Fourier transform emission spectroscopy of HfH and HfD

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The electronic emission spectra of HfH and HfD were investigated in the 476 nm to 1 μm spectral region using a Fourier transform spectrometer. The bands were excited in a hafnium hollow cathode lamp in the presence of a mixture of neon and H_2 or D_2. For HfH, two $\Delta\Omega=0$ electronic transitions with a common $\Omega''=3/2$ lower state, most probably the $X\,^2\Delta_{3/2}$ ground state, were identified at 14 495 and 19 147 cm^{-1}. These bands have been assigned as the $[14.5]3/2-X\,^2\Delta_{3/2}$ and the $[19.1]3/2-X\,^2\Delta_{3/2}$ transitions. The rotational analysis of the 0–0 and 1–1 bands of the $[14.5]3/2-X\,^2\Delta_{3/2}$ system and the 0–0 band of the $[19.1]3/2-X\,^2\Delta_{3/2}$ system provides the following equilibrium constants for the ground state of HfH: $B_e'' = 5.019\ 11(8)$ cm^{-1}, $\alpha_e'' = 0.120\ 26(11)$ cm^{-1}, and $r_e'' = 1.830\ 691(15)$ Å. For HfD, only the 0–0 band of the $[19.1]3/2-X\,^2\Delta_{3/2}$ transition at 19 134 cm^{-1} was identified. This work represents the first observation of the HfH and the HfD molecules.

I. INTRODUCTION

Diatomic transition metal hydrides are of interest to a wide range of scientists.[1–15] They serve as simple models for the study of metal–hydrogen bonding in inorganic chemistry and in surface science. The interaction of transition metals with hydrogen has important practical applications in heterogeneous catalysis where, e.g., hydrocarbons are hydrogenated or reformed. Since hydrogen is the most abundant element in the universe, metal hydrides are found in the sun and in cool stars.[16,17]

The properties of most heavy diatomic transition metal hydrides have been predicted by *ab initio* quantum chemistry, most notably by Balasubramanian and co-workers.[6,12–14] The experimental database is more meager. For example, for the possible $5d$ transition metal hydrides, experimental data are available for only LaH,[18] PtH,[19,20] AuH,[21] and, tentatively, WH.[22]

The large number of unpaired electrons in transition metal atoms results in a large number of low-lying electronic states with large orbital and spin angular momenta in metal hydride molecules. Relativistic effects, such as spin–orbit coupling, are very important for the heavy $5d$ metals. The numerous electronic states interact with each other and cause perturbations. This leads to experimental difficulty in the analysis of the spectra and in the *ab initio* prediction of molecular properties. Indeed, one of the main motivations in the study of transition metal hydrides is the confrontation between *ab initio* results and experimental reality.

We report here on the discovery of a new metal hydride molecule HfH. HfH and HfD were formed in a hollow cathode discharge lamp and the visible emission spectra were recorded with a Fourier transform spectrometer. Our analysis of the data was aided by the *ab initio* calculation of Balasubramanian and Das.[6]

II. EXPERIMENT

The spectra of HfH and HfD molecules were observed in a hafnium hollow cathode lamp. The cathode was prepared by inserting a 1 mm thick cylindrical foil of hafnium metal into a hole in a copper block. The foil was tightly pressed against the inner wall of the cathode to provide a close and uniform contact between the metal and the copper. The lamp was operated at 450 V and 387 mA current with a mixture of 1.7 Torr Ne and about 100 mTorr of H_2 or D_2.

The spectra were recorded using the 1 m Fourier transform spectrometer associated with the McMath Solar Telescope of the National Solar Observatory. The spectra in the 4800–21 000 cm^{-1} region were recorded in two experiments. The 4800–9800 cm^{-1} spectral region was recorded using InSb detectors and silicon filters with ten scans coadded in 70 min of integration. For the 9000–21 000 cm^{-1} spectral region, the spectrometer was operated with colored glass filters which transmit to the red of 495 nm and Si-diode detectors. This time a total of six scans were coadded in approximately 1 h of integration. In both cases, the spectrometer resolution was set at 0.02 cm^{-1}. The observed interferograms were transformed to provide the spectra of HfH and HfD.

