

Rotationally resolved spectroscopy of Pt₂

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High-resolution laser-induced fluorescence spectroscopy has been used to investigate the 18 163 cm⁻¹ band of Pt₂ in a supersonically cooled molecular beam. Rotational constants of the ground and excited states were extracted from the rotationally resolved spectrum and determined to be $B''_0 = 0.031\,754(12)\text{ cm}^{-1}$ and $B'_0 = 0.028\,672(11)\text{ cm}^{-1}$, respectively. These values correspond to ground- and excited-state bond lengths of $r''_0 = 2.33297(44)\text{ \AA}$ and $r'_0 = 2.455\,16(47)\text{ \AA}$, respectively. Nuclear spin statistics that are observed in the spectrum demonstrate that the ground state is of either 0_g^+ or 0_u^- symmetry. Of these, 0_g^+ is by far the more probable. Comparisons with Au₂ are made, suggesting that it may be appropriate to consider Pt₂ as having a double bond. © 2002 American Institute of Physics. [DOI: 10.1063/1.1428753]

I. INTRODUCTION

Over the past several years, considerable progress has been made in spectroscopic studies of the diatomic transition metals of the 3*d* and 4*d* periods.^{1–12} Through this work, the basic electronic structure of many of the homometallic and heterometallic 3*d* and 4*d* dimers has been discerned, and a qualitative understanding of many of these molecules has been established. One result of this work is the understanding that *d* orbital contributions to the chemical bond are more important in the left and central portions of the transition metal series than they are toward the right of the periodic table. This result follows from the differential contraction of the *nd* versus (*n* + 1)*s* orbitals, with the *nd* orbitals contracting more rapidly than the (*n* + 1)*s* orbital as nuclear charge is increased.¹³ Because of this contraction, the 3*d* orbitals are essentially unavailable for chemical bonding in the late 3*d* metals. As an example, Ni₂, NiCu, and Cu₂ have nearly identical bond energies and bond lengths,^{4,10,14–19} because the bonding in all three molecules is dominated by the 4*s*σ bond.

In contrast to the 3*d* and 4*d* transition metal dimers, our present knowledge of the 5*d* transition metal dimers is much more limited. For example, the only transition metal dimers of the 5*d* period to have received spectroscopic scrutiny at a rotationally resolved level are Au₂^{20–22} and Hg₂.^{23,24} Quantum chemical calculations on the 5*d* metal dimers are far fewer as well, probably because of the lack of experimental data and the intrinsic difficulty of performing calculations on systems for which both electron correlation and relativistic effects are important.

One of the relativistic effects that is particularly important for the 5*d* metals is the mass-velocity effect, which is a correction to the kinetic energy of the electron due to the relativistic increase in mass that occurs at high velocities.²⁵ This effect stabilizes orbitals that penetrate close to the nucleus, causing them to contract and drop in energy. It is particularly pronounced for the *s* orbitals, causing the expec-

tation value of the radial coordinate, $\langle r \rangle$, for the 6*s* orbital of gold, for example, to drop to 84% of its nonrelativistic value.²⁶ An important result of the contraction of the *s* orbitals is a concomitant expansion of the 5*d* orbitals due to improved shielding by the contracted *s* orbitals. Together, these two effects make the *d* orbitals more accessible for chemical bonding in the 5*d* series than in either the 3*d* or 4*d* transition metal series. The enhanced *d* orbital contributions to the chemical bonding in the 5*d* series explain why all of the metals with melting points above 3000 K (Ta, W, Re, and Os) lie within the 5*d* transition metal series.²⁷

While it is expected that 5*d* orbital contributions to chemical bonding are important in the 5*d* metal dimers as well, direct evidence is rather scarce. Prior to this investigation, none of the bond lengths of the open 5*d* subshell dimers had been measured, and very limited data is available on the bond dissociation energies.¹³ Vibrational frequencies of Hf₂,²⁸ Ta₂,²⁹ W₂,³⁰ Re₂,^{31,32} Pt₂,^{33–35} and Au₂¹³ have been reported, however, and these indicate significant *d* orbital contributions to the chemical bonding among the open 5*d* subshell transition metal dimers. A predissociation threshold measurement of the bond energy of Pt₂, giving a value of $D_0(\text{Pt}_2) = 3.14 \pm 0.02\text{ eV}$, also suggests substantial 5*d* bonding in this molecule,³⁶ particularly when compared to the bond energy of Au₂, $D_0(\text{Au}_2) = 2.306 \pm 0.005\text{ eV}$.²²

