

## Fourier Transform Emission Spectroscopy of the $A^1{}^3\Pi-X^3\Sigma^-$ Transition of PtO

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A new  ${}^3\Pi$  electronic state of PtO has been observed between 7100 and 8015  $\text{cm}^{-1}$  above the ground state. Three independent electronic systems connecting  $\Omega' = 0^+, 1,$  and  $2$  in the upper state to  $\Omega'' = 1$  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  $A^1{}^3\Pi-X^3\Sigma^-$  transition in Hund's case (a) notation. Molecular constants (including  $\Omega$ -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  $A^1\Sigma^+-X^1\Sigma^+$  (1) and  $D^1\Sigma^+-X^1\Sigma^+$  (2), were analyzed as  ${}^1\Sigma^+-{}^1\Sigma^+$  transitions assuming a singlet state as the ground state for the molecule. In a matrix isolation investigation of PtO and Pt<sub>2</sub>, 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  $X^1\Sigma^+$  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  $\Omega = 1$  state and was 945.929  $\text{cm}^{-1}$  above the  $X$  state. It was evident (3) that the ground state of PtO has  ${}^3\Sigma^-$ -symmetry and that the  $X$  and  $x$  states are in fact the  $\Omega = 1$  and  $0^+$  spin components which originate from a  ${}^3\Sigma^-$  state in Hund's case (c) coupling scheme (6).

We report here the discovery of a new  ${}^3\Pi$  electronic state of PtO about 7600  $\text{cm}^{-1}$  above the ground state. The emission spectra analyzed here support the assumption that the ground state of PtO is a  ${}^3\Sigma^-$  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<sub>2</sub> beamsplitter and InSb detectors. The spectral

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band pass was 1850 to 9000  $\text{cm}^{-1}$  with a resolution of 0.02  $\text{cm}^{-1}$ . 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  $\text{O}_2$  flowed at a slow rate through the cathode during the experiment. The total pressure was 3.2 Torr of which 0.4 Torr was  $\text{O}_2$ . 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  $\pm 0.001 \text{ cm}^{-1}$  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  $\text{cm}^{-1}$ . 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.

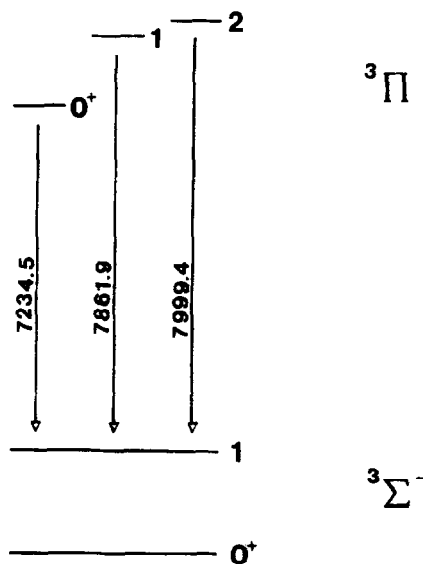


FIG. 1. Energy level diagram of the observed  $A'^3\Pi-X^3\Sigma^-$  electronic system of the PtO molecule. The energy levels are not drawn to scale.

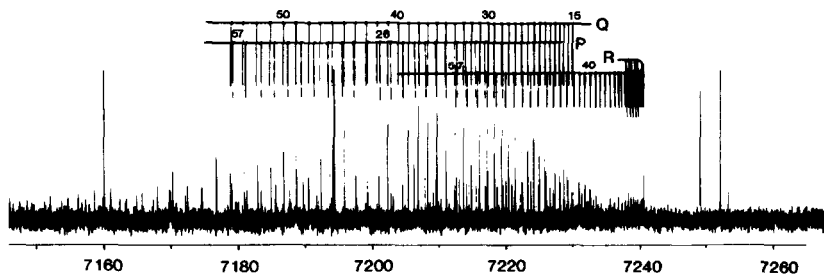


FIG. 2. The  $A'^3\Pi-X^3\Sigma^-$  transition of PtO. The  $0^+-x1$  system is shown here. Many low  $J$  lines are missing in all three branches.