In addition to the HfH and HfD bands, the final spectra also contained Hf and Ne atomic lines. The spectra were calibrated using the measurements of Ne atomic lines made by Palmer and Engleman.[23] The absolute accuracy of the wave number scale is expected to be better than ±0.002 cm^{-1}. The HfH/HfD lines have a typical width of about 0.070 cm^{-1} and appear with a maximum signal-to-noise ratio of about ten. This limits the precision of measurements to ±0.003 cm^{-1} for strong and unblended lines.

III. OBSERVATION AND ANALYSIS

The spectral line positions were extracted from the observed spectra using a data reduction program called PC-DECOMP developed by Brault of the National Solar Observatory at Kitt Peak. The peak positions were determined by fitting a Voigt line shape function to each spectral feature.

The assignment of the observed transitions of HfH and HfD was greatly facilitated by the recent theoretical calculation of the properties of HfH by Balasubramanian and Das.[6]
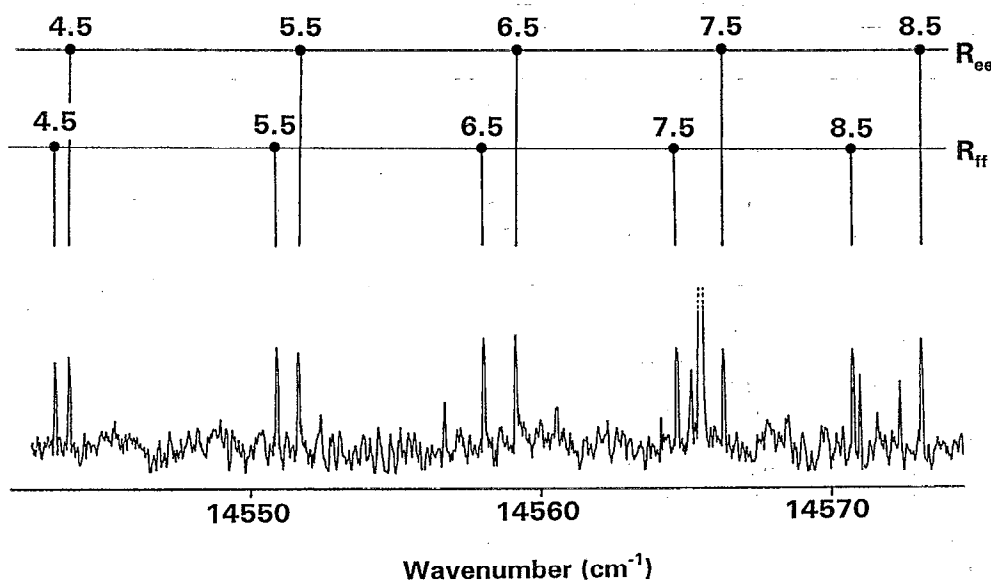
FIG. 1. A portion of the 0–0 band of the $[14.5]3/2 - X \, ^2\Delta_{3/2}$ transition of HfH.

These authors have applied the complete active space multi-configuration self-consistent field (CAS-MCSCF) and second-order configuration interaction (SOCI) methods to predict the symmetry as well as the spectroscopic constants of several electronic states of HfH. They predict the ground state of this molecule to be a $\Omega''=3/2$ state with 82% $^2\Delta_{3/2}$ and 18% $^2\Pi_{3/2}$ character. They also predict that several strong electronic transitions of HfH involving the ground $^2\Delta$ state should lie in the visible region of the spectrum.

In the present work, we have discovered two electronic transitions of HfH at 14 495 and 19 147 cm^{-1} and one transition of HfD at 19 134 cm^{-1}. The analysis of these bands indicates that the ground state of HfH and HfD is indeed an $\Omega''=3/2$ state which we denote as the $X \, ^2\Delta_{3/2}$ ground state. We assign these transitions of HfH as $[14.5]3/2 - X \, ^2\Delta_{3/2}$ and $[19.1]3/2 - X \, ^2\Delta_{3/2}$ transitions. For convenience, we have chosen to label the observed excited electronic states using the notation suggested by Linton and co-workers[24] and Friedman-Hill and Field.[25] The number in brackets represents the energy of the Ω state (with $v = 0$) measured in units of 1000 cm^{-1}. This avoids the confusion caused by naming states with conventional labels before the low-lying states have been discovered.

