulse high voltage discharge through the vapours of hafnium tetrachloride. The time delay between the dye-laser and discharge pulses could be changed within 50-250 mc sec and was controlled with the help of a photomultiplier and oscillograph Type C8-2. Optimum conditions for recording the HfCl spectrum were delay about 50 mc sec between the dye-laser and discharge pulses.

The spectrum have been photographed in the region of 550-650 nm on a DFS-3 spectrograph with a grating having 75 lines/mm in the 25-27 orders of grating with a dispersion of about 0.1 nm/mm. The hollow iron cathode lamp provided a reference spectrum. The accuracy of the measurements of the individual rotational lines is of the order of ±0.03 cm^{-1}. However for some

Table 1.

Wavelengths, wave numbers and assignments of band heads of HfCl molecule

nm	cm^{-1}	$v'-v''$	isotopic shifts	
			calc.	exp.
1	2	3	4	5
549.600	18189	3-0 R		
550.630	18156	4-1 R		
560.290	17842.94	2-0 R		
561.255	17812.26	3-1 R		
562.267	17780.26	4-2 R		
563.288	17748.12	5-3 R	13.07	13.98
564.289	17716.49	6-4 R	12.23	12.82
565.315	17684.39	7-5 R	11.38	11.94
566.343	17652.22	8-6 R	10.53	11.04
567.375	17620.17	9-7 R	9.66	9.79
568.416	17588.03	10-8 R		
569.467	17555.31	11-9 R		
571.469	17493.94	1-0 R	7.68	7.99
572.413	17465.01	2-1 R	7.00	7.17
573.370	17435.86	3-2 R	6.26	6.61
574.399	17406.55	4-3 R	5.15	5.52
575.301	17377.05	5-4 R	4.77	5.16
576.311	17346.94	6-5 R	4.06	4.30
577.311	17316.95	7-6 R	3.36	3.93
578.320	17286.67	8-7 R		
579.335	17256.36	9-8 R		
580.340	17226.52	10-9 R		
581.341	17196.85	11-10 R		
583.196	17142.15	0-0 R	-0.30	-0.32
584.093	17115.82	1-1 R	-0.91	-0.89
585.003	17089.18	2-2 R	-1.53	-1.43
585.929	17062.17	3-3 R	-2.17	-2.06
586.883	17034.62	4-4 R		
596.322	16764.74	0-1 R	-8.89	-8.30
597.184	16740.63	1-2 R	-8.48	-8.81
598.058	16716.13	2-3 R	-9.93	-9.22
598.947	16691.37	3-4 R	-10.42	-9.65
599.854	16666.09	4-5 R	-11.03	-9.89
600.768	16640.71	5-6 R	-11.59	-10.42
600,691	16615.08	6-7 R	-12.16	-10.97
602.636	16589.17	7-8 R	-12.73	-12.73
603.753	16563.09	8-9 R		
604.545	16536.80	9-10 R		
609.938	16390.57	0-2 R	-17.36	-16.82
610.780	16368.01	1-3 R	-17.81	-17.24
613.334	16299.59	4-6 R	-19.09	-18.67
614.222	16276.27	5-7 R		
615.113	16252.58	6-8 R		
616.003	16229.14	7-9 R		
616.903	16205.45	8-10 R		
617.800	16181.93	9-11 R		
618.720	16157.81	10-12 R		
619.816	16133.75	11-13 R		
620.757	16109.66	12-14 R		
621.637	16086.57	13-15 R		
622.404	16062.32	14-16 R		
623.328	16038.49	15-17 R		
624.918	15997.53	1-4 R		
625.730	15976.98	2-5 R		
638.840	15679.06	0-4 R		
639.640	15629.53	1-5 R		

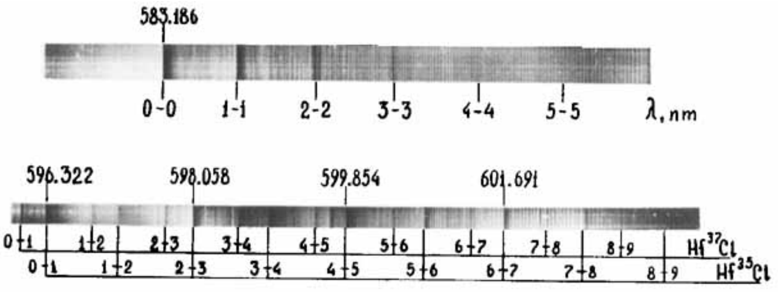

Fig.1. A portion of the HfCl electron spectrum: a) 0-0 band; b) 0-1 band.

of the weak and broad diffuse rotational lines the error of measurement is ±0.07 cm^{-1} .