Platinum has six naturally occurring isotopes,  $^{190}\text{Pt}$ , 0.01%;  $^{192}\text{Pt}$ , 0.79%;  $^{194}\text{Pt}$ , 32.9%;  $^{195}\text{Pt}$ , 33.8%;  $^{196}\text{Pt}$ , 25.3%. The isotope splitting caused by the three major isotopes ( $^{194}\text{Pt}$ ,  $^{195}\text{Pt}$ , and  $^{196}\text{Pt}$ ) was observed at high  $J$  in the  $0^+-x1$  and the  $2-x1$  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  $0^+-x1$  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

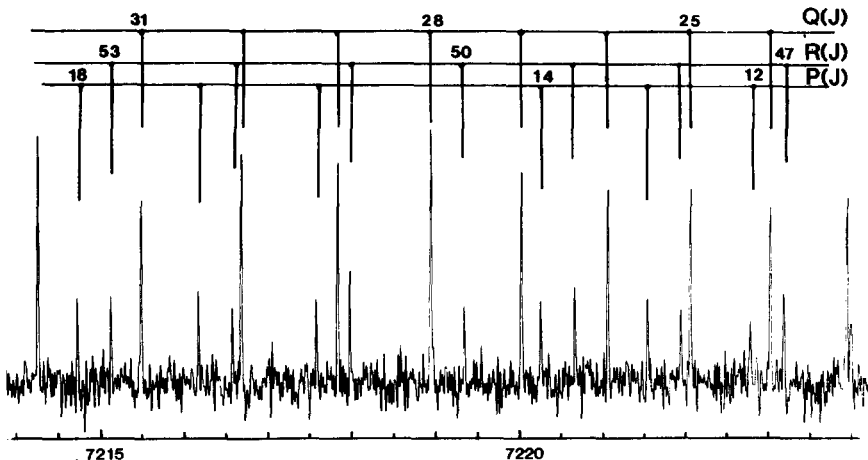


FIG. 3 A. portion of the  $0-0$  band of the  $0^+-x1$  system.

assignment we predicted the  $R$  head from the molecular constants obtained and found good agreement with the measured value of  $7241.262\text{ cm}^{-1}$ . 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  $7999\text{ cm}^{-1}$  (see Fig. 4) showed six distinct branches: two  $Q$  branches, two  $R$ , and two  $P$  branches with two  $R$  heads at  $8011.598$  and  $8012.703\text{ cm}^{-1}$ . 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

TABLE I  
Molecular Constants Obtained from the Least-Squares Fit of the  $A^1\Pi-X^3\Sigma^-$   
Electronic Transition of PtO

State	T	B	D	q	$q_D$
			$/10^{-6}$	$/10^{-3}$	$/10^{-8}$
$x1^a$	-	0.3783383(41)	0.3039(26)	0.99127(20)	0.339(15)
$0^+$	7234.53284(13)	0.3586616(40)	0.3277(19)	-	-
1	7861.89992(15)	0.36265532(27)	0.15285(11)	0.23902(27)	0.1273(15)
2	7999.42805(11)	0.36749638(16)	0.355370(41)	-	0.1630(29)

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

<sup>a</sup> From the  $0^+-x1$  transition. For the  $1-x1$  and  $2-x1$  fits these constants were held fixed.