A. Observed spectrum of HfH

The spectrum of HfH consist of two transitions with the 0–0 bands located at 14 495 and 19 147 cm^{-1}, respectively. Each of these bands consists of simple P and R branches with each line split into two components as J increases. This splitting increases as J^3 as expected for a $\Omega=3/2-3/2$ transition. The analysis of these bands indicates that both of these transitions have a common lower state.

A part of the spectrum of the 0–0 band of the $[14.5]3/2 - X \, ^2\Delta_{3/2}$ transition at 14 495 cm^{-1}, showing well-resolved Ω doubling, is presented in Fig. 1. Several perturbations were observed in the excited state of this tran-

sition. A small local perturbation can be seen in the e-parity component of the excited state at $J = 11.5$ (Table I). The perturbation in the f-parity component is more severe. All lines with J' greater than 12.5 are perturbed. After the perturbation the lines become randomly displaced and weaker in intensity, and it becomes very difficult to assign the perturbed transitions. The transitions affected by perturbations were not included in the determination of the molecular constants.

Near to the 0–0 band, there is a weaker band with an origin at 14 335.4 cm^{-1} which has been assigned as the 1–1 band. This band is also affected by several perturbations. In this band, all of the lines of both Ω-doubling components are severely perturbed for J' greater than 9.5. Therefore transitions with J' values greater than 9.5 could not be identified with certainty.

The transition at 19 147 cm^{-1} has been assigned as the 0–0 band of the $[19.1]3/2 - X \, ^2\Delta_{3/2}$ transition. A part of the spectrum of this band is provided in Fig. 2. The spacing between the consecutive lines of e-parity component varies in an erratic manner. Similarly, all of the higher J transitions of f parity are shifted from their respective positions for $J' > 12.5$. For J' greater than 18.5, it becomes impossible to identify the rotational lines. All of the perturbed transitions were excluded from the final fit, but ground state combination differences obtained from the perturbed transitions were included.

Hafnium has six naturally occurring isotopes ^{174}Hf(0.2%), ^{176}Hf(5.2%), ^{177}Hf(18.5%), ^{178}Hf(27.1%), ^{179}Hf(13.8%), and ^{180}Hf(35.2%). At higher J, the splitting into two components due to the most abundant ^{178}HfH and ^{180}HfH isotopomers becomes visible. Since in most parts of the spectrum the isotopic splitting is not resolved, we did not try to measure the line positions of

TABLE I. Observed transition wave numbers (in cm^{-1}) of the $[14.5]3/2 - X\ ^2\Delta_{3/2}$ system of HfH.