In this paper we present the first rotationally resolved study of Pt₂, which provides the first rotationally resolved spectrum of any open 5*d* subshell transition metal dimer. This, and spectroscopic studies of the remaining 5*d* metal dimers, will provide a stringent test of *ab initio* quantum chemistry for the important situation in which both electronic correlation and relativistic effects are significant. Few molecules exist for which both of these effects are important, and for which detailed, accurate spectroscopic data are also available. The rotationally resolved data presented below for Pt₂ establish the ground state bond length and symmetry, providing a reference point connecting theoretical and experimental work on the heavier transition metal dimers. Work of this type serves as an essential prerequisite to un-

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derstanding the contributions of the d electrons to the bonding in the $5d$ transition metal dimers.

II. EXPERIMENT

The rotationally resolved spectrum of Pt_2 was collected using high resolution laser-induced fluorescence spectroscopy. Preparation of diatomic platinum was accomplished by the pulsed laser ablation (Nd:YAG, 1064 nm) of a platinum metal disk followed by supersonic expansion in a pulse of helium carrier gas (70–80 psig). The jet-cooled molecules were excited at right angles to the molecular beam by a cw ring dye laser (Coherent 899-21, 0.5 MHz linewidth) pumped by an argon ion laser (Coherent Innova 200-15). A lens imaging system was used to collect the laser-induced fluorescence, which was then filtered to reduce scattered laser light and plasma emissions. The fluorescence was imaged onto a 1.6 mm slit and detected by a Hamamatsu R3896 photomultiplier tube. The output signal was preamplified and a gated integrator was used to select the signal reaching the detector during the appropriate time interval. Linearization of the wave number axis was provided by transmission peaks from a 250 MHz confocal étalon and calibration was accomplished by comparison of collected iodine absorption lines to the iodine absorption atlas of Gerstenkorn and Luc.^{37,38}

III. RESULTS

For this rotationally resolved study, conducted using a cw ring dye laser, weak fluorescence signals dictated that we seek a band with a small isotope shift, so that the absorption intensity was not broken up into separate lines for each of the isotopomers. This was a particularly serious problem for Pt_2 because five isotopomers have natural abundances over 10%, with $^{194}\text{Pt}^{195}\text{Pt}$ (22%) being the most abundant. Accordingly, a vibrational 0–0 band was sought that displayed strong fluorescence following pulsed dye laser excitation.

In the search for an appropriate band to rotationally resolve, it was discovered that our initial investigation of Pt_2^{36} was conducted with a miscalibrated dye laser. All of the band positions reported in that work, at least in the 18 000–19 000 cm^{-1} range, should be increased by $\sim 11 \text{ cm}^{-1}$.

A band displaying strong fluorescence with an unmeasurably small isotope shift was located near 18 163 cm^{-1} , as displayed in Fig. 1. Comparing this wave number to our previously reported bands of Pt_2 ,³⁶ corrected as described above, it is clear that this band is a member of the band system previously designated as System XIX. Furthermore, the 0–0 band at 18 163 cm^{-1} was not identified in the original work, so the vibrational numbering previously reported for this system must be increased by one unit for the upper electronic state. With this correction, a revised upper state vibrational frequency of $196.6 \pm 0.4 \text{ cm}^{-1}$ is obtained.

The absence of a Q -branch in the spectrum indicates that this is an $\Omega' = 0 \leftarrow \Omega'' = 0$ transition, which is confirmed by a fit of the rotational lines to the formula

$$\nu = \nu_0 + B_0' J'(J' + 1) - B_0'' J''(J'' + 1). \quad (3.1)$$

Line positions and residuals in the least-squares fit are provided in Table I, along with the fitted parameters ν_0 , B_0' ,

