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Intracavity laser absorption spectroscopy of platinum fluoride, PtF

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ABSTRACT

Two vibrational bands of an electronic transition of PtF occurring at 11 940 cm^{-1} and 12 496 cm^{-1} were recorded and analyzed. These transitions are identified as the (0,0) and (1,0) bands of an [11.9] $\Omega = 3/2$ – $X\Omega = 3/2$ electronic transition. Gas phase PtF was produced in a copper hollow cathode lined with platinum foil using a trace amount of SF_6, and the spectrum was recorded at Doppler resolution by intracavity laser absorption spectroscopy. This work represents the first published spectroscopic data on PtF. Molecular constants for the ground and excited electronic states are presented.

1. Introduction

Little information is known about the spectroscopic properties of PtF. Theoretical studies by Liu and Franke [1] predicted values for the spectroscopic parameters T_e, $\grave{u}_e$ and r_e as well as the dissociation energy for the first three electronic states of PtF. The ground state for PtF is predicted to be $X^2\Pi_{3/2}$, with $r_e = 1.873$ Å, $\omega_e = 600$ cm^{-1}, and $D_e = 4.2$ eV. Recently we located a conference abstract from Okabayashi et al. [2] reporting observation of the ground state of four PtF isotopologues by microwave spectroscopy. This abstract included a small portion of the microwave spectrum showing the $R_f(13.5)$ rotational lines of ^{194}PtF which are split by the ^{19}F nucleus ($I = ½$). Additionally they reported that the ^{195}PtF spectrum shows further splitting due to the ^{195}Pt nucleus ($I = ½$). The abstract included the bond length obtained from their analysis, $r_0 = 1.874$ Å, and an estimated vibrational frequency, $\omega_e = 580$ cm^{-1}, which are in very good agreement with the predictions of Liu and Franke [1].

In our work, two vibrational bands of a new electronic transition of PtF are reported: red-degraded bandheads are observed at 11 940 cm^{-1} and 12 496 cm^{-1}. Lines for the three main isotopologues ^{194}PtF, ^{195}PtF, and ^{196}PtF were observed for both spectral bands. We have identified the transitions as the (0,0) and (1,0) bands of a [11.9] $\Omega = 3/2$ – $X^2\Pi_{3/2}$ electronic transition. Molecular parameters for PtF are reported for each state involved in the transition.

2. Experimental details

The intracavity laser absorption spectrometer has been described previously [3–6]. Briefly, PtF molecules were produced in a hollow cathode sputter source using a Pt-lined copper cathode. An applied potential produced a discharge current of 0.40–0.80 A in 1.40–1.60 Torr of Argon. A trace amount of SF_6 was introduced and allowed to react with the platinum vapor sputtered from the cathode. Spectra are recorded as a series of overlapping ~6 cm^{-1} wide spectral segments. The generation time varied from 100 to 130 μs which results in an effective pathlength of 0.92–1.2 km for a 50 mm long cathode. Calibration is accomplished by alternatively measuring the spectrum of the intracavity PtF species and an I_2 absorption spectrum recorded from an extra-cavity iodine cell heated to approximately 600 °C. The widely used Iodine Atlas [7] served as reference. Peak positions are determined from the zero crossing-points of the first derivative spectra using Savitzky–Golay polynomial smoothing. The procedure enables the positions for isolated, unblended lines to be determined to an accuracy of better than ±0.005 cm^{-1}.

3. Results and discussion

Two vibrational bands of a new electronic transition of PtF were observed in absorption using intracavity laser spectroscopy. Red-degraded bandheads were recorded at 11 940 cm^{-1} and 12 496 cm^{-1}. The 11 940 cm^{-1} band of PtF was observed several months prior to the second band. A portion of the PtF spectrum showing the 11 940 cm^{-1} bandhead is shown in Fig. 1. Four branches were readily identified in the 11 940 cm^{-1} spectrum: two P-branches and two R-branches. As J increased, the line width slowly increased and eventually, for $J'' > 25.5$, each line split into three separate components. This rotational structure is consistent with peaks due to the three major PtF isotopologues in a (0,0) vibrational band. Since the ground state is predicted to have $\Omega = 3/2$ symmetry [1], the transition at 11 940 cm^{-1} was identified as the (0,0) band of an $\Omega = 3/2$ – $X^2\Pi_{3/2}$ electronic transition of PtF.

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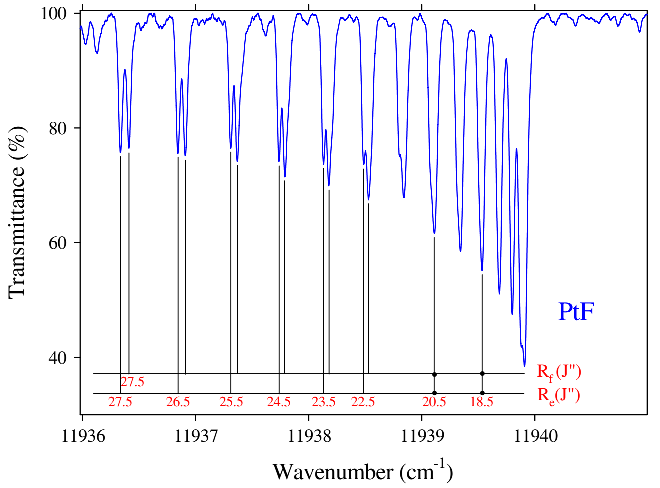

Fig. 1. A portion of the PtF spectrum near the (0,0) bandhead at 11 940 cm^{-1} recorded by intracavity laser absorption spectroscopy.