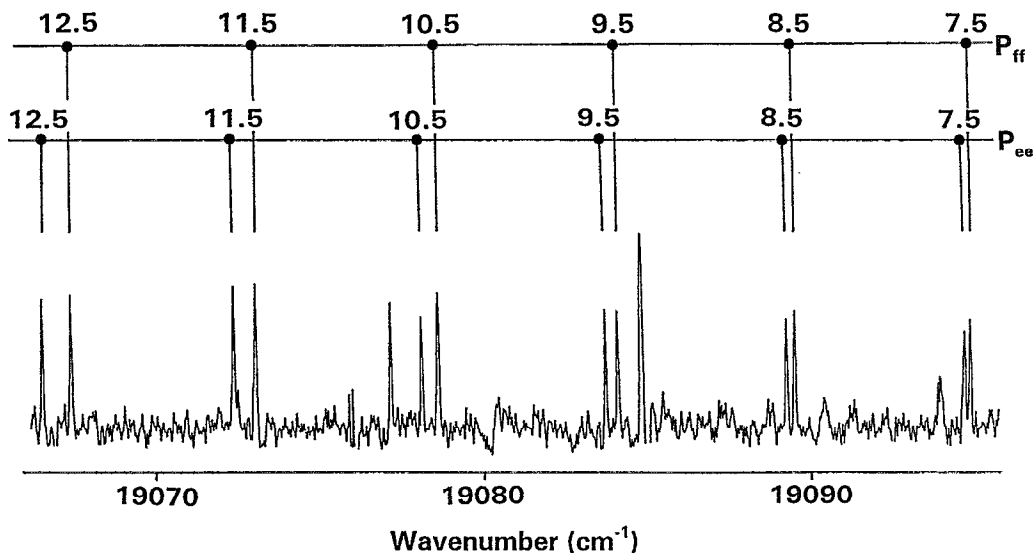| J	R_{ee}	Obs.–calc.[a]	P_{ee}	Obs.–calc.[a]	R_{ff}	Obs.–calc.	P_{ff}	Obs.–calc.[a]
				0–0 band				
1.5	14 518.231	0.001			14 518.164	−0.005		
2.5	14 527.053	0.000	14 469.427	−0.007	14 526.899	−0.010	14 469.420	0.005
3.5	14 535.564	0.007	14 458.770	0.006	14 535.268	−0.013	14 458.694	−0.006
4.5	14 543.738	−0.000	14 447.810	0.005	14 543.261	−0.003	14 447.637	−0.019
5.5	14 551.590	0.004	14 436.563	0.001	14 550.846	0.003	14 436.263	−0.012
6.5	14 559.098	0.005	14 425.039	0.002	14 558.003	0.001	14 424.547	−0.002
7.5	14 566.242	−0.003	14 413.233	0.003	14 564.630[c]	−0.093	14 412.477	0.009
8.5	14 573.027	−0.002	14 401.139	0.000	14 570.672[c]	−0.323	14 400.018	−0.005
9.5	14 579.422	−0.008	14 388.759	−0.002			14 387.117[c]	−0.092
10.5	14 585.355[c]	−0.074	14 376.086	−0.004	14 580.394[c]	−1.756	14 373.700[c]	−0.320
11.5	14 591.007	−0.002	14 363.112	−0.007	14 583.582[c]	−3.444	14 359.647[c]	−0.804
12.5	14 596.152	0.005	14 349.755[c]	−0.083			14 344.756[c]	−1.749
13.5	14 600.845[b]	0.027	14 336.244	0.009			14 328.741[c]	−3.450
14.5	14 604.996	−0.001	14 322.286	−0.012				
15.5	14 608.644	−0.008	14 308.017	0.007				
16.5	14 611.748	−0.003						
17.5	14 614.273	0.018	14 278.301	0.001				
18.5	14 616.124	−0.000	14 262.827	−0.003				
19.5			14 246.911	−0.001				
20.5			14 230.508	−0.002				
				1–1 band				
2.5	14 367.251	−0.009	14 310.723	−0.029	14 367.202	0.001	14 310.723	−0.002
3.5	14 375.782	0.007			14 375.625	−0.005		
4.5	14 384.015	0.001	14 289.961	−0.005	14 383.716	0.001	14 289.825	0.001
5.5	14 391.949	−0.003	14 279.225	0.000	14 391.408	−0.001	14 278.965	0.007
6.5	14 399.545	−0.006	14 268.251	0.007	14 398.660	0.005	14 267.781	−0.002
7.5	14 406.754	0.008	14 257.004	−0.005	14 405.378	−0.005	14 256.260	−0.003
8.5	14 413.432	−0.002	14 245.479	−0.005	14 411.460[c]	−0.048	14 244.352	−0.000
9.5			14 233.617	0.006			14 231.990	0.003
10.5			14 221.287	−0.002			14 219.046[c]	−0.051

[a]Observed–calculated line positions.
[b]Blended lines (see the text for details).
[c]Perturbed transitions not included in the final fit.

FIG. 2. A portion of the 0–0 band of the $[19.1]3/2 - X\ ^2\Delta_{3/2}$ transition of HfH.

TABLE II. Observed transition wave numbers (in cm^{-1}) of the $[19.1]3/2-X\ ^2\Delta_{3/2}$ system of HfH.