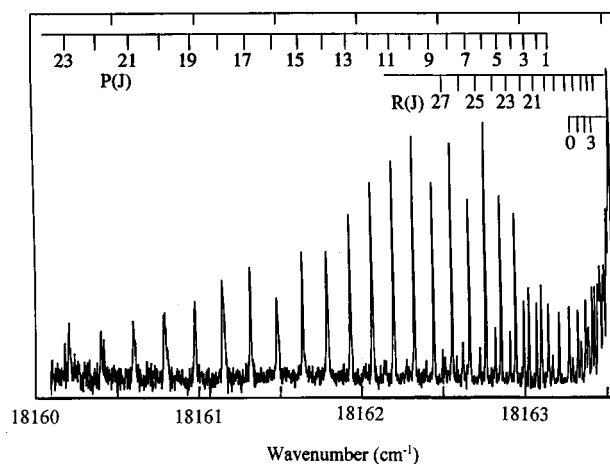


FIG. 1. Rotationally resolved scan over the 0–0 band of the System XIX–X₀⁺ system of Pt_2 .

and B_0'' . Using the average atomic weight of 195.08 amu for the isotopically unresolved lines of Pt_2 , the rotational constants may be inverted to obtain bond lengths of $r_0'' = 2.332\,97(44) \text{ \AA}$ and $r_0' = 2.455\,16(47) \text{ \AA}$, where the values in parentheses represent 1σ error limits. Although a metastable excited electronic state has been shown to be populated under these conditions, dispersed fluorescence studies conducted in this group strongly suggest that the lower level of the band displayed in Fig. 1 is the ground state of the Pt_2 molecule.³⁵

The spectrum displayed in Fig. 1 also exhibits an alternating pattern of apparent line widths that is most obvious in the high- J'' lines of the P -branch. A magnified view is presented in Fig. 2. The alternating pattern is a consequence of nuclear spin statistics in the homonuclear dimers $^{194}\text{Pt}_2$, $^{195}\text{Pt}_2$, and $^{196}\text{Pt}_2$, which have nuclear spins of $I = 0, 1/2$, and 0 , respectively. The natural abundances of these dimers are 10.8%, 11.4%, and 6.40%, respectively. The corresponding statistical weights for alternate J'' -levels in $^{194}\text{Pt}_2$, $^{195}\text{Pt}_2$, and $^{196}\text{Pt}_2$ are 1:0, 1:3, and 1:0. Evidently, the odd- J'' lines in the spectrum appear narrow because the light $^{194}\text{Pt}_2$ and heavy $^{196}\text{Pt}_2$ dimers cannot exist in an odd- J'' level of the ground state. Furthermore, the rotational lines that are absent for these isotopomers contribute with the greatest intensity in the central isotopomer, $^{195}\text{Pt}_2$. The net result is a transfer of intensity from the wings of the line into the center of the line, for odd values of J'' . The fact that it is the odd- J'' lines that are more narrow then implies that the ground-state symmetry of Pt_2 is either 0_g^+ or 0_u^- , just as was found for the isovalent Ni_2 molecule.¹⁰ Accordingly, the excited state symmetry is either 0_u^+ or 0_g^- .

IV. DISCUSSION

As previously discussed, d orbital participation in the chemical bonding is expected to be more significant in the $5d$ series of metal dimers than in either the $3d$ or $4d$ series. To judge the extent of $5d$ bonding in Pt_2 , it is useful to compare its properties to those of Au_2 . The ground state of gold dimer provides a good standard of comparison because the $5d$ orbitals are filled in atomic gold, and therefore do not