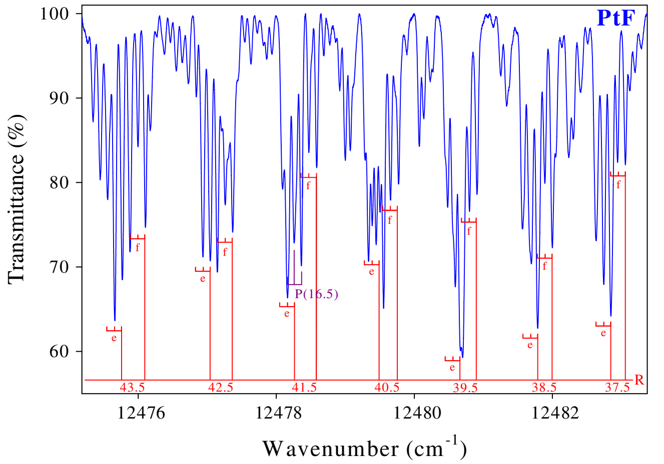

Fig. 2. A portion of the (1,0) band spectrum of PtF near 12 479 cm^{-1} recorded by intracavity laser absorption spectroscopy.

Table 1
Line positions, assignments and residuals for the (0,0) band of the [11.9] $\Omega = 3/2 - X^2\Pi_{3/2}$ electronic transition of ^{194}PtF (in cm^{-1}).

J''	P_e	o–c	P_f	o–c	R_e	o–c	R_f	o–c
3	11934.066	−0.010	11934.066	−0.010				
4	11933.378	−0.009	11933.378	−0.010				
5	11932.657	−0.003	11932.657	−0.004				
6	11931.895	0.000	11931.895	−0.001				
7	11931.093	0.003	11931.093	0.000				
8	11930.251	0.003	11930.251	0.000				
9	11929.371	0.004	11929.371	0.000				
10	11928.459	0.011	11928.459	0.005				
11	11927.506	0.016	11927.506	0.009				
12	11926.507	0.014	11926.507	0.005				
13	11925.466	0.008	11925.466	−0.003				
14	11924.394	0.009	11924.394	−0.004	11939.907	0.041*	11939.907	0.027*
15	11923.283	0.011	11923.283	−0.005	11939.799	0.014	11939.799	−0.002
16	11922.129	0.007	11922.142	0.000	11939.685	0.020	11939.685	0.000
17	11920.938	0.005	11920.961	0.004	11939.532	0.026*	11939.532	0.003
18	11919.710	0.004	11919.725	−0.007	11939.338	0.029*	11939.338	0.001
19	11918.442	0.002	11918.459	−0.011	11939.109	0.036*	11939.109	0.004
20	11917.142	0.006	11917.159	−0.012	11938.838	0.040*	11938.838	0.004
21	11915.793	0.001	11915.820	−0.012	11938.489	0.005	11938.527	0.001
22	11914.417	0.007	11914.468	0.011	11938.134	0.002	11938.178	−0.000
23	11913.001	0.012	11913.059	0.016	11937.743	0.003	11937.794	0.001
24	11911.541	0.011	11911.584	−0.006	11937.306	−0.002	11937.364	−0.004
25	11910.045	0.013	11910.118	0.017	11936.837	−0.001	11936.902	−0.004
26	11908.504	0.007	11908.580	0.009	11936.327	−0.002	11936.402	−0.003
27	11906.925	0.004	11907.005	0.000	11935.778	−0.003	11935.863	−0.002
28	11905.324	0.017	11905.400	0.000	11935.192	−0.002	11935.284	−0.003
29	11903.677	0.023	11903.756	−0.000	11934.566	−0.001	11934.671	0.000
30	11901.982	0.019	11902.072	−0.002	11933.898	−0.003	11934.015	−0.000
31	11900.227	−0.004	11900.344	−0.012	11933.194	−0.002	11933.320	−0.001
32	11898.458	−0.004	11898.586	−0.012	11932.454	0.001	11932.588	−0.001
33	11896.655	0.001	11896.787	−0.015	11931.670	0.000	11931.815	−0.002
34	11894.806	−0.001	11894.968	−0.000	11930.845	−0.000	11931.007	−0.000
35	11892.932	0.011	11893.102	0.005	11929.982	−0.001	11930.158	−0.001
36	11891.050	0.053*	11891.200	0.013*	11929.079	−0.001	11929.271	−0.000
37	11889.150	0.118*	11889.300	0.061*	11928.146	0.006	11928.354	0.007
38	11887.032	0.003	11887.246	−0.005	11927.163	0.005	11927.387	0.005
39	11884.984	−0.001	11885.212	−0.013	11926.141	0.004	11926.384	0.006
40	11882.897	−0.006	11883.149	−0.013	11925.074	−0.001	11925.336	0.001
41	11880.784	0.001	11881.055	−0.006	11923.972	−0.003	11924.252	−0.000
42	11878.619	−0.003	11878.907	−0.013	11922.848	0.013	11923.175	0.042
43	11876.421	−0.002	11876.732	−0.009	11921.658	0.004	11921.978	0.005
44	11874.184	0.000	11874.511	−0.014	11920.441	0.008	11920.780	0.005
45	11871.899	−0.006	11872.250	−0.019	11919.167	−0.004	11919.535	−0.001
46	11869.579	−0.007	11869.957	−0.018	11917.864	−0.006	11918.256	−0.003
47					11916.518	−0.011	11916.940	−0.003
48					11915.140	−0.008	11915.584	−0.003
49					11913.725	−0.001	11914.195	0.002