Fourier Transform Emission Spectroscopy of the A'3Π-X'3Σ- Transition of PtO

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A new 3Π electronic state of PtO has been observed between 7100 and 8015 cm\(^{-1}\) above the ground state. Three independent electronic systems connecting Ω' = 0', 1, and 2 in the upper state to Ω = 1 in the ground state have been recorded in emission from a Pt hollow cathode with the Fourier transform spectrometer associated with the McMath solar telescope at Kitt Peak. We interpret these three transitions as arising from the spin components of a new A'3Π-X'3Σ- transition in Hund's case (a) notation. Molecular constants (including Ω-doubling parameters) for the new electronic state have been determined from the analysis of the data. © 1991 Academic Press, Inc.

INTRODUCTION

The emission spectrum of PtO has been previously recorded in the ultraviolet and visible region of the spectrum by several workers (1–4). The first two electronic systems, the A'1Σ+-X'1Σ+ (1) and D'1Σ+-X'1Σ+ (2), were analyzed as 1Σ+-1Σ+ transitions assuming a singlet state as the ground state for the molecule. In a matrix isolation investigation of PtO and Pt\(_2\), Jansson and Scullman (5) observed several transitions assigned to PtO between 2500 and 9000 Å but none of them matched the previously measured A-X and D-X systems. The origin of this discrepancy is not clear. A few years later, Sassenburg and Scullman (3, 4) discovered additional emission bands of PtO. All these new transitions had the previously known X'1Σ+ state or a new state which they designated as the x state as the lower state. The new x state had the character of an Ω = 1 state and was 945.929 cm\(^{-1}\) above the X state. It was evident (3) that the ground state of PtO has 3Σ- symmetry and that the X and x states are in fact the Ω = 1 and 0+ spin components which originate from a 3Σ- state in Hund's case (c) coupling scheme (6).

We report here the discovery of a new 3Π electronic state of PtO about 7600 cm\(^{-1}\) above the ground state. The emission spectra analyzed here support the assumption that the ground state of PtO is a 3Σ- state.

EXPERIMENTAL DETAILS

The new electronic transition of PtO was recorded in emission with the Fourier transform spectrometer associated with the McMath solar telescope at Kitt Peak. The instrument was operated with a CaF\(_2\) beamsplitter and InSb detectors. The spectral

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band pass was 1850 to 9000 cm\(^{-1}\) with a resolution of 0.02 cm\(^{-1}\). Eight consecutive scans were coadded for a total integration time of 40 min to increase the signal-to-noise ratio. However, the signal-to-noise was relatively poor ranging from 10 for the strongest system to less than 3 for the weakest electronic transition.

Gaseous PtO was produced in a hollow cathode discharge lamp. The cathode was made of oxygen-free Cu with a platinum tube insert. A mixture of Ne and O\(_2\) flowed at a slow rate through the cathode during the experiment. The total pressure was 3.2 Torr of which 0.4 Torr was O\(_2\). At this pressure a discharge current of 190 mA yielded a stable discharge.

The strong Ne atomic lines present in the spectrum were used to provide the wave number calibration. The spectrum was calibrated to better than \(\pm 0.001\) cm\(^{-1}\) with the Ne line positions measured by Palmer and Engleman (7).

RESULTS AND ANALYSIS

PC-DECOMP, a spectral analysis program developed by J. W. Brault of the National Solar Observatory, was used for data reduction.

Three independent electronic systems each having only one strong vibrational band were identified between 7100 and 8015 cm\(^{-1}\). An energy level diagram of the observed transitions is shown in Fig. 1. These are found to be the transitions from the \(\Omega\) components of an excited state of \(^3\Pi\) symmetry to the \(\Omega = 1\) component of the \(^3\Sigma^-\) ground state of PtO. The three states which originate from a Hund's case (c) \(^3\Pi\) state with \(\Omega = 0, 1, 2\) are designated as \(0^+, 1,\) and \(2\) (the \(0^-\) state was not observed). All individual branches were picked out using an interactive color Loomis-Wood program running on a 486/33 microcomputer.

