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Electronic transitions of platinum monoboride

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The electronic transition spectrum of platinum monoboride (PtB) radical has been observed for the first time. Using laser vaporization/reaction free jet expansion and laser induced fluorescence spectroscopy, the optical spectrum of PtB in the visible region between 455 and 520 nm has been studied. Gas-phase PtB molecule was produced by the reaction of diborane (B_2H_6) seeded in argon and laser ablated platinum atom. Seven vibrational bands of the $Pt^{11}B$ radical have been recorded and analyzed. The observation of Pt isotopic molecules and the $Pt^{10}B$ isotope confirmed the carrier of the bands. Two different transition systems, namely: the [20.2]3/2–$X^2\Sigma^+$ and the [21.2]1/2–$X^2\Sigma^+$ systems were identified. PtB was determined to have an $X^2\Sigma^+$ ground state and the bond length, r_e, was determined to be 1.741 Å. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4754157]

I. INTRODUCTION

Platinum and its compounds are extremely important catalysts for hydrogenation, dehydrogenation, reductive alkylation, hydrogenation of carbonyls and selective hydrogenation of nitro compounds.[1] Despite the fact that many complex reactions involving Pt are very well known, fundamental knowledge of simple diatomic molecules formed from Pt and main group elements are not ready available and only a few of this class of molecules have been studied. For the diatomic Pt-containing molecules with the first row main group elements, gas-phase experimental work has only been reported for PtC,[2,3] PtN,[4,5] and PtO[6] molecules. For PtB and PtF, however, nothing is experimentally known. Theoretically, a computational study using density functional theory has been performed by Kalamse *et al.*[7] in which they predicted spectroscopic properties including ground state symmetry, bond length, and vibrational frequency of 5*d* transition metal (TM) mononitrides and monoborides. In order to understand better the reactivity of Pt compounds, it is essential to learn about their molecular and electronic properties. The analysis of optical spectra recorded under conditions sufficient to resolve rotational fine structure and magnetic hyperfine structure can provide such information.

We have been studying TM monoborides and are interested in their molecular and electronic structure. In this work, we report the analysis of [20.2]3/2–$X^2\Sigma^+$ and [21.2]1/2–$X^2\Sigma^+$ systems of the PtB molecule recorded between the spectral region 455 and 520 nm using the technique of laser vaporization/reaction free jet expansion and laser induced fluorescence (LIF) spectroscopy. Spectra of isotopic molecules were observed, which confirmed the carrier of the spectrum. Molecular constants for the [21.2]1/2, [20.2]3/2, and $X^2\Sigma^+$ states are reported. A molecular orbital (MO) energy level diagram has been used to understand the observed electronic states.

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II. EXPERIMENT

The laser vaporization/reaction assembly with free jet expansion setup and LIF spectrometer used in this work has been described in Refs. 8 and 9. A brief description of the relevant experimental conditions for obtaining the PtB spectrum is provided here. Pulses from a Nd:YAG laser with wavelength 532 nm and energy 5–6 mJ, were focused onto the surface of a platinum rod to generate platinum atoms. The PtB molecules were formed from the reaction of platinum atoms with 0.5% diborane (B_2H_6) seeded in argon. A pulsed optical parametric oscillator (OPO) laser pumped by another Nd:YAG laser with wavelength set to 355 nm produced tunable output in the ultraviolet and visible regions, which was used to excite the jet cooled PtB molecule. The energy output from the OPO laser was typically about 10 mJ per pulse, its wavelength was measured by a wavelength meter with an accuracy around ± 0.02 cm^{-1}, and the laser linewidth was estimated to be 0.07 cm^{-1}. The emitted light was directed into a 0.25 m monochromator and subsequently detected by a photomultiplier tube (PMT). The monochromator was used for recording the wavelength resolved fluorescence spectrum, and also acted as an optical filter in recording the LIF spectrum. The PMT output was fed into a fast oscilloscope for averaging and storage. Due to insufficient resolution to resolve isotopic transition lines of the Pt atom, molecular transition lines are often crowded together and the linewidth observed was much worse than 0.07 cm^{-1}.