VIBRATIONAL AND ROTATIONAL ANALYSIS

Numerous bands (59) were measured in the region 550-700 nm, about 38 of with being recorded for the first time. The recorded HfCl bands as well as their assignment with the data from Ref. [3] are listed in Table 1. The vibrational assignments of the bands have well supported by a study of chlorine isotope effect.

The spectrum consists of seven discrete groups of bands degraded to longer wavelengths. Each group is identified as a sequence with v = 0, +1, +2, +3, +4. From intensity consideration, the group at λ = 583.196 nm is easily identified as the $\Delta v = 0$ sequence. Fig. 1 is a reproduction of the $\Delta v = 0$ and $\Delta v = -1$ sequences. The sequence $\Delta v = 0$ consists of four bands with vibrational quantum numbers (0,0), (1,1), (2,2), (3,3), (4,4). The sequence $\Delta v = -2$ consists of bands with vibrational quantum numbers $v' = v'' = 15$. From considerations of the electronic configuration for the ground and first excited

Table 2.

Molecular constants of the HfCl molecule (cm^{-1})

Constants	A1/2	X1/2
ν_{00}	17126.33	
w	353.05(0.09)	379.65(0.09)
$w_e\chi_e$	1.132(0.007)	1.054(0.006)
B_0	0.21486(22)	0.21801(21)
D_0	$1.5\ 10^{-7}$	$1.2\ 10^{-7}(0.8)$

states of HfCl and related molecules, the transition of A-X system is expected to be $^2\Sigma-^2\Pi_{1/2}$. However, an examination of the rotational structure of all band reveals the presence of only two branches P and R. This feature can be seen from the enlargement of the 0-0 band in Fig.1. The branch which forms the head is easily identified as the R branch.

The fact that no splitting of rotational lines has been observed even at high J values, strongly indicates that this transition is a case (c) equivalent (1/2-1/2) of $^2\Sigma-^2\Pi_{1/2}$ transition in Hund s case (a).

A vibrational analysis of the system designated as A1/2 -X1/2 was carried out leading to the following formula:

$$\nu_{v'v} = \nu_e + [\ \omega'_e(v'+1/2) - \omega_e\chi'_e(v'+1/2)^2\ ] - [\omega''_e(v''+1/2) - \omega_e\chi''_e(v'+1/2$$

The isotopic separations are calculated and compared with the experimentally observed values. The agreement is found to be quite satisfactory with Table 1. This confirms the vibrational analysis of the band system. The wave numbers, classification, and isotopic shifts due to ^{35}Cl and ^{37}Cl data are displayed in Table 1.