![Energy level diagram of the observed \(A^3\Pi-X^3\Sigma^-\) electronic system of the PtO molecule. The energy levels are not drawn to scale.](image-url)
Platinum has six naturally occurring isotopes, $^{190}$Pt, 0.01%; $^{192}$Pt, 0.79%; $^{194}$Pt, 32.9%; $^{195}$Pt, 33.8%; $^{196}$Pt, 25.3%. The isotope splitting caused by the three major isotopes ($^{194}$Pt, $^{195}$Pt, and $^{196}$Pt) was observed at high $J$ in the $0^+ - x 1$ and the $2- x 1$ systems. However, the intensity of these lines was so poor that we refrained from fitting each isotopomer independently.

The electronic system lying at the lowest wavenumber was the most intense. Only one vibrational band was found in this region, as shown in Fig. 2. This band showed a strong $Q$ branch and two weaker $P$ and $R$ branches of almost equal intensity as expected for a transition with $\Delta \Omega = \pm 1$ and one $\Omega = 0$ state. The spectrum was assigned to the $0^+ - x 1$ electronic transition of PtO. The rotational levels of the $0^+$ state have all $e$ parity while the levels in the $1$ state are split into $e$ and $f$ parity levels by $\Omega$-type doubling. The spectrum was weak so the rotational assignment was complicated by the large number of missing low $J$ lines. Fortunately, the assignment could be carried out using a least-squares fitting program and a fast computer. We started with an initial guess and then shifted the assignment simultaneously in all three branches to minimize the variance of the fit. As a final test for the validity of the
assignment we predicted the \( R \) head from the molecular constants obtained and found good agreement with the measured value of 7241.262 cm\(^{-1}\). The molecular constants of the lower state were found to be identical (within experimental error) with the values for the \( x1, v = 0 \) state as determined by Sassenberg and Scullman (3, 4) from their analysis of several emission spectra attributed to PtO. The observed band was therefore assigned to the 0–0 band, which seemed the most reasonable choice on the basis of the Franck-Condon principle. A portion of this band is shown in Fig. 3 and the determined molecular constants are presented in Table I. The line positions and the differences between the observed and calculated values are shown in Table II.

The assignment for the other two systems was even more complicated due to lower intensity of the transitions. Each system showed only one vibrational band. The stronger system centered around 7999 cm\(^{-1}\) (see Fig. 4) showed six distinct branches: two \( Q \) branches, two \( R \), and two \( P \) branches with two \( R \) heads at 8011.598 and 8012.703 cm\(^{-1}\). The \( Q \) branches were almost 10 times stronger than \( R \) and \( P \) branches which showed almost equal intensity. The transition was assigned as the 2–\( x1 \) system of PtO (see Fig. 5). In a 2 state the \( \Omega \)-doubling of the rotational levels also occurs but the splitting is smaller since the interaction is of second order. The rotational assignment was carried out in a manner similar to that for the 0\(^+\)–\( x1 \) system. Fortunately, we were able to fix the ground constants to the values previously obtained, greatly facilitating the assignment. However, the large number of missing lines in the spectrum required multiple shifts until all six branches fitted together and the variance of the overall fit was a minimum. Finally, both the upper and lower state constants were varied in the least-squares fit. As expected, the molecular constants obtained in this way did not change significantly from the values obtained in the fit with fixed lower state constants. The values obtained for the molecular constants of the lower state of this transition confirm the assignment to the \( v = 0 \) level of the \( x1 \) state. The best

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Note. The values are given in inverse centimeters with one standard deviation enclosed in parentheses.