J	R_{ee}	Obs.–calc.[a]	P_{ee}	Obs.–calc.	R_{ff}	Obs.–calc.[a]	P_{ff}	Obs.–calc.[a]
				0–0 band				
1.5	19172.364	0.004						
2.5	19182.170	−0.014	19122.812	0.009	19181.847[b]	1.807		
3.5	19191.942	−0.007	19112.889	−0.002	19190.301[b]	1.245		
4.5	19201.677	0.011	19102.922	−0.009	19198.221[b]	0.317		
5.5	19211.336	−0.005	19092.944	−0.000	19206.586	0.000	19091.293[b]	1.232
6.5	19220.936[b]	−0.037	19082.960	0.008	19215.114	0.006	19079.522[b]	0.319
7.5	19230.581	0.031	19072.970	0.004	19223.386[b]	−0.094	19068.225	−0.004
8.5	19240.045	−0.001	19062.961[b]	−0.034	19232.016[b]	0.305	19057.151	−0.003
9.5	19249.426	0.004			19240.113[b]	0.298	19045.922[b]	−0.074
10.5	19258.604	−0.014	19043.065	−0.005	19247.807	0.003	19035.073[b]	0.301
11.5	19267.932[b]	0.383	19033.066	−0.001			19023.778[b]	0.273
12.5	19277.166[b]	1.059					19012.208	−0.003
13.5	19286.843[b]	2.697	19013.118[b]	0.403				
14.5	19295.752[b]	4.259						
15.5	19304.389[b]	6.464	18993.960[b]	2.703				
16.5	19312.897[b]	9.716	18984.007[b]	4.253				
17.5	19321.360[b]	14.414	18973.913[b]	6.445				
18.5			18963.849[b]	9.706				
19.5			18953.893[b]	14.422				

[a]Observed–calculated line positions.
[b]Perturbed transitions not included in the final fit.

individual isotopomers. For split lines, an average line position was measured.

The observed transition wave numbers of the $[14.5]3/2-X\ ^2\Delta_{3/2}$ transition of HfH are provided in Table I and those of the $[19.1]3/2-X\ ^2\Delta_{3/2}$ transition are provided in Table II. Note that an absolute e/f parity assignment could not be made so that the parity was chosen to make p_D positive in the [14.5] 3/2 state.

B. Observed spectrum of HfD

For the HfD molecule, only the $[19.1]3/2-X\ ^2\Delta_{3/2}$ transition with a band origin at 19 134 cm^{-1} was identified in our spectra. A part of the spectrum of this band is provided in Fig. 3. The structure of this band of HfD is also perturbed, as is the case for the corresponding band of HfH. The higher J transitions above $J' = 12.5$ involving both Ω-doubling com-
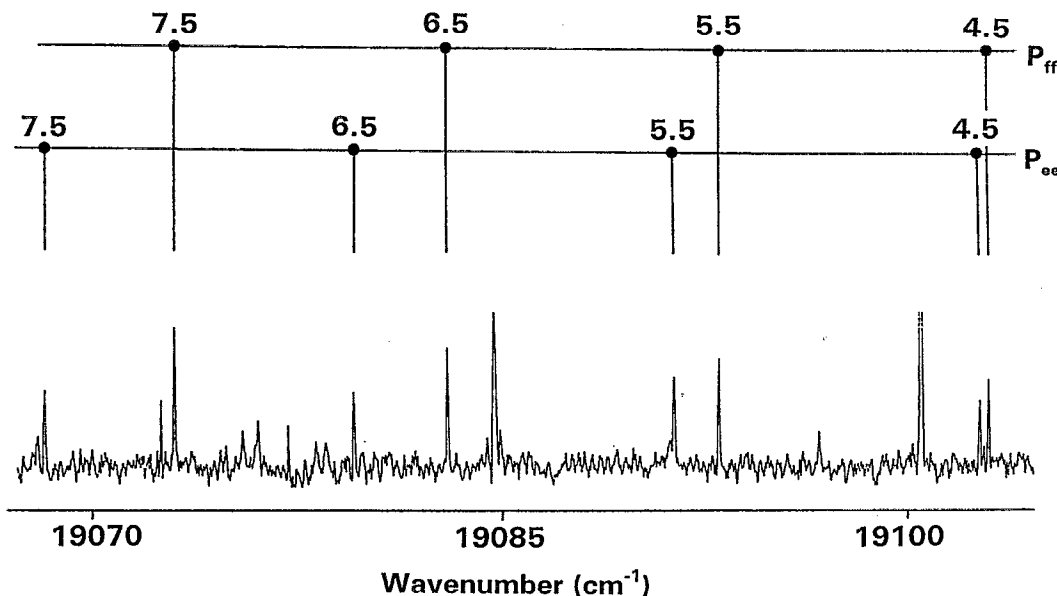

FIG. 3. A portion of the 0–0 band of the $[19.1]3/2-X\ ^2\Delta_{3/2}$ transition of HfD.

