

Dispersed fluorescence spectroscopy of jet-cooled AgAu and Pt₂

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Dispersed fluorescence spectroscopy has been used to study jet-cooled AgAu and Pt₂. Fluorescence resulting from the excitation of five bands of the $A \leftarrow X^1\Sigma^+$ system of AgAu was dispersed, and 51 measured ground state vibrational levels were fit to provide ground state vibrational constants of $\omega_e'' = 198.22 \pm 0.11 \text{ cm}^{-1}$ and $\omega_e''x_e'' = 0.512 \pm 0.002 \text{ cm}^{-1}$. A Franck–Condon calculation was performed using the experimental values of the ground and excited state vibrational frequencies and anharmonicities, providing an estimate of the change in bond length upon excitation of the $A \leftarrow X$ system of $\Delta r_e = 0.214 \pm 0.005 \text{ \AA}$. Fluorescence resulting from four different excitations of Pt₂ was dispersed, providing vibrational constants for the ground and two low-lying excited states. Ground state vibrational constants of $\omega_e = 222.3 \text{ cm}^{-1}$ and $\omega_e x_e = 0.62 \text{ cm}^{-1}$ were obtained, based on the analysis of 16 measured ground state vibrational levels. In addition, a low-lying excited state was located at $T_0 = 2877 \text{ cm}^{-1}$, with $\omega_e = 197 \text{ cm}^{-1}$. This state perturbed the ground state, from which it was deduced that it has the same symmetry as the ground state. A comparison to theoretical calculations suggests that both states have 0_g^+ symmetry. Finally, a metastable state of Pt₂ lying at an unknown energy was determined to have $\omega_e = 211 \text{ cm}^{-1}$, $\omega_e x_e = 0.4 \text{ cm}^{-1}$. © 2001 American Institute of Physics. [DOI: 10.1063/1.1407273]

I. INTRODUCTION

The open d subshells of the transition metals make the electronic structure of transition metal clusters quite complex, even for diatomic molecules. The factors that govern the bonding in these molecules are often complicated and difficult to sort out, with phenomena such as exchange effects, spin–orbit coupling, and ion-pair and d orbital contributions to the bonding varying in importance as one moves from one metal molecule to another. Among the transition metal dimers, the coinage metal dimers are by far the most easily understood. In the ground states of these species the d orbitals are filled and highly contracted such that when two $d^{10}s^1$ atoms combine the bonding is dominated by the s orbitals, which overlap to form a σ^2 bond, giving a ground term of $^1\Sigma_{(g)}^+$ symmetry. The d orbital contributions to the bonding in other transition metal diatomics may be tested by comparisons of the bond energies, bond lengths, and vibrational frequencies to those of the corresponding coinage metal analogs.

In a 1993 review¹ the experimental data and factors affecting the electronic structure in the coinage and nickel group dimers have been discussed. For the nickel group dimers, the open d orbitals both greatly increase the number of low-lying excited electronic states and create the possibility of d orbital contributions to the bonding.^{1,2} To make further comparisons of the chemical bonding in the nickel and copper groups, more experimental data about each group is needed. Toward this end, we have performed dispersed fluorescence studies on the least well known of the coinage metal

diatomics, AgAu, and on the nickel group dimer most likely to display significant d orbital contributions to the bonding, Pt₂.

II. EXPERIMENT

Laser-induced fluorescence spectroscopy was used to investigate supersonically cooled Pt₂ and AgAu molecules. The instrument has been described in detail previously.³ The molecules were formed by pulsed laser ablation (Nd:YAG, 1064 nm) of either a pure platinum metal disk, or an AgAu (2:1) alloy metal disk, followed by supersonic expansion in helium carrier gas (120 psi). The metal targets were prepared by melting in an electric arc furnace a 12 g sample of platinum, or silver and gold metals in a 2:1 Ag: Au molar ratio for the AgAu (2:1) sample. The bond energy of Au₂, $2.305 \pm 0.005 \text{ eV}$,⁴ is much greater than that of Ag₂ ($1.65 \pm 0.03 \text{ eV}$),² and is also somewhat greater than the bond energy of AgAu ($2.06 \pm 0.10 \text{ eV}$).⁵ To decrease the probability of displacement reactions such as $\text{AgAu} + \text{Au} \rightarrow \text{Ag} + \text{Au}_2$ occurring in the cluster formation zone, as well as the cost of the sample, the Ag: Au ratio was increased from the 1:1 ratio, which might be considered optimal for the formation of a 1:1 mixed metal molecule, and a 2:1 Ag: Au alloy was used instead.