TABLE II

Line Positions of the 0-0 Band of the  $0^+ - x1$  Electronic Transition of PtO

J	Q(J)	o-c	P(J)	o-c	R(J)	o-c
5			7230.3342	-70		
6			7229.3912	91		
7			7228.3882	59		
8			7227.3456	32		
9			7226.2622	0		
10			7225.1413	-4		
11	7232.0001	-4	7223.9867	58		
12	7231.5387	-13	7222.7761	-36		
13	7231.0400	-12	7221.5356	-27		
14	7230.5025	-13	7220.2515	-51		
15	7229.9297	16	7218.9410	64		
16	7229.3121	-19	7217.5725	2		
17	7228.6627	14	7216.1668	-29		
18	7227.9678	-25	7214.7231	-36		
19	7227.2395	-13	7213.2419	-17		
20	7226.4732	3	7211.7166	-34		
21	7225.6562	-3	7210.1549	-13		
22	7224.8215	-1	7208.5500	-20		
23	7223.9384	2	7206.9078	3	7240.5870	-7
24	7223.0169	6	7205.2210	-17	7240.3326	-3
25	7222.0559	1	7203.4968	-7	7240.0381	6
26	7221.0574	5	7201.7327	7	7239.6985	-28
27	7220.0194	1	7199.9257	-6	7239.3227	-16
28	7218.9410	-23	7198.0807	8	7238.9071	5
29	7217.8279	-8	7196.1945	12	7238.4487	7
30	7216.6759	5	7194.2683	20	7237.9509	23
31	7215.4846	10	7192.2989	0	7237.4113	30
32	7214.2526	-6	7190.2937	26	7236.8265	-6
33	7212.9827	-13	7188.2427	-3	7236.2060	10
34	7211.6765	2	7186.1544	1	7235.5451	32
35	7210.3298	0			7234.8346	-33
36	7208.9445	-1			7234.0944	15
37	7207.5210	2			7233.3106	39
38	7206.0580	-2			7232.4794	-1
39	7204.5573	4			7231.6088	-24
40	7203.0163	-4			7230.7024	6
41	7201.4374	-4			7229.7490	-23
42	7199.8200	-1			7228.7580	-5
43	7198.1641	6			7227.7264	-1
44	7196.4669	-12			7226.6501	-21
45	7194.7348	10			7225.5438	72
46	7192.9601	-5			7224.3793	-4
47	7191.1483	-1			7223.1775	-39
48	7189.2975	3			7221.9390	-26
49	7187.4069	-2			7220.6616	11
50	7185.4784	4			7219.3383	4
51					7217.9720	-17
52					7216.5670	-11
53					7215.1207	1
54					7213.6348	32
55					7212.1008	-3
56					7210.5279	-7
57					7208.9147	1
58					7207.2625	39
59					7205.5625	17
60					7203.8241	30
61					7202.0452	57

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.

The system centered at  $7834 \text{ cm}^{-1}$ , 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  $7870.884 \text{ cm}^{-1}$  (see Fig. 6). The presence of  $\Omega$ -doubling of the rotational levels

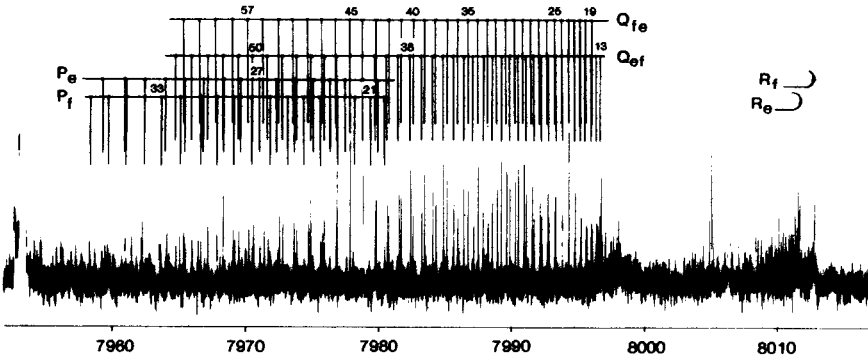


FIG. 4. The  $A'^3\Pi-X^3\Sigma^-$  transition of PtO. The 2-x1 system is shown here.

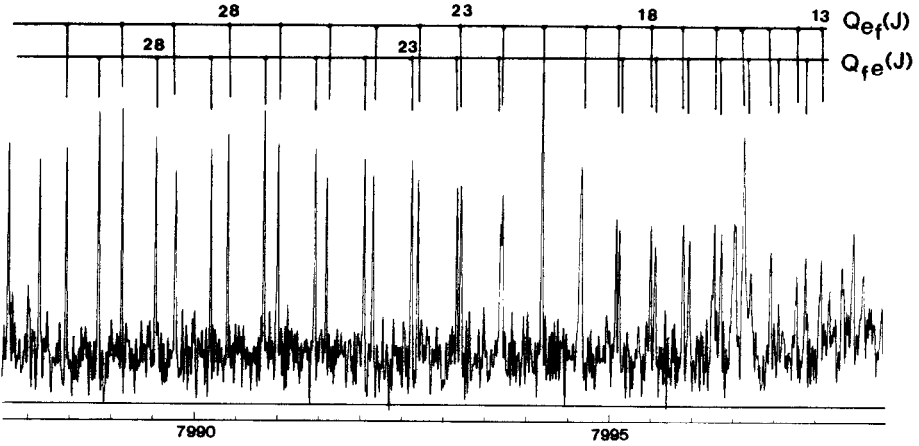


FIG. 5 A. portion of the 0-0 band of the 2-x1 system of PtO.