TABLE I. Measured and fitted rotational line positions for Pt₂.^a

Line	Measured wave number (cm ⁻¹)	Residual (cm ⁻¹)	Line	Measured wave number (cm ⁻¹)	Residual (cm ⁻¹)
P(1)	18 163.1671	0.0011	P(23)	18 160.2071	0.0044
P(2)	18 163.0987	-0.0002	R(0)	18 163.2877	0.0013
P(3)	18 163.0221	0.0006	R(1)	18 163.3396	0.0006
P(4)	18 162.9412	-0.0005	R(2)	18 163.3838	0.0014
P(5)	18 162.8528	-0.0003	R(3)	18 163.4227	0.0014
P(6)	18 162.7595	-0.0013	R(4)	18 163.4556	0.0012
P(7)	18 162.6598	-0.0021	R(5)	18 163.4808	0.0025
P(8)	18 162.5532	-0.0022	R(12)	18 163.4991	-0.0027
P(9)	18 162.4400	-0.0018	R(13)	18 163.4719	0.0017
P(10)	18 162.3209	-0.0017	R(14)	18 163.4418	0.0028
P(11)	18 162.1941	-0.0000	R(15)	18 163.4079	0.0016
P(12)	18 162.0629	-0.0001	R(16)	18 163.3663	0.0019
P(13)	18 161.9265	-0.0012	R(17)	18 163.3194	0.0014
P(14)	18 161.7851	-0.0034	R(18)	18 163.2664	0.0008
P(15)	18 161.6339	-0.0020	R(19)	18 163.2064	0.0010
P(16)	18 161.4798	-0.0039	R(20)	18 163.1409	0.0006
P(17)	18 161.3144	-0.0007	R(21)	18 163.0690	0.0004
P(18)	18 161.1489	-0.0034	R(22)	18 162.9913	-0.0002
P(19)	18 160.9739	-0.0029	R(23)	18 162.9078	-0.0011
P(20)	18 160.7871	0.0033	R(24)	18 162.8174	-0.0013
P(21)	18 160.5998	0.0038	R(25)	18 162.7225	-0.0032
P(22)	18 160.4058	0.0048	R(26)	18 162.6190	-0.0026

^aRotational lines were fitted to the formula $\nu = \nu_0 + B'J'(J'+1) - B''J''(J''+1)$, providing values of $\nu_0 = 18\,163.231\,70(52)\text{ cm}^{-1}$, $B' = 0.028\,672(11)\text{ cm}^{-1}$, and $B'' = 0.031\,754(12)\text{ cm}^{-1}$. Inversion of these values using the average atomic mass of Pt gives $r_0' = 2.455\,16(47)\text{ \AA}$ and $r_0'' = 2.332\,97(44)\text{ \AA}$.

contribute to the bonding. The bond in gold dimer consists of a single σ -bond arising from the $6s$ - $6s$ atomic orbital overlap.

The measured bond length of Pt₂, $r_0(\text{Pt}_2) = 2.332\,97(44)\text{ \AA}$, is 0.14 \AA shorter than the bond length of Au₂, $r_0(\text{Au}_2) = 2.472\,953(2)\text{ \AA}$.³⁹ This is a significant difference, indicating substantial $5d$ orbital participation in the chemical bond. This agrees with the previous finding that the bond energy of Pt₂, $D_0(\text{Pt}_2) = 3.14 \pm 0.02\text{ eV}$,³⁶ is about 36% greater than that of Au₂, $D_0(\text{Au}_2) = 2.306 \pm 0.005\text{ eV}$.²² Finally, the ground-state vibrational frequency of Pt₂ has been measured to be $215 \pm 15\text{ cm}^{-1}$ in a photoelectron study,³³

$222.46 \pm 0.66\text{ cm}^{-1}$ in a gas-phase dispersed fluorescence study,³⁵ and $197.4 \pm 3.3\text{ cm}^{-1}$ in a matrix isolation luminescence study.³⁴ Employing the gas-phase dispersed fluorescence measurement of $222.46 \pm 0.66\text{ cm}^{-1}$, we find a 16.5% increase in vibrational frequency compared to Au₂, for which $\omega_e'' = 190.9\text{ cm}^{-1}$.¹³ It is perhaps more relevant to compare force constants for these molecules. Again, Pt₂ is found to have a significantly stronger bond, with a force constant 34.5% greater than that of Au₂. By any measure, the $5d$ electrons contribute substantially to the chemical bond in Pt₂, and it may be appropriate to consider Pt₂ as having a double bond.

It is useful to compare the measured Pt₂ bond length to the results of theoretical calculations, so that the required level of theoretical treatment may be ascertained. A detailed complete active space self-consistent field calculation, followed by a first-order configuration interaction with spin-orbit effects included, was performed on Pt₂ in 1987 by Balasubramanian.⁴⁰ The ground state was calculated to be a 0_g^+ state with $r_e = 2.456\text{ \AA}$, $\omega_e = 189\text{ cm}^{-1}$, and $D_e = 1.97\text{ eV}$. While the symmetry of the ground state is in agreement with our findings, the calculated bond length is 0.12 \AA too long and the vibrational frequency is 33 cm^{-1} too low. More importantly, the calculated bond energy represents only 63% of the measured value. Indeed, the calculated results on Pt₂ provide almost identical parameters as those found by the same author in his investigation of Au₂ ($r_e = 2.517\text{ \AA}$; $\omega_e = 193\text{ cm}^{-1}$; $D_e = 2.05\text{ eV}$).⁴¹ This suggests that the theoretical treatment employed for Pt₂ was simply not adequate for the description of $5d$ bonding in this system. It appears that a more extensive treatment of electron