The laser ablated metal atoms were entrained in a pulse of helium carrier gas and traveled through a 5.9 cm long \times 2 mm diam channel before expansion into vacuum (2×10^{-4} Torr) through a 2 mm orifice. The resulting jet-cooled molecular beam was crossed at right angles by a Nd:YAG-pumped tunable dye laser beam ($\approx 0.7 \text{ cm}^{-1}$ resolution) 1 cm downstream from the exit orifice to excite the

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molecules. Fluorescence was collected at right angles to the molecular beam and to the excitation laser beam, and dispersed with a 0.25 m monochromator. The intensity of the fluorescence in the case of AgAu permitted the monochromator slits to be narrowed to widths in the range of 0.10–0.20 mm, corresponding to a resolution of 3–7 Å. The weaker fluorescence signal for Pt₂ required a somewhat greater slit width of 0.35 mm, corresponding to a resolution of 12 Å.

In addition to diatomic AgAu, a large quantity of Au₂ was produced when the 2:1 Ag:Au sample was used. Although diatomic gold has intense transitions in the frequency range of the AgAu transitions that were excited in this study, its spectrum is sufficiently sparse⁶ that fluorescence originating from Au₂ could be readily identified. Diatomic silver has no transitions in the frequency range probed here, so we are confident that the dispersed fluorescence data collected for AgAu does truly originate from this molecule.

III. RESULTS

A. Dispersed fluorescence spectra of AgAu

Fluorescence resulting from excitation of the 0–0, 2–0, 3–0, 11–0, and 18–0 bands of the $A \leftarrow X^1\Sigma^+$ system of AgAu was dispersed, and the 51 observed vibronic levels of the $X^1\Sigma^+$ ground state were fitted to extract ground state vibrational constants. The $v'-0$ bands of the $A \leftarrow X^1\Sigma^+$ system have been previously recorded at a resolution limited by the probe dye laser (0.7 cm⁻¹). This resolution is much better than that obtained in the present dispersed fluorescence experiments, so the previously reported $v'-0$ band frequencies were used to calibrate the present data. Table I lists the band positions observed in fluorescence, along with the residuals from the fit. From this fit, values of $\omega_e'' = 198.22 \pm 0.11$ cm⁻¹, and $\omega_e''x_e'' = 0.512 \pm 0.002$ cm⁻¹ were obtained for the $X^1\Sigma^+$ ground state of AgAu. Here, as in the remainder of this paper, the error limits that are reported are the 1 σ error limits generated by a standard least-squares fitting procedure.⁷ They are undoubtedly somewhat too optimistic, but it is unclear to the authors how to devise more reliable error limits. In any case, the resulting vibrational frequency is in surprisingly good agreement with the estimated value of 196 cm⁻¹ obtained in the previous resonant two-photon ionization (R2PI) study by the analysis of isotope shifts.⁶

Figures 1 and 2 display the fluorescence resulting from the excitation of the 2–0 and 3–0 bands, respectively. Two nodes are clearly visible in the fluorescence intensity pattern displayed in Fig. 1 for excitation of the $v' = 2$ level of the A state, and three nodes are observed in the fluorescence from $v' = 3$ displayed in Fig. 2. These intensity patterns confirm the assignment of the vibrational levels previously reported⁶ and provide sufficient data for a Franck–Condon estimate of the change in bond length upon electronic excitation. The Franck–Condon analysis was performed using Morse potentials for the upper and lower states, with the potentials given by the measured ground and excited state⁶ vibrational frequencies and anharmonicities. A comparison of the measured and calculated Franck–Condon factors for the 2– v'' and 3– v'' bands, corrected for the wavelength-dependent grating

efficiency and photomultiplier quantum efficiency, provides an estimate of the bond length change upon electronic excitation as 0.214 ± 0.005 Å.

In a review of the nickel and copper group diatomic metals, it was noted that the measured bond lengths of Cu₂, Ag₂, Au₂, CuAg, and CuAu may be reproduced to an accuracy of 0.012 Å by assigning covalent bond radii of 1.107, 1.263, and 1.233 Å to Cu, Ag, and Au, respectively.¹ These covalent radii predict a ground state bond length of 2.496 Å for AgAu.¹ On this basis the A state bond length may be estimated as 2.71 Å, with a probable error of 0.02 Å.

The great intensity of the $A \leftrightarrow X^1\Sigma^+$ system in AgAu is revealed by the short fluorescence lifetime reported previously, $\tau \approx 39$ ns.⁶ Assuming that the A state decays entirely by fluorescence to the ground state, this implies an absorption oscillator strength of $f \approx 0.08$ for this system,⁶ making it very strong indeed. It is the intensity of this band system that permitted the slits to be narrowed on the monochromator to give improved resolution, while simultaneously permitting a large number of vibrational bands to be observed. To obtain the best possible values for the vibrational constants of the ground state, the 18–0 band was excited in the hope of observing fluorescence to high vibrational levels of the ground state. Figure 3 demonstrates that this was indeed the case, with fluorescence to $v'' = 53$ observed. This greatly reduced the uncertainty in the fitted ground state vibrational constants ω_e'' and $\omega_e''x_e''$.

