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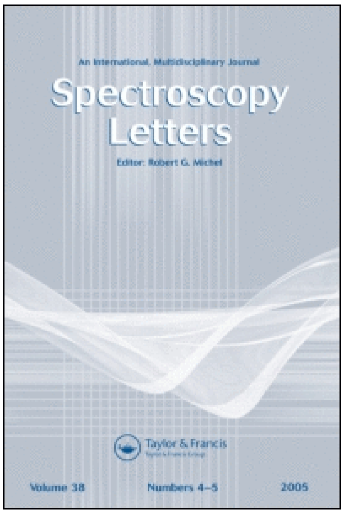

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Spectroscopy of Hafnium Monohalides

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SPECTROSCOPY OF HAFNIUM MONOHALIDES

Key words: intracavity laser method, electronic spectra, hafnium halides, HfF, HfCl, HfBr and HfI molecules, molecular constants.

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ABSTRACT

The modern intracavity laser method has been applied to study electronic spectra of the hafnium monohalides molecules. Results of new investigation of HfF and HfBr molecules are presented: the bands at 589.3, 590.6, and 593.1 nm observed in intracavity laser spectra of HfF_4 have been assigned to the bands of HfF or ionized HfF; new molecular constants of the HfBr molecule have been obtained. Spectroscopic studies of HfCl and HfI molecules are discussed, and the most reliable molecular constants of HfCl, HfBr, and HfI molecules are recommended.

INTRODUCTION

There has been recent interest in spectroscopic study of simple molecules containing transition metal because their electronic spectra can provide profound information on nature and strengths of various intermolecular interactions. This information serves as a good basis for an ab initio calculation and gives new understanding of chemical bonding between atoms in molecules.

In this paper, we review spectroscopic information about diatomic hafnium halides. To date, there are scarce spectroscopic data on monohalides which contain metal of the f-elements. Our first spectroscopic research of hafnium halides has dealt with the HfCl molecule. The study was performed by a conventional spectroscopic method in 1975 [1].

Then, we developed **a highly sensitive intercavity laser method** which allows us to record absorption spectra containing many more bands compared to that obtained by conventional spectroscopic methods. This intracavity method is based on a depression of intensity in the spectrum of laser generation at wavelengths corresponding to the absorption spectrum of the substance which is inserted into a cavity.

We have been applying this method to spectroscopic study of diatomic hafnium halides since 1982 [2].

We describe the new spectroscopic study of the HfF and HfBr molecules performed by this intracavity laser spectroscopic method, review spectroscopic information about hafnium monohalides, and recommend the most reliable molecular constants of hafnium monohalides on the basis of the critical analysis of spectroscopic data available up to now.

EXPERIMENT

The basic experimental set-up has been described previously in [3]. Briefly, the set-up consists of a pulse dye laser, a discharge tube, and a 4 m grating-mounted spectrograph. Solid hafnium tetrahalides are placed into the discharge tube. Thereafter the tube is pumped down, filled up with argon or with a mixture of argon and hydrogen or NH_3. The total pressure is about 1-2 Torr. If it is necessary, the tube is heated to increase the partial pressure of hafnium tetrahalides. There are two electrodes in the tube. A capacitor which was charged up to 10 kV is connected with these electrodes. The tube is inserted into the cavity of a pulse dye laser. A pulse generator initiates a capacitor discharge in the tube. This discharge produces a plasma where various species (including diatomic) are formed. After a time delay, the pulse generator initiates a flash of the dye laser. An emission spectrum of the dye laser serves as a continuous background to record absorption spectra of the diatomic halides. The pulse of laser can be delayed in respect to the pulse of electric discharge. This time delay can be changed within 10-2000 ms and allows us to obtain molecular spectra which are almost free from atomic lines. The accuracy of the measurements of the sharp unblended lines in molecular spectra is about 0.03 cm^{-1}.

RESULTS AND DISCUSSION

HfF molecule.

The HfF species has not previously been characterised spectroscopically. We considered the location of the most intensive bands in the spectra [4-10] of titanium and zirconium halides. It was found that location of the bands of these florid-containing molecules spectra tended to be shifted to ultraviolet compared to the position of these bands of other halides containing the same metal. We came to the conclusion that the spectrum of HfF molecules can be found at the ultraviolet limits of the spectra of other hafnium halides.