TABLE III. Observed transition wave numbers (in cm^{-1}) of the $[19.1]3/2-X\ ^2\Delta_{3/2}$ system of HfD.

J	R_{ee}	Obs.-calc.[a]	P_{ee}	Obs.-calc.[a]	R_{ff}	Obs.-calc.	P_{ff}	Obs.-calc.
				0–0 band				
1.5	19 146.138	0.012			19 146.138	−0.001		
2.5	19 150.981[b]	0.019	19 121.115[b]	0.026	19 150.981	−0.013	19 121.115[b]	0.022
3.5	19 155.732	−0.001	19 115.936	0.013	19 155.789	−0.007	19 115.936	−0.001
4.5	19 160.440	0.007	19 110.724[b]	0.021	19 160.528	−0.013	19 110.724	−0.011
5.5	19 165.052	−0.004	19 105.431	0.005	19 165.237	0.009	19 105.494	0.006
6.5	19 169.591	−0.005	19 100.092	0.004	19 169.860	0.007	19 100.190	−0.006
7.5	19 174.039	−0.008	19 094.689	0.002	19 174.419	0.006	19 094.857	−0.001
8.5	19 178.398	−0.004	19 089.220	0.001	19 178.923[b]	0.020	19 089.474	−0.001
9.5	19 182.651	−0.000	19 083.672	−0.006	19 183.322	0.005	19 084.043	0.000
10.5	19 186.787	0.000	19 078.057	−0.002	19 187.653	0.001	19 078.557	−0.003
11.5	19 190.800	−0.000	19 072.357	−0.001	19 191.899	−0.001	19 073.024	−0.001
12.5	19 194.684	0.004	19 066.565	−0.002			19 067.427	−0.005
13.5	19 198.422	0.005	19 060.682	0.004	19 200.053[c]	−0.053		
14.5	19 201.988	−0.012	19 054.689	0.006	19 204.102[c]	0.052		
15.5	19 205.397[c]	−0.018	19 048.581	0.006	19 207.677[c]	−0.199	19 050.202[c]	−0.062
16.5	19 208.524[c]	−0.128	19 042.344	0.001			19 044.452[c]	0.059
17.5			19 035.961[c]	−0.015			19 038.235[c]	−0.201
18.5			19 029.333[c]	−0.132			19 031.811[c]	−0.574
19.5			19 022.526[c]	−0.270				

[a]Observed–calculated line positions.
[b]Perturbed transitions not included in the final fit.
[c]Blended lines (see the text for details).

ponents are perturbed and were excluded from the final fit. The ground state combination differences up to $\Delta_2 F''(18.5)$ for the perturbed transitions were included in the final fit. The observed wave numbers for the $[19.1]3/2-X\ ^2\Delta_{3/2}$ transition of HfD are provided in Table III.

The observed wave numbers of the different bands were initially fitted separately as Hund's case (c) states using the expression

$$F(J) = T_v + BJ(J+1) - D[J(J+1)]^2 + H[J(J+1)]^3$$
$$\pm 1/2[p(J+1/2) + p_D(J+1/2)^3 + p_H(J+1/2)^5].$$

In the final fit, the transitions of HfH having a common ground state were combined together in order to obtain a single set of constants for $v=0$ of the $X\ ^2\Delta_{3/2}$ state.

IV. RESULTS AND DISCUSSION

The molecular constants obtained for HfH and HfD are provided in Tables IV and V, respectively. The rotational constants of Table IV provide the following equilibrium constants: $B_e = 5.019\ 11(8)$ cm^{-1} and $\alpha_e = 0.120\ 25(11)$ cm^{-1} for the ground state of HfH. Using the usual isotopic relationships[26] $B_e^i = \rho^2 B_e$ and $\alpha_e^i = \rho^3 \alpha_e$, the B_e and α_e values for HfD were predicted to be 2.525 61 and 0.042 92 cm^{-1}, respectively. This provides a predicted B_0 value for HfD of 2.504 15 cm^{-1}, in agreement with our experimental value of 2.517 749(72) cm^{-1}. HfD does not have a determinable Ω-doubling constant in the ground state and this parameter is very small $[p_D = -6.05(15) \times 10^{-5}\ cm^{-1}]$ for HfH. This is consistent with our assignment of the ground state of

TABLE IV. Rotational constants (in cm^{-1}) obtained for the $[14.5]3/2-X\ ^2\Delta_{3/2}$ and $[19.1]3/2-X\ ^2\Delta_{3/2}$ electronic transitions of HfH. The numbers in parentheses are one standard deviation in the last digit.