III. RESULTS AND DISCUSSION

A. Low-resolution broadband spectrum

The LIF spectrum of PtB in the visible region between 455 and 520 nm was recorded. Figure 1 is a broadband scan of the PtB spectrum, showing two electronic transition band systems, namely, the [20.2]3/2–$X^2\Sigma^+$ and the [21.2]1/2–$X^2\Sigma^+$ systems. Seven vibrational bands were recorded for these two systems, summarized in Figure 2. Due to the fact that platinum has six isotopes and four of them are abundant [^{194}Pt

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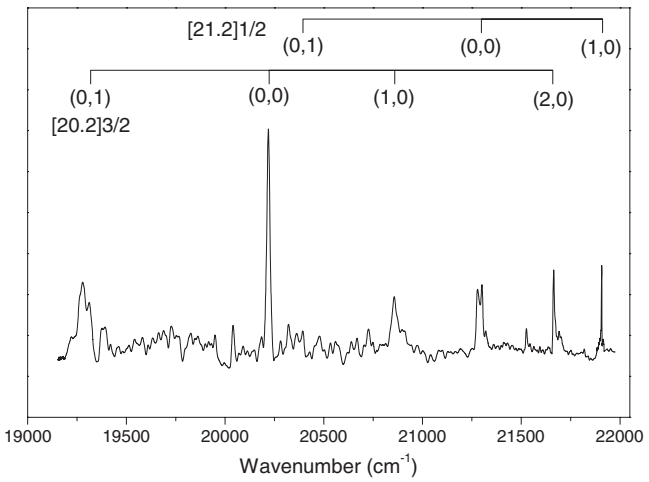

FIG. 1. Low-resolution LIF spectrum of PtB.

(32.9%), ^{195}Pt (33.8%), ^{196}Pt (25.3%), ^{198}Pt (7.2%)], these mass differences cause the rotational constants of each isotope to change very slightly and, hence, the rotational energy; consequently, the observed spectrum appears to be more complicated. Spectra of Pt and B isotopic species were observed, which provides direct evidence that the carrier of the spectrum is PtB. It is well known that the platinum atom has large spin–orbit interactions (a large ζ parameter:[10] ζ_{5d}(Pt) = 4221 cm^{-1} and the energy gaps between the ($5d^96s^1$) ^{3}D term are 775.9 and 10132.0 cm^{-1}, respectively, for the $^3D_2$–$^3D_3$ and $^3D_1$–$^3D_3$ separations[11]), so that the S and Λ of the excited states of PtB molecule are no longer good quantum number. The upper states conform to the Hund's case (c) coupling scheme; it is more appropriate to label or describe individual spin component using its respective Ω value.[12] The branches fit the pattern of a $^2\Pi_\Omega$–$^2\Sigma$ transition, where Ω = 1/2 or 3/2. As the excited states of PtB are undoubtedly highly mixed by the spin–orbit interactions, it is important to note that the same pattern would be expected for any Ω = 1/2 or 3/2 upper state that gains its intensity by spin–orbit mixing with a $^2\Pi_{1/2}$ or $^2\Pi_{3/2}$ state. In such situation, the branches could be identified and labeled as if the upper states were pure $^2\Pi_{1/2}$ or $^2\Pi_{3/2}$ states. A list of measured transition lines of the observed [20.2]3/2–$X^2\Sigma^+$ and [21.2]1/2–$X^2\Sigma^+$ systems is available from the supplementary material.[13]

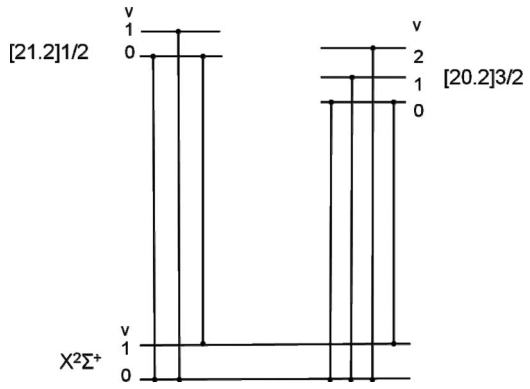

FIG. 2. Observed vibrational transitions of PtB.