Intracavity laser spectroscopic method has been employed to find spectra of HfF. The spectral region of 560-590 nm has been investigated. Powdery HfF_4 (99.98% purity) has been placed into the discharge tube. We supposed that the HfF molecule can be produced in a plasma of electric discharge. The experiments were conducted using very different conditions. The recorded spectra show extremely complicated and obscured structure. We were able to detect only three molecular bands at 589.3 nm, 590.6 nm, and 593.1 nm. It seemed natural to assign the bands to HfF or ionized HfF since no identifiable impurity spectra were found in association with them. The analysis of this molecular spectrum has turned out to be impossible now.

HfCl molecule.

The spectrum of HfCl molecule was first obtained in our laboratory by a conventional spectroscopic method in 1975 [1].

The detailed study of the HfCl molecule spectra was carried out by modern intracavity laser method in our laboratory in 1993

[11]. 59 bands (38 bands are new ones) were recorded in the region 550-700 nm. The vibrational analysis was performed in detail. Rotational analysis of the 0-0 bands was carried out for the first time. This analysis indicated that Hund's case (c) of angular moment coupling applied to this molecule. The recommended vibrational and rotational constants are given in the Table 3.

HfBr molecule.

The electronic spectrum of HfBr molecule was discovered by T.Savithry at. el. in 1973 and the tentative vibration analysis of the spectrum was performed [12]. Results of our first conventional spectroscopic study of HfBr molecule was published in 1982 [2]. Now we report on detailed research carried out by the intracavity laser method. The purpose of this research is to obtain more bands to be able to calculate the accurate value of vibrational constants.

Tetrabromide of hafnium, $HfBr_4$ (99.98% purity), is used for production of HfBr in a discharge tube. The time delay about 50-100 ms between the discharge and day-laser pulses is the best magnitude to record molecular spectrum.

The spectrum of HfBr extends from 550 to 700 nm. All known bands have been recorded, besides the 20 new bands detected. All bands are clearly red-shaded.

The structure of HfBr spectrum is similar to the structure of HfCl spectrum which was rotationally analyzed in [11]. By analogy with a spectrum of HfCl molecule, the spectrum of HfBr was assigned to A1/2-X1/2 transition.

The spectrum consists of seven band groups. Each group is assigned to a vibrational sequence. The most intensive group at 620.5 nm is identified as the $d\upsilon=0$ sequence. Figure 1. shows microdensitometer tracing of the spectrum of (0,0) and (1,1) bands. The other groups which are arranged in the red and the violet from the $d\upsilon=0$ sequence are assigned to the $d\upsilon= \pm1, \pm2, \pm3, \pm4$ sequences.

The vibrational analysis of bands recorded was performed. The molecular constants are listed in Table 3.

There are six naturally occurring isotopes in hafnium:- ^{180}Hf(35%), ^{178}Hf(27%), ^{179}Hf(13.75%), ^{177}Hf(18.56%), ^{176}Hf