Constants	$X\ ^2\Delta_{3/2}$		$[14.5]3/2$		$[19.1]3/2$
	$v=0$	$v=1$	$v=0$	$v=1$	$v=0$
T_v	0.0	x[a]	14 494.801 0(24)	$x+14$ 335.400 3(56)	19 147.333 5(61)
B_v	4.958 981(52)	4.838 73(10)	4.801 25(15)	4.712 52(46)	4.899 76(31)
$10^4 \times D_v$	1.745 2(30)	1.582 8(71)	2.510(18)	2.33(11)	0.551(66)
$10^7 \times H_v$	0.041 2(15)	0.041 2[b]	0.86(16)	−9.88(78)	−3.58(35)
p_v	...	...	...	...	−0.4542(40)
$10^3 \times p_{D_v}$	−0.060 5(15)	−0.927(22)	2.244(28)	0.226(64)	−5.40(10)
$10^5 \times p_{H_v}$	...	0.287(16)	−0.212(44)	2.21(19)	1.559(54)
$10^7 \times p_{L_v}$	...	...	−0.0422(78)	−1.01(15)	...

[a]The vibrational interval in the ground state is undetermined due to lack of off-diagonal vibrational bands.
[b]Fixed to the value for the $v=0$ vibrational level.

TABLE V. Rotational constants (in cm^{-1}) obtained from the [19.1]3/2$-X$ $^2\Delta_{3/2}$ electronic transitions of HfD. The numbers in parentheses are one standard deviation in the last digit.

Constants	X $^2\Delta_{3/2}$ $v=0$	[19.1]3/2 $v=0$
T_v	0.0	19 133.774 0(21)
B_v	2.517 749(72)	2.491 941(64)
$10^5 \times D_v$	4.610(44)	6.872(24)
$10^9 \times H_v$	2.84(78)	...
$10^4 \times p_{D_v}$	...	−5.006(14)

HfH and HfD as a $^2\Delta_{3/2}$ state. Almost the entire Ω-doubling splitting in the rotational lines arises from the relatively large Ω doubling in the excited states, consistent with substantial $^2\Pi_{3/2}$ character. For a $^2\Pi_{3/2}$ state, the leading term in the Ω-doubling expression is p_D, as observed for the [14.5]3/2 state. The [19.1]3/2 state is clearly anomalous because a large value for p is also necessary. Balasubramanian and Das[6] have predicted strong $^2\Pi-X$ $^2\Delta$, $^2\Delta-X$ $^2\Delta$, and $^2\Pi-X$ $^2\Delta$ transitions at 15 000, 17 000, and 19 000 cm^{-1}, respectively. As mentioned by Balasubramanian and Das[6] in their paper, these values could be in error by as much as 5000 cm^{-1} due to the neglect of spin–spin coupling in their calculations. Although these predictions are very suggestive, it is not possible to assign definitely the observed excited states of HfH to the excited electronic configurations proposed by these authors. The excited states of HfH are mixtures of many configurations.[6]

The rotational constants obtained from the fit were used to evaluate the equilibrium bond lengths in the ground X $^2\Delta$ and the excited [14.5]3/2 states of HfH (Table VI). The observed ground state bond length of 1.830 691(15) Å agrees well with the theoretical value of 1.854 Å obtained by Balasubramanian and Das.[6]

The X $^2\Delta$ state of HfH arises from the $1\sigma^2 2\sigma^2 1\delta^1$ electronic configuration.[6] It is interesting to note that this regular state is the early transition metal analog of the inverted X $^2\Delta$ state of the late transition metal hydride PtH.[20]

In the absence of $\Delta v \neq 0$ bands associated with any of the observed transitions, we are unable to determine the vibrational constants for the electronic states. The [14.5]3/2$-X$ $^2\Delta_{3/2}$ transition of HfD was not observed because it is weaker than the green bands, and the HfD transitions were not as strong as those of HfH.