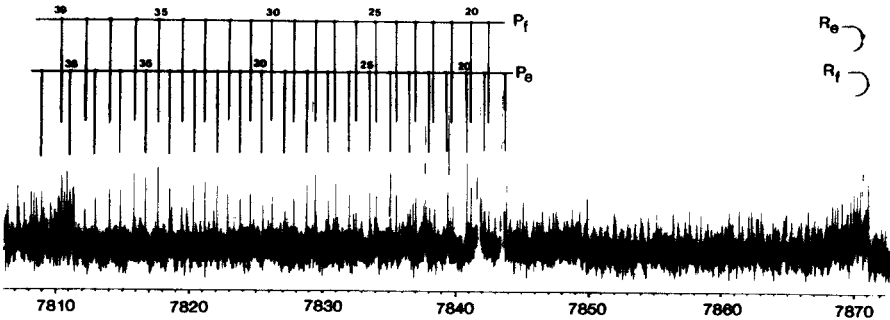


FIG. 6. The  $A'^3\Pi-X^3\Sigma^-$  transition of PtO. The 1-x1 system is shown here.

TABLE III

Line Positions of the 0-0 Band of the  $2-\pi 1$  Electronic Transition of PtO

J	$Q_{fe}(J)$	o-c	$Q_{of}(J)$	o-c	$P_{ee}(J)$	o-c	$P_{ff}(J)$	o-c
11	7997.9388	82			7989.8478	2		
12	7997.6514	-67	7997.8130	2	7988.8375	-32	7989.9926	142
13	7997.3601	-28	7997.5465	31	7987.8225	114	7988.9964	10
14	7997.0408	-40	7997.2525	-7	7986.7604	16	7987.9991	76
15	7996.6983	-56	7996.9417	-4	7985.6907	68	7986.9665	-6
16	7996.3415	13	7996.6159	57	7984.5782	-81	7985.9262	43
17	7995.9549	12	7996.2548	-27	7983.4640	-19	7984.8462	-99
18	7995.5436	-7	7995.8813	-26	7982.3286	57	7983.7709	14
19	7995.1055	-65	7995.4883	-11	7981.1632	61	7982.6600	-22
20	7994.6462	-106	7995.0736	-4	7979.9735	49	7981.5402	61
21	7994.1782	-4	7994.6462	85	7978.7622	50	7980.3850	-3
22	7993.6893	119	7994.1782	-21	7977.5206	-25	7979.2204	48
23	7993.1507	-26	7993.6893	-127	7976.2721	59	7978.0258	6
24	7992.6047	-14	7993.2008	-19	7974.9857	-7	7976.8253	114
25	7992.0341	-17	7992.6816	-7	7973.6908	69	7975.5830	9
26	7991.4419	-6	7992.1388	-21	7972.3614	30	7974.3326	35
27	7990.8261	1	7991.5786	5	7971.0093	-7	7973.0575	22
28	7990.1870	7	7990.9923	-23	7969.6423	35	7971.7645	39
29	7989.5223	-13	7990.3901	3	7968.2579	133	7970.4445	-6
30	7988.8375	0	7989.7617	-20	7966.8285	11	7969.1070	-15
31	7988.1275	-6	7989.1156	-9	7965.3912	41	7967.7760	250
32	7987.3953	-2	7988.4476	-3	7963.9283	43	7966.3724	-1
33	7986.6386	-8	7987.7560	-19	7962.4384	7	7964.9748	18
34	7985.8594	-6	7987.0445	-22	7960.9173	-110	7963.5567	44
35	7985.0569	-2	7986.3123	-18	7959.3958	0	7962.1075	-31
36	7984.2316	9	7985.5592	-8	7957.8495	95	7960.6523	45
37	7983.3798	-10	7984.7830	-15	7956.2580	-32	7959.1621	-18
38	7982.5076	2	7983.9861	-13	7954.6601	10	7957.6579	48
39	7981.6112	10	7983.1670	-18	7953.0277	-59	7956.1369	-6
40	7980.6903	9	7982.3286	0	7951.3807	-42	7954.5906	59
41	7979.7474	25	7981.4661	-6	7949.7223	95	7953.0277	120
42	7978.7622	-144	7980.5819	-13	7948.0212	39	7949.8124	-13
43	7977.7937	93	7979.6756	-23	7946.3227	244	7948.1272	121
44	7976.7682	-1	7978.7622	115	7944.5583	25	7946.5442	182
45	7975.7330	48	7977.7937	-80	7942.7977	80	7944.8607	108
46	7974.6678	36	7976.8254	-54	7941.0015	13	7943.1754	232
47	7973.5837	77	7975.8378	-1	7939.1865	-5	7941.4327	-2
48	7972.4709	71	7974.8187	-34	7937.3388	-112	7939.7101	182
49	7971.3339	66	7973.7835	-26	7935.5125	232	7937.9318	25
50	7970.1694	28	7972.7257	-14	7933.5962	-86	7936.1436	-13
51	7968.9899	84	7971.6385	-63	7931.7001	36	7934.3435	48
52	7967.7760	39	7970.5375	-47	7929.7974	331	7932.5117	12
53	7966.5510	127	7969.4184	20	7927.8204	123	7930.6478	-127
54	7965.2965	167	7968.2579	-103	7925.8361	82	7928.8035	150
55	7964.0133	165	7967.0906	-69	7923.8555	319	7926.9180	235
56	7962.6979	88	7965.9068	24				
57	7961.3762	195	7964.6866	-21				
58			7963.4536	32				
59			7962.1831	-62				
60			7960.9173	118				