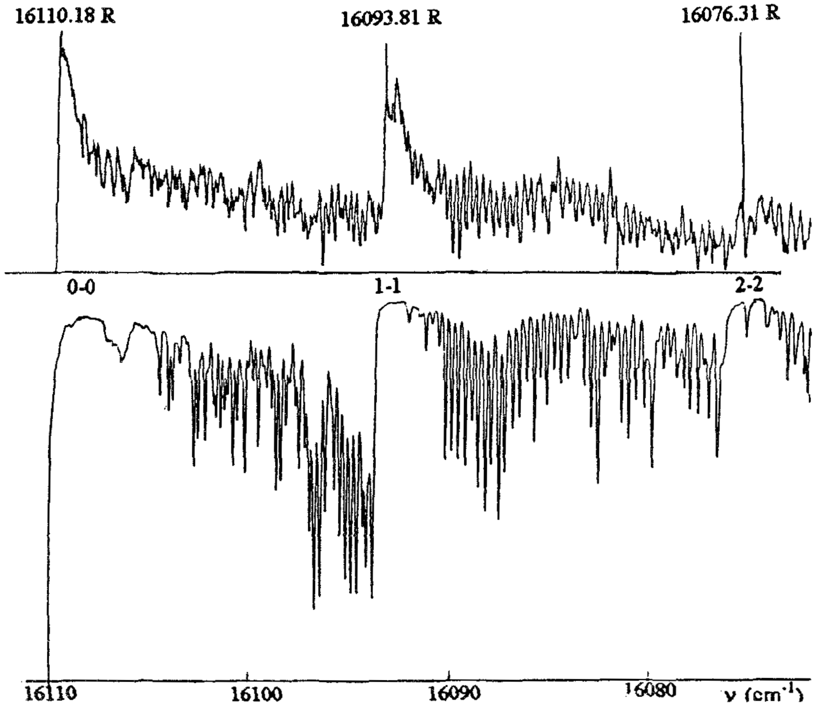

Fig. 1. Microdensitometer tracing of the intracavity dye laser absorption spectrum of HfBr 0-0 sequence. a) delay-200ms, b) delay 60 ms.

(5.25%), ^{174}Hf(0.165%); and in bromine, there are two naturally occurring isotopes ^{79}Br(50.5%) and ^{81}Br(49.5%). The heads of the bands are split due to the occurrence of isotopomeres. The splitting of heads appearing from isotopic species ^{180}Hf^{79}Br and ^{180}Hf^{81}Br was remarkable. These splitting are shown in Figure 2.

Assignments (υ'-υ"), wavelengths (λ), wave numbers (ν), and isotopic shifts (dν) of band heads of ^{180}Hf^{79}Br and ^{180}Hf^{81}Br molecules (cm^{-1}) are listed in Table 1.

As can be seen from Table 1 , isotopic shifts recorded are in good agreement with shifts calculated on the basis of molecular constants obtained.

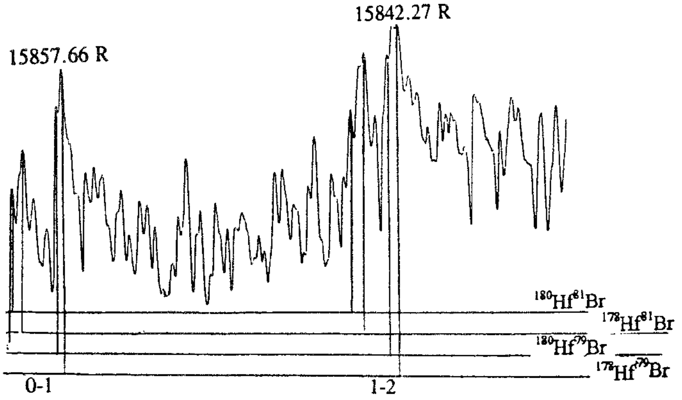

Fig.2. Microdensitometer tracing of the intracavity dye laser absorption spectrum of HfBr 0-1sequence. The splitting of heads appeared from isotopi species ^{180}Hf^{79}Br ^{180}Hf^{81}Br are shown.

TABLE 1.

Assignments (υ'-υ''), wavelengths (λ), wave numbers (ν), and isotopic shifts (dν) of band heads of ^{180}Hf^{79}Br and ^{180}Hf^{81}Br molecules (cm^{-1}).

υ'-υ''	λ(nm)	ν (cm^{-1})	dν (cm^{-1}) obs.	calc.
3-0	594.584	16813.48 R	6.1	5.84
4-1	595.426	16790.20 R	5.8	5.64
5-2	596.263	16766.40 R	5.5	5.42
2-0	602.911	16581.49 R	4.1	3.91
3-1	603.697	16560.18 R	3.8	3.62
4-2	604.480	16538.69 R	3.5	3.47
5-3	605.370	16514.25 R	-	3.20
1-0	611.564	16346.93 R	2.08	1.94

TABLE 1.(Continued)