B. Dispersed fluorescence spectra of Pt₂

Dispersed fluorescence spectra were also recorded for four excitations of Pt₂. The resulting fluorescence band positions are reported in Table II. Three of the four excitation bands, at 17 041, 17 522, and 18 167 cm⁻¹, led to resonance fluorescence to the same lower state. Sixteen vibrational levels were observed for this state, which were analyzed to provide $\omega_e = 222.26 \pm 0.31$ cm⁻¹ and $\omega_e x_e = 0.62 \pm 0.02$ cm⁻¹. The excitation features at 17 041 and 17 522 cm⁻¹ correspond to excitations of the 7–0 and 10–0 bands of System XVI, as reported in our previous publication,⁸ while the excitation at 18 167 cm⁻¹ represents a new feature that cleanly fits into the progression labeled System XIX. Although System XIX is an intense band system, poor Franck–Condon factors prevented us from recognizing the band at 18 167 cm⁻¹ as a member of this system in our original paper.⁸ With the identification of this as the 0–0 band of this system, the previously published vibrational numbering must now be revised by 1 unit, giving corrected spectroscopic constants of $T_0 = 18 162.7$ cm⁻¹, $\omega_e' = 196.6$ cm⁻¹, and $\omega_e'x_e' = 2.41$ cm⁻¹. Based on the intensity of the observed transitions at 17 041, 17 522, and 18 167 cm⁻¹, we believe that the lower state of these bands is the ground state of Pt₂.

Figure 4 displays the dispersed fluorescence spectrum that is obtained following the excitation of Pt₂ at 18 167 cm⁻¹, which is now assigned as the 0–0 band of System XIX. The spectrum is contaminated by scattered excitation laser light at 18 167 cm⁻¹, but otherwise the Franck–Condon pattern is almost as expected for excitation of a 0–0 band in which a significant change in bond length occurs. A gradual

TABLE I. Band positions of the $A \rightarrow X^1\Sigma^+$ system of AgAu.^a

Band	Wave number	Residual ^b	Band	Wave number	Residual ^b	Band	Wave number	Residual ^b
0-12	19688.6	-1.4	3-11	20217.0	2.4	11-5	22192.8	-4.6
0-11	19872.9	-3.1	3-10	20401.9	0.3	11-4	22385.5	-5.0
0-10	20068.2	5.3	3-7	20969.7	1.1	11-3	22579.0	-5.6
0-9	20249.5	-1.4	3-6	21160.7	1.1	11-2	22776.7	-3.1
0-8	20436.6	-3.3	3-5	21353.8	2.1	11-1	22972.5	-3.4
0-7	20627.1	-2.8	3-3	21742.0	3.1	11-0	23169.5	-3.6
0-6	20824.7	3.7	3-2	21933.2	-0.9	18-53	14777.9	-8.3
0-5	21017.0	4.0	3-1	22129.3	-1.0	18-51	15076.0	0.9
0-4	21204.1	-2.0	3-0	22334.6	7.2	18-50	15228.2	7.1
0-3	21399.0	-1.3	11-40	16091.1	6.9	18-49	15354.7	-13.4
0-2	21594.1	-1.3	11-39	16241.9	0.4	18-48	15510.2	-5.9
0-1	21790.3	-1.3	11-38	16406.8	7.1	18-47	15658.0	-7.1
0-0	21993.7	4.9	11-37	16566.6	7.6	18-45	15961.4	-5.0
2-21	18284.4	-6.6	11-36	16724.9	5.5	18-44	16122.0	3.5
2-20	18459.4	-8.3	11-35	16877.3	-3.4	18-43	16270.6	-1.0
2-19	18641.2	-4.2	11-34	17046.5	3.4	18-42	16430.0	4.2
2-18	18819.4	-4.8	11-33	17219.2	12.7	18-38	17063.5	10.7
2-17	19004.9	0.9	11-32	17377.4	6.5	18-31	18190.8	1.4
2-16	19183.4	-1.3	11-31	17541.8	5.5	18-30	18355.7	-0.2
2-15	19364.7	-1.9	11-30	17701.0	-1.8	18-28	18697.7	5.8
2-14	19546.2	-3.3	11-29	17872.8	2.5	18-27	18865.4	4.0
2-13	19733.4	0.0	11-28	18035.3	-3.5	18-25	19202.8	-0.8
2-12	19919.7	1.4	11-27	18212.2	3.8	18-24	19374.6	-1.6
2-11	20106.0	1.8	11-26	18369.1	-9.8	18-22	19723.2	-1.3
2-10	20292.2	1.1	11-25	18546.6	-3.9	18-21	19898.7	-1.5
2-9	20478.5	-0.6	11-24	18726.6	3.4	18-19	20252.3	-2.3
2-8	20670.6	2.5	11-23	18904.4	7.6	18-18	20434.0	0.6
2-7	20861.1	3.0	11-22	19070.2	-1.2	18-17	20608.8	-4.4
2-6	21050.5	1.3	11-21	19244.7	-2.4	18-16	20787.2	-6.8
2-4	21439.9	5.5	11-20	19427.9	4.1	18-14	21156.6	-2.1
2-3	21629.1	0.6	11-19	19599.1	-2.5	18-13	21346.0	3.4
2-2	21826.1	2.5	11-18	19773.7	-6.6	18-12	21532.0	4.5
2-1	22023.9	4.1	11-17	19961.5	1.4	18-11	21715.6	2.2
2-0	22223.2	6.2	11-16	20140.5	-0.4	18-10	21910.8	10.5
3-22	18223.6	-2.2	11-15	20329.9	7.1	18-9	22085.0	-3.3
3-20	18572.9	-5.3	11-14	20503.2	-2.4	18-8	22278.9	1.6
3-19	18750.0	-5.9	11-13	20689.6	0.1	18-7	22464.0	-3.3
3-18	18931.5	-3.2	11-12	20868.8	-5.6	18-6	22663.2	4.8
3-17	19112.9	-1.5	11-11	21058.6	-1.7	18-5	22847.7	-2.8
3-16	19293.2	-2.0	11-10	21245.9	-1.4	18-4	23041.4	-2.2
3-15	19475.2	-1.9	11-9	21434.8	-0.5	18-2	23430.7	-2.1
3-14	19659.4	-0.5	11-8	21617.9	-6.4	18-1	23636.7	7.7
3-12	20035.9	7.1	11-6	21998.8	-6.5	18-0	23828.6	2.4