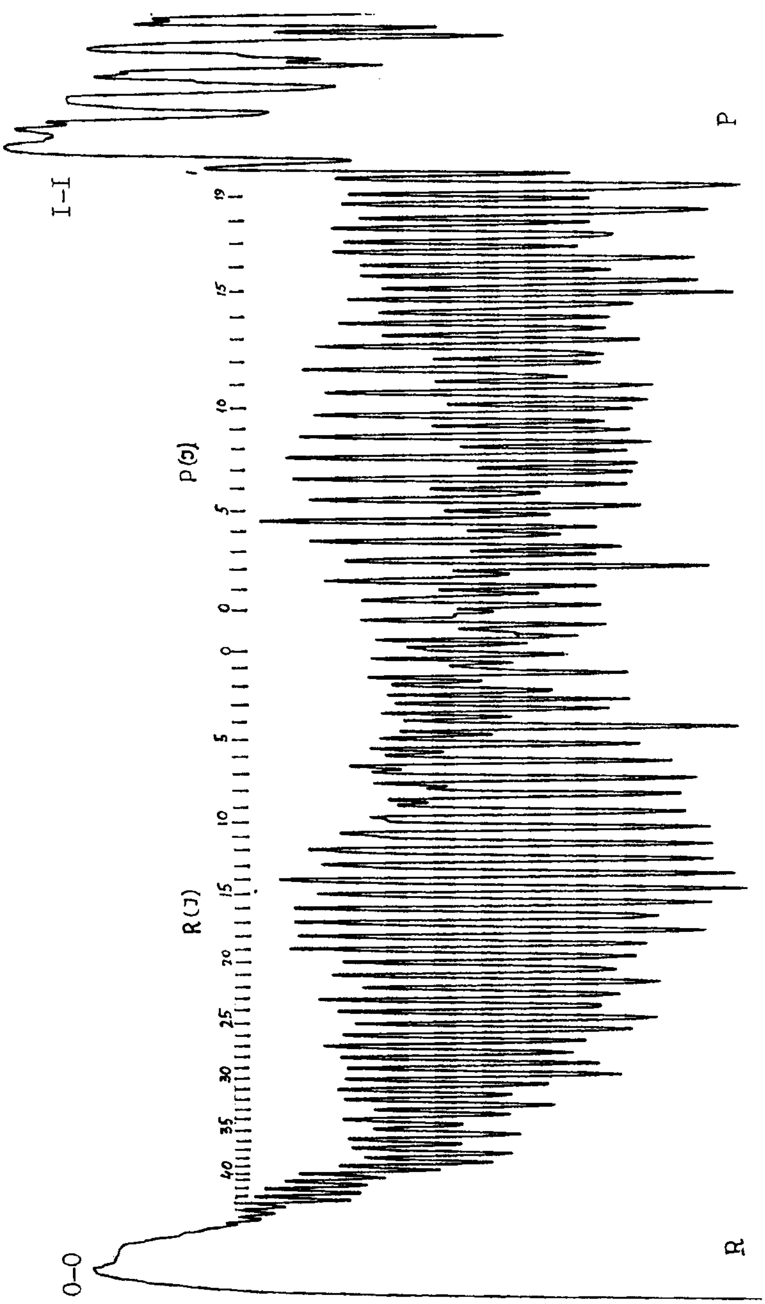

Fig.2. Microdensitometr tracing of the intracavity dye laser absorption spectrum of HfCl 0-0 band.

ROTATIONAL ANALYSIS

The rotational analysis was performed for the (0,0) and (0,1) bands. The bands analyzed consist of two branches R and P. The relative numbering for the bands has been found by finding of agreement between the combination differences Δ_2F = R(J-1)-P(J+1) for both the (0,0) and the (1,0) bands. Absolute numbering has been found by the requirement that $\Delta_2F(J) = 4B(J+1/2)$ plotted as function of J should go through zero at J=-1/2. The molecular constants of HfCl derived from the rotational analysis are given in Table 2. The rotational constants B and D and the band origins were calculated by the least-squares method using the following relations:

$$\Delta_2F(J) = 4B(J+1/2)-8D(J+1/2)^3$$

$$R(J-1)+P(J) = 2\nu_0+2(B'-B'')J^2-2(D'-D'')J^2(J+1)^2$$

Fig.2 is reproducton of the microdensitometr tracing of the intracavity dye laser absorption spectrum of HfCl 0-0.

DISSOCIATION ENERGY

The linear extrapolation of vibrational energy levels for ground and exited states results in following dissociation energy $D_{lin}(X_{1/2}) = 34187\ cm^{-1}$, $D_{lin}(A_{1/2}) = 27520\ cm^{-1}$. Obviously it is not necessary to consider under dissociation of the formation of excited chlorine atom due to high energy of the first excitation term (80000 cm^{-1}). Therefore one should suppose, that A1/2 dissociation of HfCl molecule of the state takes place in the formation of atom Sl in the state $^2P_{3/2}$ and the atom Hf in the state ^3P with the energy exitation 8983.75 cm^{-1} or in the state a'D with energy exitation 10535.5 cm^{-1}. The found values of dissotiation energy result in ,the exitation energy $E_{at} = T_e + D'-D'' = 10485\ cm^{-1}$ good agree to a'D.

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