υ'-υ"	λ(nm)	ν (cm^{-1})	dν (cm^{-1})	
			obs.	calc.
*	611.620	16346.14 *	-	-
2-1	612.283	16327.80 R	1.81	1.75
*	612.310	16327.01 *	-	-
3-2	613.01	16308.69 R	1.57	1.54
*	613.02	16308.19 *	-	-
4-3	613.825	16286.82 R	1.47	1.42
*	613.851	16286.08 *	-	-
5-4	614.652	16264.87 R	-	1.13
0-0	620.554	16110.18 R	-0.06	-0.05
1-1	621.184	16093.81 R	-0.23	-0.22
*	621.205	16093.28 *	-	-
2-2	621.861	16076.31R	-0.43	-0.38
*	621.90	16075.26 *	-	-
3-3	622.55	16058.61 R	-0.67	-0.56
*	622.618	16056.78 *	-	-
4-4	623.360	16037.67 R	-	-0.73
0-1	630.436	15857.66 R	-2.30	-2.24
1-2	631.048	15842.27 R	-2.36	-2.36
2-3	631.726	15825.26 R	-2.52	-2.49
3-4	634.409	15808.18 R	-2.78	-2.63
4-5	633.187	15788.76 R	-	-2.75
5-6	633.990	15768.75 R	-2.99	-2.93
0-2	640.58	15606.20 R	-4.48	-4.37
1-3	641.15	15592.80 R	-4.9	-4.47
2-4	641.84	15575.90 R	-5.1	-4.46
0-3	650.919	15358.65 R	-6.70	-6.48

TABLE 2.

Assignments (υ'-υ"), wavelengths (λ), and wave numbers (ν) of band heads of HfI molecule (cm^{-1}).

υ'-υ"	λ(nm)	ν(cm^{-1})	υ'-υ"	λ(nm)	ν(cm^{-1})
4-0	658.47	15182.4	4-4	687.99	14531.13
3-0	665.19	15029.0	5-5	688.36	14523.33
4-1	665.70	15017.7	6-6	688.73	14515.4
5-2	666.18	15006.8	7-7	689.12	14507.3
2-0	672.06	14875.5	8-8	689.51	14499.0
3-1	672.58	14864.0	9-9	689.94	14490.0
4-2	673.02	14854.25	0-1	694.50	14394.82
5-3	673.47	14844.45	1-2	694.78	14389.0
1-0	679.29	14717.21	2-3	695.07	14383.12
2-1	679.68	14708.84	3-4	695.36	14377.05
3-2	680.07	14700.4	4-5	695.66	14370.93
4-3	680.46	14691.9	0-2	702.50	14231.0
5-4	680.86	14683.35	1-3	702.70	14227.0
0-0	686.64	14559.71	2-4	703.00	14221.8
1-1	686.98	14552.51	0-3	710.60	14069.0
2-2	687.33	14545.40	1-4	710.75	14065.45
3-3	687.66	14538.10			

There are specific features in some bands: heads of these bands could not be assigned to any isotopomeres of the HfBr. Nature of these heads is not identifiable up to now. These heads are marked by sign * in Table 1.

The bands throughout the spectra are strongly overlapped and the rotational analysis could not be implemented. The rotational structure of the HfBr spectrum is similar to that of the HfCl spectrum.

TABLE 3.

Molecular constants recommended for HfCl, HfBr, and HfI (cm^{-1})

	HfCl	HfBr	HfI
ν_{00}	17126.33±0.1	16119.0±0.1	14562.9±0.1
ω'_e	353.05±0.1	238.41±0.1	159.2±0.1
$\omega'_e x'_e$	1.13±0.01	1.10 ±0.1	0.71±0.02
ω''_e	379.65±0.1	255.07±0.15	165.90±0.1
$\omega''_e x''_e$	1.05±0.01	0.86 ±0.15	0.64±0.02
B'_0	0.21486(22)	~0.137	
B''_0	0.21801(21)		
D'_0	$1.5\times10^{-7}\pm0.3$	1×10^{-7}	
D''_0	$1.2\times10^{-7}\pm0.3$		

HfI molecule

The electronic emission spectrum of HfI molecule was reported by T.Savithry at. el. in 1973 and the vibration assignment was carried out. It was possible to calculate the first vibrational quantum of excited and ground states only [13].

The results of our conventional spectroscopic study of HfI molecule was published in 1982 [2]. All known bands which are known in the literature have been recorded, besides 15 new bands were detected. On the basis of all available data we calculated vibrational frequencies and coefficients of anharmonisity. These constants are given in the Table 3. These data have not been known previously.

Assignments (υ'-υ"), wavelengths (λ), and wave numbers (ν) of band heads of HfI molecule which are known at present are given in Table 2.

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