^aBands listed above were fit to the standard equation $\nu = T_0 + \omega'_e v' - \omega'_e x'_e (v'^2 + v') - \omega''_e v'' + \omega''_e x''_e (v''^2 + v'')$, yielding fitted values for the ground state of $\omega''_e = 198.22 \pm 0.11 \text{ cm}^{-1}$, and $\omega''_e x''_e = 0.512 \pm 0.002 \text{ cm}^{-1}$. The band positions of the $v' = 0$ bands, taken from the higher resolution resonant two-photon ionization (R2PI) spectrum, were used to calibrate the dispersed fluorescence data. The constants obtained in the previous R2PI study (Ref. 6) for the excited state were $T_0 = 21\,995.97 \pm 0.86 \text{ cm}^{-1}$, $\omega'_e = 115.73 \pm 0.18 \text{ cm}^{-1}$, and $\omega'_e x'_e = 0.74 \pm 0.01 \text{ cm}^{-1}$.

^bDefined as $\nu - \nu_{\text{calc}}$.

increase in intensity of the $0-v''$ fluorescence bands is observed with increasing v'' , followed by a decrease as the vibrational wave functions get out of phase. Two additional vibronic features are evident in this spectrum, however, at $15\,280$ and $15\,086 \text{ cm}^{-1}$. These represent fluorescence to the $v'' = 0$ and $v'' = 1$ levels of a new electronic state lying 2877 cm^{-1} above the ground state. The $v'' = 0-7$ levels of this new electronic state are also observed in fluorescence excited at $17\,041 \text{ cm}^{-1}$, and this allows the vibrational frequency of the 2877 cm^{-1} state to be determined as $\omega_e = 197.3 \pm 1.8 \text{ cm}^{-1}$.

The dispersed fluorescence spectrum displayed in Fig. 4

clearly shows that the $v'' = 0, 1$ levels of the new electronic state perturb the $v'' = 12-15$ vibrational levels of the ground state, causing these levels to gain intensity in fluorescence. The mixing of vibronic levels of the 2877 cm^{-1} state with those of the ground state implies that both of these electronic states have the same Hund's case (c) symmetry, since the Hamiltonian matrix elements that could cause mixing of states having different Ω values would be expected to be less than 1 cm^{-1} in magnitude for the rotational levels populated in our molecular beam, and would lead to negligible state mixing. An examination of the low-lying electronic states calculated by Balasubramanian⁹ then suggests that both the

