

Electronic transitions of platinum monofluoride



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ABSTRACT

Electronic transition spectrum of platinum monofluoride (PtF) between 431 and 560 nm has been investigated using the technique of laser vaporization/reaction with free jet expansion and laser induced fluorescence spectroscopy. Eight vibrational bands had been observed but only six of them were analyzed, they were grouped into four electronic transitions: the $[18.9]^2\Pi_{3/2} - X^2\Pi_{3/2}$, the $[18.9]^2\Pi_{3/2} - [0.04]^2\Delta_{5/2}$, the $[19.9]^2\Delta_{5/2} - X^2\Pi_{3/2}$ and the $[23.2]^2\Delta_{5/2} - X^2\Pi_{3/2}$ transitions. Accurate molecular constants have been determined for the $[23.2]^2\Delta_{5/2}$, $[19.9]^2\Delta_{5/2}$, $[18.9]^2\Pi_{3/2}$ and $[0.04]^2\Delta_{5/2}$ electronic states. The agreement between experimental determined molecular constants and those from *ab initio* calculations incorporating the spin-orbit coupling is generally good.

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1. Introduction

For molecules formed from platinum and fluorine atoms, the platinum difluoride (PtF₂), platinum tetrafluoride (PtF₄) and platinum hexafluoride (PtF₆) are commonly known stable molecules. Recently, the molecular structure of the PtF_{2n} (n = 1–3) molecules have been investigated theoretically by Wesendrup and Schwerdtfeger [1], the calculated molecular geometry and Pt–F bond length of these molecules are: nearly linear with 1.862 Å for PtF₂, almost square planar with 1.857 Å for PtF₄, and octahedral with 1.890 Å for PtF₆. For the PtF₆ molecule, all the experimentally determined Pt–F bond lengths are around 1.850 Å, which indicates the molecule is very close to or completely octahedral in structure [2]. Furthermore, density-functional theory (DFT) calculations with two-component zeroth-order regular approach including spin-orbit interaction supported that the PtF₆ molecule is a diamagnetic octahedral molecule with a closed-shell ground state [3], which not only describes the octahedral structure and also explains the Pt–F bond length is shorter in PtF₆ than in an isolated PtF molecule. It would be interesting to understand in detail the electronic structure of a single Pt–F bond and learn about the bonding characteristics involving the *d* orbitals. In addition, the degenerated *d* orbital also leads to a wealth of low-lying electronic states with energies very sensitive to electron correlation in this molecule.

The electronic structure of PtF was first studied by Liu and Franke [4] using relativistic *ab initio* and density functional theory (DFT) calculations, they reported calculated spectroscopic properties for the three lowest-lying Λ -S electronic states namely: $^2\Sigma^+$,

$^2\Pi$ and $^2\Delta$ states. The $^2\Sigma^+$ state was calculated to be the ground state, however, when the spin-orbit coupling was incorporated into the calculation, the ground state was predicted to be the $^2\Pi_{3/2}$ ($\Omega = 3/2$) sub-state, followed by the $^2\Sigma^+$ ($\Omega = 1/2$) state and then the $^2\Delta_{5/2}$ ($\Omega = 5/2$) sub-state. Subsequently, Zou et al. [5] also performed detailed theoretical calculations on the same three low-lying states using multi-reference configuration interaction with single and doubles (MRCI) with relativistic core potential (RECP), they also reported their spectroscopic constants. First experimental observation of PtF was performed by O'Brien and coworkers [6] using intra-cavity laser absorption spectroscopy with a copper hollow cathode molecular source and recorded the (1, 0) and (0, 0) bands of the $[11.9]\Omega = 3/2 - X^2\Pi_{3/2}$ electronic transition in the near infrared region. They confirmed the $X^2\Pi_{3/2}$ is the ground state and reported molecular constants for both the ground and excited states. The same group later on also reported the identification of a new $[12.5]^2\Sigma^+ - A^2\Sigma^+$ transition [7]. Using microwave spectroscopy, Okabayashi et al. [8] studied in detail the rotational and hyperfine structures of the $X^2\Pi_{3/2}$ state and, using their determined molecular constants, they estimated the ground state vibrational frequency, ω_e , to be 582 cm⁻¹. The permanent electric dipole moment and the hyperfine structure of the $[11.9]\Omega = 3/2 - X^2\Pi_{3/2}$ transition were measured by Steimle and coworkers [9] using laser induced fluorescence (LIF) spectroscopy.