* From the 0\(^+\)–\( x1 \) transition. For the 1–\( x1 \) and 2–\( x1 \) fits these constants were held fixed.
### Table II

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The system centered at 7834 cm⁻¹, the weakest of all, was analyzed in a similar manner. This spectrum, which has been assigned to the $1-x1$ transition of PtO, showed four weak branches, two $P$ branches and two $R$ branches with two $R$ heads at 7870.471 and 7870.884 cm⁻¹ (see Fig. 6). The presence of $\Omega$-doubling of the rotational levels

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estimate for vibrational assignment of the band was again 0–0. Molecular constants and the line positions of this transition are reported in Tables I and III, respectively.
EMISSION SPECTRUM OF PtO

**Fig. 4.** The $A^3\Pi - X^3\Sigma^-$ transition of PtO. The 2–1 system is shown here.

**Fig. 5 A.** portion of the 0–0 band of the 2–1 system of PtO.

**Fig. 6.** The $A^3\Pi - X^3\Sigma^-$ transition of PtO. The 1–1 system is shown here.
in both states is responsible for the doubling in the $R$ and $P$ branches. Although a $Q$ branch is allowed by the electric dipole selection rules, its intensity is very small and is only rarely observed. The intensity of the $P$ branches was only slightly larger than the intensity of $R$ branches. In fact, the $R$ branches were so weak that only a few lines near the $R$ heads could be measured from the spectrum. Analysis proceeded as before and on the basis of the values of the lower state molecular constants we assigned this band as a $0–0$ vibrational band again. The molecular constants of this band are shown in Table I. The line positions and the differences between observed and calculated line positions are given in Table IV. The fit of this band is not as good as the fits of the other two bands because of the poor signal-to-noise ratio.
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**DISCUSSION**

From the $\sigma^2\delta^4\pi^2$ electronic configuration of PtO three states are possible, namely, $1\Sigma^+$, $3\Sigma^-$, and $1\Delta$. The $3\Sigma^-$ is the ground state according to Hund's rules. We have not been able to locate any published ab initio calculations on PtO. However, NiO, although poorly characterized experimentally due to its highly perturbed spectra (8-10), has been the subject of several calculations (11, 12). In NiO the ground state is calculated (11, 12) and observed to be $X^3\Sigma^-$ (10). Both of the ab initio calculations (11, 12) on NiO predict low-lying $3\Pi$ states.
Since PtO is clearly a Hund's case (c) molecule we approached the problem of analyzing the spectrum by treating each component of the triplet state as independent states. The $0^+ - x1$ transition was treated as a $^1\Sigma^+ - ^1\Pi$ transition, the $1-x1$ as a $^1\Pi - ^1\Pi$ transition, and the $2-\chi1$ transition as a $^1\Delta - ^1\Pi$ transition. The following term values expressions were used:

$$F(J) = B_e J(J + 1) - D_e [J(J + 1)]^2$$

for $^1\Sigma^+$ states

$$F(J) = B_e J(J + 1) - D_e [J(J + 1)]^2 \pm qJ(J + 1)/2$$

$$\pm q_d [J(J + 1)]^2/2$$

for $^1\Pi$ states

$$F(J) = B_e J(J + 1) - D_e [J(J + 1)]^2 \pm qJ(J + 1)/2$$

$$\pm q_d [J(J + 1)]^2/2$$

for $^1\Delta$ states.
EMISSION SPECTRUM OF PtO

where the upper (lower) sign refers to $e$ ($f$) parity. The $\Omega$-doubling appears as $\Lambda$-doubling in this treatment and therefore we preserve the notation for the coefficients $q$ and $q_D$.

If the 2, 1, and $0^+$ states were to arise from an isolated $^3\Pi$ state then the 1 state would be midway between the $0^+$ and 2 states and the rotational constant would be equal to the average of the $B$'s for the 2 and $0^+$ states. Unfortunately, this was not the case. The 1 state lies at higher energy than expected and the $B$ value is different from the predicted value (Table I). This clearly indicates that the 1 state of PtO is strongly perturbed by other electronic states of appropriate symmetry and confirms the Hund's case (c) character of the $A'(^3\Pi$ state of PtO.

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