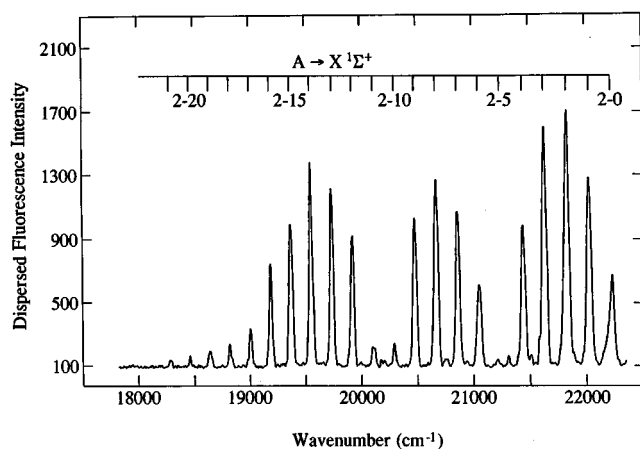


FIG. 1. Dispersed fluorescence resulting from excitation of the 2–0 band of the $A \leftarrow X^1\Sigma^+$ system of AgAu.

ground state and the 2877 cm^{-1} state are of 0_g^+ symmetry, because the ground state is calculated to be of 0_g^+ symmetry and another state of this symmetry is calculated to lie 3064 cm^{-1} higher in energy, in quite good agreement with the 2877 cm^{-1} energy difference reported here. Other pairs of states of the same symmetry include a pair of 4_u states calculated to lie at 1074 and 8259 cm^{-1} (a separation of 7185 cm^{-1}), a pair of 1_u states calculated at 3556 and 8180 cm^{-1} (a separation of 4624 cm^{-1}), a pair of 2_g states calculated at 5838 and 11286 cm^{-1} (a separation of 5448 cm^{-1}), and a pair of 1_g states calculated at 5935 and 8282 cm^{-1} (a separation of 2347 cm^{-1}).⁹ Although the experimental data reported here provide no information about the symmetry of the ground and 2877 cm^{-1} state by themselves, a comparison with the theoretical calculations certainly suggests that both states are of 0_g^+ symmetry. For this reason, this assignment is tentatively adopted in the remainder of this paper. Proof of this assignment will require a rotationally resolved study of the Pt_2 molecule, which is currently in progress.

The fourth vibronic excitation investigated, at 16453 cm^{-1} , corresponds to the 3–0 band of our previously published System XVII.⁸ This excitation results in weaker fluo-

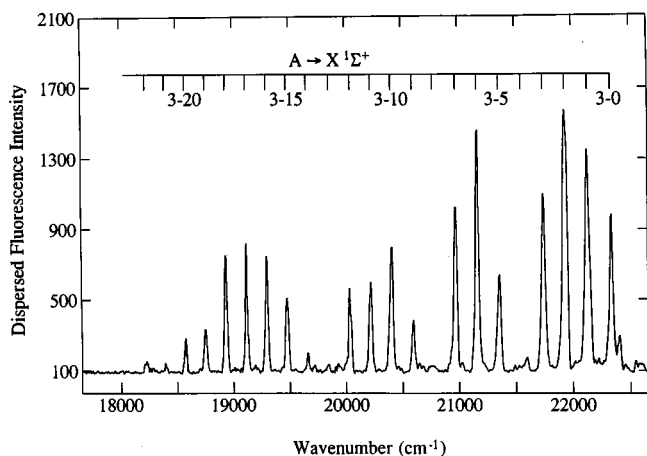


FIG. 2. Dispersed fluorescence resulting from excitation of the 3–0 band of the $A \leftarrow X^1\Sigma^+$ system of AgAu.

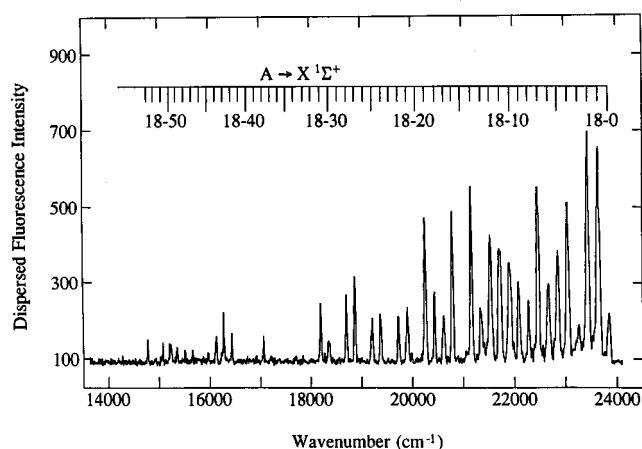


FIG. 3. Dispersed fluorescence resulting from excitation of the 18–0 band of the $A \leftarrow X^1\Sigma^+$ system of AgAu.

rescence than is found for the other three excitations, and produces resonant fluorescence to a state with $\omega_e = 210.85 \pm 0.59\text{ cm}^{-1}$, $\omega_e x_e = 0.42 \pm 0.03\text{ cm}^{-1}$, as displayed in Fig. 5. Evidently, a metastable electronic state of Pt_2 is populated in our jet-cooled sample, and excitation out of this metastable state is responsible for the 16453 cm^{-1} band. Based on the relative weakness of this band, combined with the fact that three out of the four excitations studied originate from the state with $\omega_e = 222.26 \pm 0.31\text{ cm}^{-1}$, we believe that the state with $\omega_e = 222.26 \pm 0.31\text{ cm}^{-1}$ is the ground state of Pt_2 . Spectroscopic constants for the three observed low-lying electronic states of Pt_2 , labeled the $X0_g^+$, A , and $[2.9]0_g^+$ states, are collected in Table III.