In this work, we report rotationally resolved LIF spectroscopic study of the PtF molecule in the visible region. Eight vibrational bands were observed and six of them were analyzed in detail; they have been assigned to four new electronic transitions. Accurate molecular constants have been determined for the involved electronic states.

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2. Experiment

PtF molecules were produced by the reaction of laser-ablated platinum atoms with sulfur hexafluoride (SF₆) under supersonic free jet conditions. Experimental procedure and apparatus for studying metal halides and recording their laser induced fluorescence (LIF) spectrum have been discussed in detail in previous publication [10], only a brief description of the experimental conditions will be given here. Pulses of 532 nm, 1 mJ and 10 ns from a Nd:YAG laser were focused onto the surface of platinum rod to produce Pt atoms in gas-phase. A pulsed valve, synchronized with an appropriate delay, released a gas mixture of 5% SF₆ in argon to react with Pt atoms. The Nd:YAG laser – pulsed valve system was operated at 10 Hz. A pulsed tunable dye laser, operated with Coumarin dyes, was pumped by another Nd:YAG laser with wavelength set to 355 nm producing tunable laser output in the visible region, which was used to excite the jet-cooled PtF molecule. The LIF signal was collected by a lens system and directed to a monochromator and eventually detected by a photomultiplier tube (PMT). The monochromator was used for two purposes (i) obtaining resolved fluorescence spectrum of the excited molecule relaxing to various lower levels; (ii) working as an optical filter for the removal of unwanted laser scattering from both the ablation and excitation lasers. The PMT output was fed into a fast oscilloscope for averaging and storage. The wavelength of the dye laser was measured using a wavelength meter with accuracy around $\pm 0.02 \text{ cm}^{-1}$. Due to the presence of unresolved isotopic structure from many platinum nuclei, the molecular linewidth of some bands recorded was as large as 0.2 cm^{-1} .

3. Results and discussion

In our low resolution scan, molecular transition bands of both PtF and PtS molecules were observed, which is shown in Fig. 1. Due to the fact that the rotational constants for the PtS molecule are much smaller than that of PtF, the transition bands of the PtS molecule could easily be identified in our broadband spectrum. In addition, molecular transition bands of PtS in the visible region were studied in detail by Steimle and coworkers [11,12], we did not pursue any further these bands. For PtF, the high resolution laser induced fluorescence spectrum in the visible region between 431 and 560 nm was recorded. Among the eight vibrational bands observed only six of them were analyzed in detail, they have been assigned to be the (ν , 0) bands with $\nu = 0-4$ of the $[18.9]^2\Pi_{3/2} - X^2\Pi_{3/2}$ transition, and the (0, 0) band of the $[18.9]^2\Pi_{3/2} - [0.04]^2\Delta_{5/2}$ transition, the (0, 0) band of the $[19.9]^2\Delta_{5/2} - X^2\Pi_{3/2}$ transition, and the (0, 0) band of the $[23.2]^2\Delta_{5/2} - X^2\Pi_{3/2}$ transition. Fig. 2 depicts the electronic transitions that have been studied so far. Since the platinum element has six isotopes and four of them are having appreciable abundance [¹⁹⁴Pt (32.9%), ¹⁹⁵Pt (33.8%), ¹⁹⁶Pt (25.3%), ¹⁹⁸Pt (7.2%)], these mass differences cause the rotational structure and energy of each isotope to change very slightly

and, hence, the transition spectrum observed consists of all isotopic molecules and appears to be more complicated. The observed transitions are discussed individually. Accurate molecular constants have been determined for the $[23.2]^2\Delta_{5/2}$, $[19.9]^2\Delta_{5/2}$, $[18.9]^2\Pi_{3/2}$ and $[0.04]^2\Delta_{5/2}$ states. The line list of all the measured line positions of the analyzed bands is available from the Journal archive.