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.

TABLE III—Continued

J	$R_{ff}(J)$	o-c	$R_{ee}(J)$	o-c
4	8002.8902	-57		
5	8003.5379	106	8003.5021	475
6			8004.0999	379
7			8004.6759	371
8	8005.3093	125	8005.2373	1206
9	8005.8299	-150	8005.7560	20
10				
11	8006.8832	43	8006.7470	-101
12	8007.3656	10	8007.2128	298
13	8007.8368	74	8007.6395	-944
14	8008.2805	75		
15	8008.6955	-6	8008.4487	-94
16	8009.0803	-177	8008.8350	67
17	8009.4856	67	8009.1767	12
18	8009.8378	-100	8009.4856	-140
19	8010.1758	-19	8009.7996	-12
20	8010.5067	114	8010.0804	16
21			8010.3382	45
22	8011.0788	114	8010.5645	-9
23			8010.7785	45
24				
25	8011.7652	-12	8011.1232	18
26	8011.9554	-15		
27	8012.1168	-90	8011.3635	-122
28	8012.2663	-73	8011.4607	-70
29	8012.3841	-157	8011.5319	-44
30			8011.5874	60
31			8010.7274	-34
32			8010.5067	-76
33			8010.2681	-57
34	8011.6844	-47	8010.0096	5
35	8011.4607	-50	8009.7174	-27
36	8011.2286	87	8009.4066	-3
37	8010.9398	-119	8009.0803	111
38	8010.6487	-124	8008.6955	-117
39	8010.3383	-96	8007.9066	-29
40	8010.0096	-25	8007.4645	-92
41	8009.6543	7	8007.0168	36
42	8009.2706	-18	8006.5157	-123
43	8008.4487	74	8006.0093	-86
44	8007.9928	13	8005.4803	-25
45	8007.5155	-31	8004.3338	-39
46	8007.0168	-57	8003.7250	-24
47	8006.5157	124	8003.0922	4
48	8005.9664	57	8002.4383	74
49	8005.3889	-59	8001.7492	44
50	8004.8119	58	8001.0429	100
51	8004.1882	-45	8000.3024	68
52	8003.5379	-184	7999.5460	135
53	8002.8902	-60		
54	8002.2125	2		
55	8001.5017	-29		
56	8000.7723	-6		
57	8000.0072	-100		