IV. DISCUSSION

A. AgAu

The dispersed fluorescence study of AgAu has provided the first direct measurement of the ground state vibrational constants of this molecule, resulting in $\omega_e'' = 198.22 \pm 0.11\text{ cm}^{-1}$ and $\omega_e'' x_e'' = 0.512 \pm 0.002\text{ cm}^{-1}$. The measured value of $\omega_e'' = 198.22 \pm 0.11\text{ cm}^{-1}$ is in surprisingly good agreement with the previous rough estimate based on isotopic shift data of 196 cm^{-1} .⁶ This compares to values of 173 – 209 cm^{-1} reported in theoretical calculations on this molecule.^{10–14} The 198 cm^{-1} vibrational frequency found for AgAu is comparable to the ground state vibrational frequencies of the corresponding homonuclear diatomics, $^{107}\text{Ag}_2$ and $^{197}\text{Au}_2$, which possess values of ω_e'' of 192.4 and 190.9 cm^{-1} , respectively.¹ While AgAu might be expected to have a vibrational frequency close to the average of those of Ag_2 and Au_2 , it is instead found to have a slightly larger vibrational frequency than either of its homonuclear counterparts. This anomalous result becomes more understandable when the vibrational force constants are compared. These fall in an order that is in agreement with the bond energies, namely 1.17×10^5 , 1.61×10^5 , and $2.11 \times 10^5\text{ dynes/cm}$ for Ag_2 , AgAu, and Au_2 , respectively. Indeed, the vibrational force constant for AgAu ($1.61 \times 10^5\text{ dynes/cm}$) is in almost exact agreement with the average of the Ag_2 and Au_2 force constants, which is $1.64 \times 10^5\text{ dynes/cm}$.

TABLE II. Bands of Pt₂ observed in dispersed fluorescence.

Excitation frequency (cm ⁻¹)	System	Band	Measured frequency (cm ⁻¹)	Residual (cm ⁻¹) ^c	Excitation frequency (cm ⁻¹)	System	Band	Measured frequency (cm ⁻¹)	Residual (cm ⁻¹) ^c				
16 453	System XVII→A ^a	3-0	16 453.6	5.8	17 041	System XVI→[2.9]0 _g ^{+b}	7-5	13 178.4	5.5				
		3-1	16 237.3	-0.5			7-6	12 974.6	-1.7				
		3-2	16 029.2	0.6			7-7	12 779.5	-0.2				
		3-3	15 813.9	-6.4			17 521	System XVI→X0 _g ^{+b}	10-0	17 521.2	-1.2		
		3-4	15 612.7	-0.2					10-1	17 299.5	-1.8		
		3-6	15 197.9	-2.6					10-2	17 079.1	-2.4		
		3-7	14 996.0	0.4					10-3	16 861.7	-1.3		
		3-8	14 788.3	-3.2					10-4	16 647.0	1.4		
		3-9	14 588.9	0.6					10-5	16 433.2	3.7		
		3-11	14 187.4	3.0					10-6	16 218.5	3.9		
		3-12	13 982.8	-1.0					10-7	15 996.8	-4.2		
		3-13	13 787.5	3.6					10-8	15 790.5	1.9		
		3-15	13 386.0	-0.8					18 167	System XIX→X0 _g ^{+b}	0-0	18 166.8	3.6
		3-16	13 194.9	5.3			0-1	17 940.0			-2.2		
		3-17	12 994.7	1.6			0-2	17 724.3			1.9		
		3-18	12 797.6	0.1			0-3	17 501.8			-2.0		
		3-19	12 596.8	-6.0			0-4	17 287.4			0.9		
		17 041	System XVI→X0 _g ^{+b}	7-0			17 040.9	0.7			0-5	17 068.6	-1.8
				7-1			16 818.1	-1.1			0-6	16 854.9	-0.6
7-2	16 599.0			-0.4	0-7	16 640.4	-1.4						
7-4	16 165.9			2.4	0-8	16 431.6	2.2						
7-5	15 948.4			1.0	0-9	16 219.4	1.2						
7-13	14 262.2			-0.5	0-11	15 795.6	-3.9						
7-15	13 851.5			-2.4	0-12	15 591.5	-0.5						
7-16	13 650.4			-0.9	0-13	15 384.2	-1.6						
7-17	13 451.1			1.1	0-14	15 180.6	-0.1						
System XVI→[2.9]0 _g ^{+b}	7-0			14 158.8	1.0	0-15	14 980.1	3.2					
	7-1			13 960.7	0.1	0-16	14 775.7	1.4					
	7-2			13 763.6	0.1	System XIX→[2.9]0 _g ^{+b}	0-0	15 280.5	-1.8				
	7-3			13 565.5	-1.0		0-1	15 086.8	1.8				
	7-4			13 365.9	-3.7								