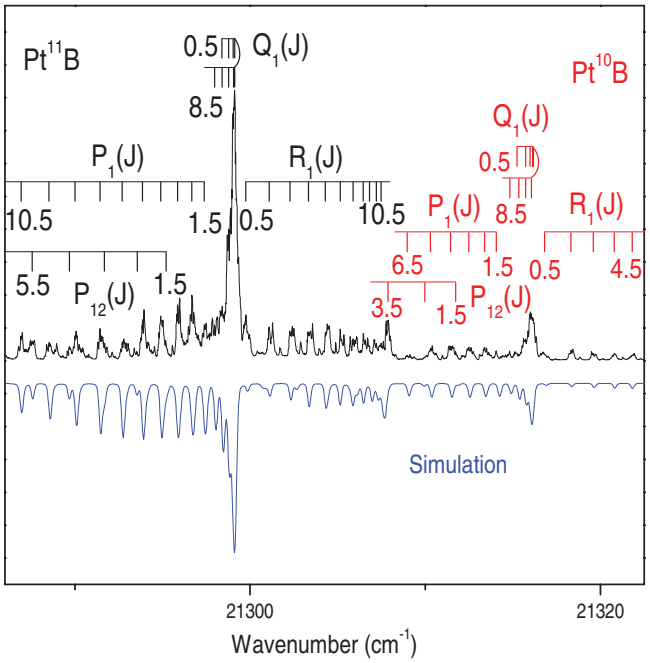

FIG. 3. The (0, 0) band of the [21.2]1/2–$X^2\Sigma^+$ transition of PtB.

B. [21.2]1/2–$X^2\Sigma^+$ system

The LIF spectrum of the (0, 0), (1, 0), and (0, 1) bands were recorded. Figure 3 shows the band head region of the (0, 0) of the [21.2]1/2–$X^2\Sigma^+$ system of PtB. Four branches were identified and they fit the pattern of an Ω = 1/2–$X^2\Sigma^+$ transition.[12] In order to further confirm the observed band belongs to the Ω = 1/2–$X^2\Sigma^+$ transition, we compare this band with a simulated spectrum. A $^2\Pi_{1/2}$–$X^2\Sigma^+$ transition spectrum was simulated using the PGOPHER software[14] with a temperature of 50 K, and a spectral linewidth broadened to 0.25 cm^{-1}. As shown in Figure 3, there is very good agreement between the observed and the simulated spectra. Figure 3 also shows the isotopic transition lines of the Pt isotopes are crowded together, which effectively makes the transition line width wider than normal. At about 16 cm^{-1} to the higher frequency side of the Pt^{11}B band, we found the same transition band of the Pt^{10}B isotope. The different in intensity of these two bands fit the 4:1 ratio of the abundance of ^{11}B:^{10}B. The assignment of transition lines is relatively easily; other vibrational bands have also been rotationally analyzed. The standard labeling of the branches is used, as if the upper state were a pure $^2\Pi_{1/2}$ state. Thus, there are six branches, two pairs of which are unresolved, giving branches, labeled as P_{12}; $P_1 + Q_{12}$ (not resolved from one another, due to the small value of the ground state spin-rotation parameter, γ, and of the Λ- doubling in the upper state); $Q_1 + R_{12}$ (also not resolved); and R_1. In order to simplify the labels in Figure 3, the unresolved double branches are labeled as P_1 (instead of $P_1 + Q_{12}$) and Q_1 (instead of $Q_1 + R_{12}$).