## 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.



TABLE IV

Line Positions of the 0-0 Band of the 1-x1 Electronic Transition of PtO

J	P <sub>ee</sub> (J)	o-c	P <sub>ff</sub> (J)	o-c	R <sub>ee</sub> (J)	o-c	R <sub>ff</sub> (J)	o-c
8	7854.9555	1512						
9	7853.9415	151						
10	7852.8887	83	7852.9677	-2				
11	7851.8003	-23	7851.9132	61				
12	7850.6988	59	7850.8062	-96				
13	7849.5452	-63	7849.6862	-82				
14	7848.3792	9	7848.5189	-238				
15	7847.1701	-33	7847.3645	37				
16	7845.9396	26	7846.1519	32				
17	7844.6744	55	7844.9136	69				
18			7843.6376	31				
19	7842.0380	-5	7842.3315	-10				
20	7840.6740	-23	7840.9962	-44				
21	7839.2932	105	7839.6402	14				
22	7837.8603	23	7838.2467	-7				
23	7836.4007	-16	7836.8250	-13				
24	7834.9171	16	7835.3736	-20				
25	7833.3954	-23	7833.8928	-27	7870.8724	193		
26	7831.8482	-10	7832.3821	-39	7870.7965	54	7870.2728	-87
27	7830.2698	-2	7830.8435	-37	7870.7059	62	7870.1507	-5
28	7828.6573	-29	7829.2757	-36	7870.5871	83	7869.9806	-87
29	7827.0191	-7	7827.6795	-28	7870.4496	209	7869.8131	160
30	7825.3472	-19	7826.0528	-35	7870.2728	233	7869.5654	-88
31	7823.6480	0	7824.3976	-37	7870.0556	145	7869.3198	-12
32	7821.9168	-1	7822.7165	-12	7869.8131	94	7869.0364	-9
33	7820.1544	-12	7821.0036	-19	7869.5654	280	7868.7186	-47
34	7818.3685	39	7819.2641	-6	7869.2582	158	7868.3859	66
35	7816.5455	19	7817.4951	-5	7868.9203	17	7868.0039	-13
36	7814.6949	18	7815.6994	13	7868.5742	78	7867.6010	-2
37	7812.8155	24	7813.8771	45	7868.1901	44	7867.1529	-146
38	7810.9043	6	7812.0226	36	7867.7712	-56	7866.7060	19
39	7808.9687	36	7810.1410	34	7867.3405	8	7866.2170	57
40	7807.0018	44	7808.2321	37			7865.6931	40
41	7804.9901	-108	7806.2914	-3	7866.3835	19	7865.1374	-4
42	7802.9754	-2	7804.3374	99	7865.8658	50	7864.5471	-101
43	7800.9245	28	7802.3333	-28	7865.3184	60	7863.9417	-63
44	7798.8325	-69	7800.3201	26	7864.7517	151	7863.3053	-46
45	7796.7289	2	7798.2815	94	7864.1369	34	7862.6138	-295
46	7794.5905	5	7796.2041	44	7863.5064	32	7861.9207	-276
47	7792.4263	29	7794.1043	36	7862.8502	42	7861.2015	-235
48			7791.9674	-79	7862.1543	-76	7860.4387	-350
49			7789.8221	-15	7861.4371	-140		
50			7787.6458	1				
51			7785.4475	56				
52			7783.2122	-1				

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<sup>+</sup>-x1 transition was treated as a <sup>1</sup>Σ<sup>+</sup>-<sup>1</sup>Π transition, the 1-x1 as a <sup>1</sup>Π-<sup>1</sup>Π transition, and the 2-x1 transition as a <sup>1</sup>Δ-<sup>1</sup>Π transition. The following term values expressions were used:

$$F(J) = B_v J(J+1) - D_v [J(J+1)]^2 \quad \text{for } ^1\Sigma^+ \text{ states}$$

$$F(J) = B_v J(J+1) - D_v [J(J+1)]^2 \pm qJ(J+1)/2 \pm q_D [J(J+1)]^2/2 \quad \text{for } ^1\Pi \text{ states}$$

$$F(J) = B_v J(J+1) - D_v [J(J+1)]^2 \pm q_D [J(J+1)]^2/2 \quad \text{for } ^1\Delta \text{ states,}$$

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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