^aThis excitation is believed to originate from a low-lying electronic state that was not quenched in the molecular beam. This band was fit to the equation $\nu = T - \omega_e''v'' + \omega_e''x_e''(v''^2 + v'')$, with T corresponding to the excitation frequency of 16 453 cm⁻¹. This excitation corresponds to the 3-0 band of System XVIII, as defined in Ref. 8.

^bBands were first shifted by subtracting the excitation frequency to provide the absolute energy of the lower level of the emission band. Bands terminating in the same lower state were fit in a global fit to the standard equation $\nu = T_0 - \omega_e''v'' + \omega_e''x_e''(v''^2 + v'')$, with T_0 providing the term energy of the low-lying state relative to $v = 0$ of the ground state. Again, bands are identified according to the band system labels given in Ref. 8.

^cDefined as $\nu - \nu_{\text{calc}}$.

The Franck-Condon determination of the bond length change upon electronic excitation in the $A \leftarrow X^1\Sigma^+$ system, given as $\Delta r = 0.214 \pm 0.005$ Å, provides the first experimental information relating to the bond length of this molecule. Based on the frequency of the $A \leftarrow X^1\Sigma^+$ band system and the Knudsen effusion measurement of the AgAu bond energy, it has been suggested that the A electronic state correlates to the Ag $4d^{10}5s^1$, $^2S_{1/2} + Au 5d^96s^2$, $^2D_{5/2}$ excited state of the separated atoms, and corresponds to a $4d_{\text{Ag}}^{10}5d_{\text{Au}}^9(^2D_{5/2})\sigma^2\sigma^{*1}$ electronic configuration.⁶

Further, it has been suggested that this electronic configuration is strongly mixed with the $^1\Sigma^+$ ion-pair state that results when Ag⁺, $4d^{10}5s^0$, 1S is combined with Au⁻, $5d^{10}6s^2$, 1S .⁶ Both of these excited configurations are expected to lead to an increase in bond length and a decrease in vibrational frequency when the molecule is excited from the ground state to the A state. The $4d_{\text{Ag}}^{10}5d_{\text{Au}}^9(^2D_{5/2})\sigma^2\sigma^{*1}$ electronic configuration corresponds to the excitation of an electron from a nonbonding $5d_{\text{Au}}$ orbital to an antibonding σ^{*} orbital, reducing the bond order from 1.0 to 0.5. Similarly,

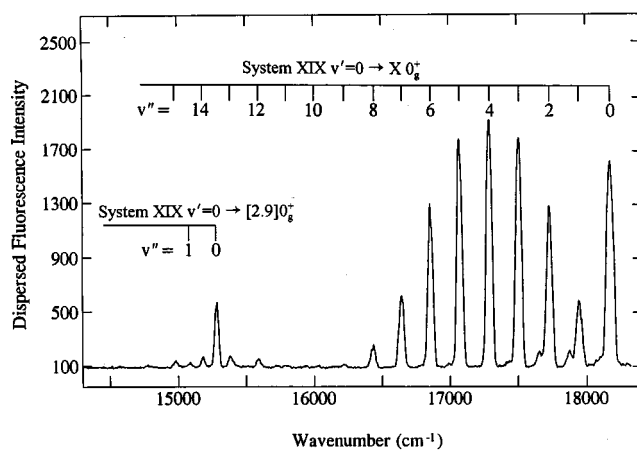


FIG. 4. Dispersed fluorescence resulting from excitation of Pt₂ at 18 167 cm⁻¹, which is now assigned as the 0-0 band of the previously reported System XIX. In addition to fluorescence to the ground state, fluorescence to the [2.9]0_g⁺ state is also observed. The apparent intensity at the excitation frequency is increased by scattered laser light, and small features to the red of the 0-1 and 0-2 bands are caused by transitions excited in jet-cooled Pt₂ by amplified spontaneous emission in the pump dye laser.