The molecular Hamiltonian and matrix elements for a $^2\Sigma^+$ state in case (b) coupling scheme has been discussed by Amiot *et al.*,[15] and was used to calculate the energy levels of a $^2\Sigma^+$ state

$$\hat{H} = B\hat{R}^2 - D\hat{R}^4 + \gamma\hat{R}\cdot\hat{S}, \quad (1)$$

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TABLE I. Molecular constants for [20.2]3/2, [21.2]1/2, and the $X^2\Sigma^+$ states of $Pt^{11}B$ and $Pt^{10}B$ (cm^{-1}).[a]

		$Pt^{11}B$			$Pt^{10}B$		
State	v	T	B_{eff}		T	B_{eff}	
[21.2]1/2	1	21911.99(1)	0.4814(2)				
	0	21298.06(1)	0.4699(3)		21314.94(1)	0.5152(9) [0.5144][c]	
[20.2]3/2	2	21659.86(2)	0.4695(3)				
	1	20858.68(2)	0.4843(3)				
	0	20222.43(1)	0.4995(3)				
		T	B	γ	T	B	γ
$X^2\Sigma^+$	1	903.60(1)	0.5245(3)	0.007[b]			
	0	0.00	0.5274(2)	0.007(3)	0.0	0.5800(9) [0.5773][c]	0.007[b]

[a]Error in parentheses are one standard deviation in unit of the last significant figure quoted.
[b]Value fixed in the least-squares fit.
[c]Value calculated from isotopic relationships using $Pt^{11}B$.

where B and D are, respectively, the rotational and centrifugal distortion constants, and γ is the spin-rotation constant. $\hat{R}$ and $\hat{S}$ are the rotational and spin angular momentum operators, respectively. For the energy level expressions of the upper $\Omega' = 1/2$ state, the rotational energy levels were calculated using the expression[11]

$$T'(J) = T_o + B_{eff}J(J+1) - D_{eff}[J(J+1)]^2, \qquad (2)$$

where B_{eff} and D_{eff} are the effective rotational and centrifugal distortion constants for $\Omega' = 1/2$ state. Molecular constants for the [21.2]1/2, and $X^2\Sigma^+$ states were retrieved using a least squares fitting program. The transition lines of observed vibrational bands were fitted in two stages. Initially, each band was fitted individually and, in the final stage, all bands were merged together in a single fit. With our relatively low temperature molecular source, the highest J value observed was 17.5, so the centrifugal distortion constant D was set to zero in the fit. The obtained molecular constants for the $Pt^{11}B$ are listed in Table I. The equilibrium molecular constants obtained are given in Table II. The vibrational separation, $\Delta G_{1/2}$, for the [21.2]1/2 and the $X^2\Sigma^+$ states was determined to be 613.93 and 903.60 cm^{-1}, respectively. The bond length r_o determined for the [21.2]1/2 and the $X^2\Sigma^+$ states are, respectively, 1.856 Å and 1.752 Å. Table I also presents the observed molecular constants for the $Pt^{10}B$ isotope; the calculated values from the isotopic relationship using $Pt^{11}B$ are also included.[12] The agreement of the isotopic molecular constants is very good, which confirms unambiguously that the carry of the spectrum is PtB. The residuals from the least squares fit of the lines of the observed [20.2]3/2–$X^2\Sigma^+$ system is also available in the supplementary material.[13]

TABLE II. Equilibrium molecular constants for $Pt^{11}B$ (cm^{-1}).

State	Parameter	$Pt^{11}B$
[21.2]1/2	T_o	21298.06(1)
	$\Delta G_{1/2}$	613.9(2)
	B_e	0.4642(5)
	r_e (Å)	1.868(5)
	α_e	−0.0115(5)
[20.2]3/2[a]	T_o	20222.43(1)
	$\Delta G_{1/2}$	636.26(2)
	$\Delta G_{3/2}$	801.18(2)
	B_o	0.4995(3)
	r_o (Å)	1.800(3)
$X^2\Sigma^+$	$\Delta G_{1/2}$	903.60(1)
	B_e	0.5342(6)
	r_e (Å)	1.741(6)
	α_e	0.0173(6)
	γ_o	0.007(3)

[a]This state is perturbed, molecular constants reported are for the v = 0 level.

C. [20.2]3/2–$X^2\Sigma^+$ system

For this transition, we recorded and analyzed the (0, 0), (1, 0), (2, 0), and (0, 1) bands.