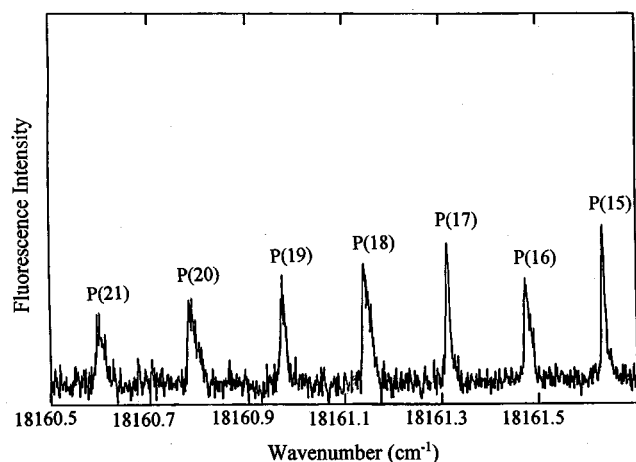


FIG. 2. Magnified view of the high- J P -lines, illustrating the alternation in line width that identifies the ground state of Pt₂ as having $\Omega'' = 0_g^+$ or 0_g^- . The more probable assignment of the ground state is $\Omega'' = 0_g^+$.

correlation and/or relativistic effects is required to properly treat Pt₂.

A more recent calculation by Wang and Carter, employing a correlation-consistent configuration interaction generalized valence bond approach has also been reported, again treating relativistic effects.⁴² The prediction of a ³Σ_g⁻ ground state with $r_e = 2.74 \text{ \AA}$, $\omega_e = 161 \text{ cm}^{-1}$, and $D_e = 1.16 \text{ eV}$ is in even worse agreement with experiment.

A large number of other calculations have been reported on diplatinum.^{43–53} Many of these are more concerned with larger platinum clusters, and consider Pt₂ only in passing.^{43–45} Others state that a “correct description of the Pt–Pt bonding is beyond the scope of our treatment.”⁴⁶ Density-functional calculations have provided bond lengths ranging from 2.25 to 2.58 Å, with bond energies in the range of 2.09–4.92 eV.^{47–50} None of these density functional calculations obtain accurate values of all three parameters r_e , ω_e , and D_e , however. In calculations which provide reasonable bond lengths, for example, the bond energies are greatly overestimated.^{49,50} Likewise, calculations which provide more reasonable bond energy estimates, or which underestimate the bond energy, lead to significant overestimates of the bond length.^{47,48}

These comparisons demonstrate that *ab initio* quantum chemistry is currently unable to provide accurate results for the open 5*d* subshell metal dimers. Proper treatment of such systems remains an important goal for theoretical chemists.

V. CONCLUSION

Using high-resolution laser-induced fluorescence spectroscopy, platinum dimer has been rotationally resolved for the first time. This is the third 5*d* transition metal dimer and the first open 5*d* subshell transition metal dimer to be rotationally resolved. The ground-state Pt₂ rotational constant and bond length have been determined to be $B''_0 = 0.031754(12)$ and $r''_0 = 2.33297(44) \text{ \AA}$, respectively. The ground-state symmetry is either 0_g⁺ or 0_u⁻, which cannot be distinguished in these experiments.

This investigation provides additional evidence of the importance of 5*d* contributions to the chemical bonding in the transition metal dimers of the 5*d* series. These contributions are expected to become even more important as one moves toward the center of the 5*d* period. Rotationally resolved studies of the remaining 5*d* dimers are expected to provide an important point of comparison between theory and experiment. It is our hope that this study of Pt₂ and upcoming studies of other 5*d* dimers will assist theoreticians in the development of methods that are capable of treating the 5*d* transition metals to chemical accuracy.

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