TABLE VI. Equilibrium constants (in cm^{-1}) for the X $^2\Delta_{3/2}$ and the [14.5]3/2 electronic states of HfH.

Constants	X $^2\Delta_{3/2}$	(14.5)3/2
B_e	5.019 11(8)	4.845 62(28)
α_e	0.120 25(11)	0.088 73(48)
r_e(Å)	1.830 691(15)	1.863 191(53)

V. CONCLUSION

Two electronic transitions for HfH and one for HfD have been observed in the visible region by Fourier transform spectroscopy. The ground state has been identified as a $^2\Delta$ state consistent with the theoretical predictions of Balasubramanian and Das.[6] The excited states, with larger Ω doubling, most probably originate from $^2\Pi$ states with $\Omega'=3/2$. The excited states are involved in several perturbations with unidentified close-lying electronic states. The present observation is the first detection of the HfH and the HfD molecules in the gas phase.

ACKNOWLEDGMENTS

[1] C. J. Cheetham and R. F. Barrow, Adv. High Temp. Chem. 1, 7 (1967).
[2] R. E. Smith, Proc. R. Soc. London Ser. A 332, 113 (1973).
[3] P. R. Scott and W. G. Richard, Chem. Soc. Spec. Period. Rep. 4, 70 (1976).
[4] A. D. McLean, J. Chem. Phys. 79, 3392 (1983).
[5] M. Krauss and W. J. Stevens, J. Chem. Phys. 82, 5584 (1985).
[6] K. Balasubramanian and K. K. Das, J. Mol. Spectrosc. 145, 142 (1991).
[7] J. A. Martinho and J. L. Beauchamp, Chem. Rev. 90, 629 (1990).
[8] J. B. Schilling, W. A. Goddard III, and J. L. Beauchamp, J. Am. Chem. Soc. 108, 582 (1986); 109, 5573 (1987).
[9] P. B. Armentrout and J. L. Beauchamp, Acc. Chem. Res. 22, 315 (1989).
[10] L. B. Knight and W. Weltner, J. Mol. Spectrosc. 40, 317 (1971).
[11] A. Lagerqvist, H. Neuhaus, and R. Scullman, Proc. Phys. Soc. 83, 498 (1964).
[12] J. Li and K. Balasubramanian, J. Chem. Phys. 94, 4415 (1990).
[13] J. Z. Wang and K. Balasubramanian, J. Mol. Spectrosc. 138, 204 (1989).
[14] K. Balasubramanian and D. W. Liao, J. Chem. Phys. 88, 317 (1988).
[15] T. D. Varberg, R. W. Field, and A. J. Merer, J. Chem. Phys. 92, 7123 (1990).
[16] O. Engvold, H. Wöhl, and J. W. Brault, Astron. Astrophys. Suppl. Ser. 42, 209 (1980).
[17] B. Lindgren and G. S. Olofsson, Astron. Astrophys. 84, 300 (1990).
[18] K. Bernard and R. Bacis, Can. J. Phys. 54, 1509 (1976).
[19] B. Caving and R. Scullman, Phys. Scr. 9, 33 (1984) (and references therein).
[20] M. C. McCarthy, R. W. Field, R. Engleman, and P. F. Bernath, J. Mol. Spectrosc. 158, 208 (1993).
[21] U. Ringström, Nature 198, 981 (1963); Ark. Fys. 27, 277 (1964), and references therein.
[22] J. F. Garvey and A. Kuppermann, J. Phys. Chem. 92, 4583 (1988).
[23] B. A. Palmer and R. Engleman, Atlas of Thorium Spectrum (Los Alamos National Laboratory, Los Alamos, NM, 1983).
[24] C. Linton, M. Dulick, R. W. Field, P. Carette, P. C. Leyland, and R. F. Barrow, J. Mol. Spectrosc. 102, 491 (1983).
[25] E. J. Friedman-Hill and R. W. Field, J. Mol. Spectrosc. 155, 259 (1992).
[26] G. Herzberg, Spectra of Diatomic Molecules (Van Nostrand, New York, 1950).