The observed branches are quite similar to the [21.2]1/2–$X^2\Sigma^+$ system, but the branches are labeled as P_2, Q_2, R_2, and R_{21}. Figure 4 depicts the (0, 0) band of this transition, which shows clearly all these branches. The observation of $P_2(2.5)$ confirms that the upper state has $\Omega' = 3/2$. The measured transition lines of an individual band were fitted initially and eventually all bands were merged together in the final fit. The molecular constants determined for the

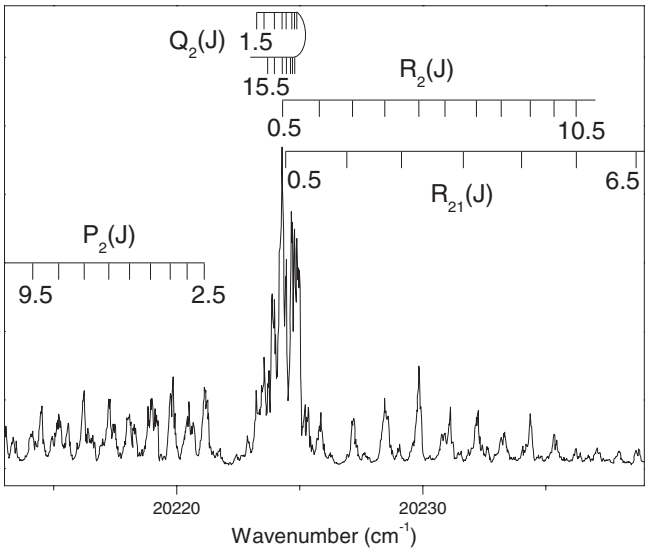

FIG. 4. The (0, 0) band of the [20.2]3/2–$X^2\Sigma^+$ transition of PtB.

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[20.2]3/2 are also listed in Table I. For the [20.2]3/2 state, the vibrational separations $\Delta G_{1/2}$ and $\Delta G_{3/2}$ measured are 636.26 and 801.18 cm^{-1}, respectively. When compared with the vibrational separation of [21.2]1/2, it is quite likely that the v = 2 level is perturbed, however, it is difficult at this stage to fully understand the origin of this perturbation.

D. Electronic configurations and electronic states

Using a MO energy level diagram, we could examine the observed transitions in this work.[15] The MO energy levels are formed from the 6*s* and 5*d* atomic orbitals (AOs) of the Pt atom and the 2p AO of the B atom. The lowest energy 1σ and 1π MOs and the higher energy 3σ and 2π MOs are the bonding and anti-bonding orbitals formed from the Pt $5d\sigma$ and $5d\pi$ AOs and the main group B $2p$ AO. The 2σ MO is mostly the Pt 6*s* AO. The 1δ MO is the Pt $5d\delta$ AO, because there is no other δ symmetry orbital nearby. The PtC molecule has a $X^1\Sigma^+$ ground state,[2] and the electronic configuration is $(1\sigma)^2(1\pi)^4(1\delta)^4(2\sigma)^2$. Since PtC has one more electron than the PtB molecule, therefore, if one electron is taken away from the outer most orbital (i.e., 2σ orbital), the ground state of PtB would be

$$(1\sigma)^2(1\pi)^4(1\delta)^4(2\sigma)^1 \rightarrow X^2\Sigma^+ \quad (3)$$

and low-lying electronic states can be obtained by promoting one electron from the ground configuration to higher energy MOs; they are

$$(1\sigma)^2(1\pi)^4(1\delta)^3(2\sigma)^2 \rightarrow {}^2\Delta_i, \quad (4)$$

$$(1\sigma)^2(1\pi)^4(1\delta)^4(2\pi)^1 \rightarrow {}^2\Pi, \quad (5)$$

$$(1\sigma)^2(1\pi)^4(1\delta)^4(3\sigma)^1 \rightarrow {}^2\Sigma^+, \quad (6)$$

$$(1\sigma)^2(1\pi)^4(1\delta)^3(2\sigma)^1(2\pi)^1 \rightarrow {}^2\Pi(2), {}^2\Phi(2), {}^4\Pi, {}^4\Phi. \quad (7)$$

From our observed spectrum, there is no doubt that the $X^2\Sigma^+$ state is the ground state of PtB, and it fits very well with the condition that only one unpaired electron is in the 2σ orbital. For the upper state of our observed transitions, due to the situation that there is large spin–orbit mixing of the excited states in PtB, the electronic state are only labeled by their Ω value. It is a difficult task to work out the electronic configurations of upper states giving rise to the observed $\Omega = 1/2$ and 3/2 states; however, a simple consideration of promoting one electron from the ground configuration to various higher energy MOs gives many configurations that could be responsible for the $\Omega = 1/2$ and 3/2 states as indicated in configurations (4), (5), and (7).