3.1. The $[18.9]^2\Pi_{3/2} - X^2\Pi_{3/2}$ transition

Five bands were observed for this transition, three bands located at 18,861, 19,399 and 19,926 cm^{-1} were recorded and rotationally analyzed, they are respectively the (0, 0), (1, 0) and (2, 0) bands of this transition. The (3, 0) and (4, 0) bands were also observed, however, due to heavy overlap of various isotopic molecular transition lines, they are too complicated to be analyzed in this work. Fig. 3 shows the (0, 0) band of this transition with the P, Q and R branches resolved, the band structure is simple because transition lines from the isotopic molecules are overlapped. Rotational analysis showed that the first lines of the branches are respectively P (2.5), Q (1.5) and R (1.5) lines, confirming the band is consistent with a $\Omega' = 1.5 - \Omega'' = 1.5$ transition. Further analysis indicated that the molecular constants of the lower state agreed very well with those determined for the ground state [9], which confirmed the transition band is from the $X^2\Pi_{3/2}$ state. Moreover, the R and P branches are stronger in intensity than the Q branch, which is consistent with a $\Delta\Lambda = 0$ transition. Consequently, the transition was assigned to be the $[18.9]^2\Pi_{3/2} - X^2\Pi_{3/2}$ transition. The observed line positions were fit to a standard formula [13]

$$\nu = \nu_0 + B'J'(J' + 1) - D'[J'(J' + 1)]^2 - \{B''J''(J'' + 1) - D''[J''(J'' + 1)]^2\} \quad (1)$$

where the ' and '' refer to the upper and lower states, respectively. The ν_0 is the band origin, and B and D are rotational and centrifugal distortion constants. We performed least squares fit to line positions of individual vibrational bands at the beginning and in the final fit all bands were merged together to yield only one set of molecular constants for each vibrational level. Molecular constants determined are reported in Table 1, the overall RMS error of the merged fit was about 0.03 cm^{-1} . Fig. 4 depicts the (1, 0) band and the resolved structure are transition lines from the more abundant ¹⁹⁴PtF, ¹⁹⁵PtF, ¹⁹⁶PtF and ¹⁹⁸PtF isotopes. The upper spectrum in the figure is our measured spectrum and the lower spectrum was simulated using the PGOPHER program [14]. For the simulated spectrum, the $\nu = 1$ level molecular constants were obtained from the least squares fitting of the observed line positions and the lower state constants are those of Steimle and coworkers [9]. A rotational temperature of 100 K was used in the simulation; the agreement between the two spectra is excellent.

The wavelength resolved fluorescence (WRF) spectrum of both bands shows two sets of vibrational progressions: they are respec-

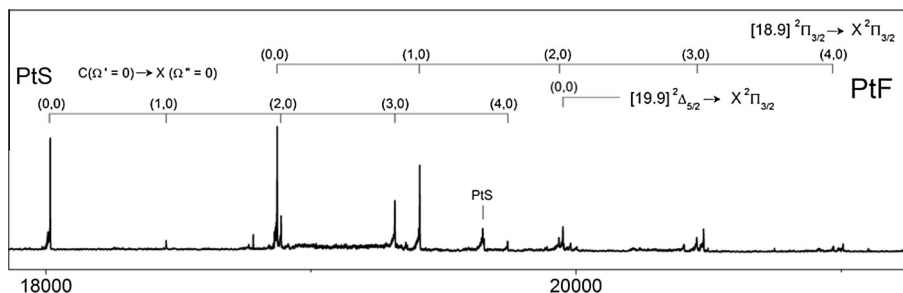


Fig. 1. Broadband scan of the visible region showing both PtF and PtS transition bands.

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