Kalamse *et al.*[7] using density functional method based B3LYP functional with LANL2DZ and SDD basis set calculations predicted the ground state bond length and vibrational frequency of PtB to be 906 cm^{-1} and 1.809 Å, respectively. The vibrational separation is in good agreement with our determined value of 903.6 cm^{-1}, but the bond length is very different from our 1.741 Å. In addition, their suggested electronic configuration for the ground state agreed with the configuration (3) discussed above. The relatively small value of the ground state spin-rotation constant, γ, is generally reasonable for diatomic molecules formed from transition metal and main group elements[16] and also indicates that there is no nearby Π state making contributions to this parameter.[10] The large uncertainty in the spin-rotation constant reflects that only low J lines were measured in this work.

TABLE III. Ground state symmetry, bond length (r_o), and vibrational frequency ($\Delta G_{1/2}$) of group 10 monoborides and diatomic Pt molecules.

Molecule	NiB[a]	PdB[b]	PtB	PtC[c]	PtN[d]	PtO[e]
Elec. Conf.	σ^1	σ^1	σ^1	σ^2	$\sigma^2\pi^1$	$\sigma^2\pi^2$
Symmetry	$^2\Sigma^+$	$^2\Sigma^+$	$^2\Sigma^+$	$^1\Sigma^+$	$^2\Pi$	$^3\Sigma^-$
r_o (Å)	1.698	1.728	1.752	1.677	1.686[f]	1.727[g]
$\Delta G_{1/2}$ (cm^{-1})	768.5	753.98	903.6	1041.4	936.7[f]	841.1

[a]Reference 15.
[b]Reference 18.
[c]Reference 3.
[d]Reference 5.
[e]Reference 6.
[f]Value of the $^2\Pi_{1/2}$ component.
[g]Value of the 0^+ component of the $^3\Sigma^-$.

It is interesting to compare the spectroscopic properties of PtB with the neighboring platinum molecules PtC, PtN, and PtO, and to compare PtB with the other group 10 monoborides: NiB,[17,18] PdB.[19,20] Table III compares the ground state symmetry, bond length (r_o) and vibrational frequency ($\Delta G_{1/2}$) of these diatomic transitional metal containing molecules. The group 10 monoborides all have the same ground state configuration ($2\sigma^1$) and therefore, all have $^2\Sigma^+$ ground states. The bond lengths of NiB, PdB, and PtB follow the trend of increasing atomic radius as one moves down the periodic table. The larger vibrational frequency of PtB suggests that the molecule is more tightly bound than NiB and PdB, however. The ground states of the diatomic Pt-containing molecules formed from the $2p$ main group elements follow the orbital filling order expected from the molecular orbital diagram. Among the PtX molecules (X = B, C, N, O), only PtC has a closed shell. This molecule also has the shortest bond length and highest vibrational frequency, consistent with the population of the antibonding 2π orbital in PtN ($2\sigma^2 2\pi^1$) and PtO ($2\sigma^2 2\pi^2$).

We report here the observation of optical spectrum of the PtB molecule for the first time. Our analysis of the rotational structure of the observed spectrum indicated the ground state of PtB is $X^2\Sigma^+$, and the equilibrium bond length, r_e, is determined to be 1.741 Å. Molecular constants for two upper states, namely: [21.2]1/2 and [20.2]3/2 are also reported. A MO energy level diagram has been used to discuss the electronic configurations giving rise to the observed states.

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Colin Western (University of Bristol, UK) for permissions to use the PGOPHER software.

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