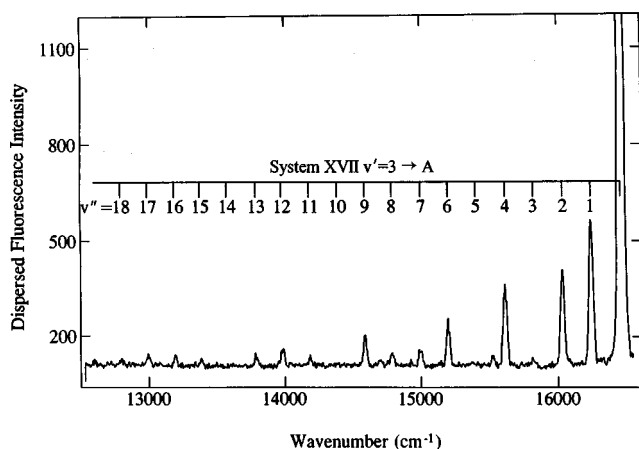


FIG. 5. Dispersed fluorescence resulting from excitation of Pt₂ at 16 453 cm⁻¹, which corresponds to the 3–0 band of the previously reported System XVII. This excitation is thought to originate from an unquenched low-lying state. This signal was very weak, and the apparent intensity at the excitation frequency is due mostly to scattered laser light.

the ion pair state corresponds to a $4d_{Ag}^{10}5d_{Au}^{10}\sigma^1\sigma^{*1}$ electronic configuration with a nominal bond order of 0. The significant bond lengthening upon electronic excitation, as deduced from the Franck–Condon analysis, and the decrease in vibrational frequency from 198.22 ± 0.11 to 115.73 ± 0.18 cm⁻¹,⁶ are in complete agreement with these configurational assignments.

B. Pt₂

The dispersed fluorescence study of Pt₂ has provided values of the vibrational constants of the ground state of $\omega_e'' = 222.26 \pm 0.31$ cm⁻¹ and $\omega_e''x_e'' = 0.62 \pm 0.02$ cm⁻¹. This represents a significant improvement over the value of $\omega_e = 215 \pm 15$ cm⁻¹ obtained in a previous photoelectron spectroscopic study of Pt₂⁻,¹⁵ and is significantly higher than the value of 197.4 ± 3.3 cm⁻¹ obtained in a luminescence spectrum of mass-selected Pt₂ in a cryogenic argon matrix.¹⁶ Our measured value of ω_e for the ground state is also approximately 18% greater than that predicted in the most detailed *ab initio* investigation reported to date.⁹ The ground state vibrational frequency measured for Pt₂ in the present study is approximately 17% greater than that of Au₂,¹ suggesting that the 5*d* orbitals may be actively engaged in chemical

TABLE III. Low-lying states of Pt₂ observed in dispersed fluorescence.

State	Relative energy (cm ⁻¹)	ω_e (cm ⁻¹)	$\omega_e x_e$ (cm ⁻¹)
[2.9]0 _g ^{+a,b}	2876.8 ± 10.1	197.3 ± 1.8	0.06 ± 0.22
A ^b	^c	210.85 ± 0.59	0.42 ± 0.03
X0 _g ^{+b}	0	222.26 ± 0.31	0.62 ± 0.02

^aBelieved to correspond to the state labeled V in Ref. 15.

^bThe Ω values of all experimentally known states of Pt₂ are presently unknown. However, the ground state borrows intensity from the [2.9] state, indicating that they have the same symmetry. A comparison to theoretical calculations of Ref. 9 suggests that both are 0_g⁺ states.

^cThe term energy of the low-lying state with $\omega_e = 210.85 \pm 0.59$ cm⁻¹ is unknown.

bonding in diatomic platinum. This suggestion also finds support in the enhanced bond energy of Pt₂ (3.14 ± 0.02 eV)⁸ as compared to Au₂ (2.305 ± 0.005 eV).⁴

In addition to this measurement of the ground state vibrational constants, two low-lying states of Pt₂ were observed in the present dispersed fluorescence experiments. The [2.9]0_g⁺ state was observed in fluorescence after excitation from the ground state of the molecule. This enabled its term energy to be accurately measured as 2876.8 ± 10.1 cm⁻¹. Its vibrational constants were determined as $\omega_e' = 197.3 \pm 1.8$ and $\omega_e'x_e' = 0.06 \pm 0.22$ cm⁻¹. This is in close agreement with the state designated as band V in the photoelectron spectroscopic study, which was listed as occurring at a term energy of 2912 ± 81 cm⁻¹, with $\omega_e' = 205 \pm 25$ cm⁻¹.¹⁵ Again, a significant improvement in the precision of these parameters has been achieved in the present study.

The second low-lying state identified in this study remained populated in the jet-cooled Pt₂ beam for a distance of at least 1 cm downstream of the expansion orifice. It was only from the fact that fluorescence to the state from which the absorption originated gave a vibrational frequency different from the ground state that this low-energy state was recognized.

Fluorescence was only observed in this instance back down to the state from which the absorption originated, so it is impossible to know the energy of this state relative to the ground state. Because neither the term energy nor the Ω value of this state are known, the state is only labeled as the A state in Table III. The only experimental knowledge of this state that is available from the present experiments are its vibrational constants, $\omega_e = 210.85 \pm 0.59$ cm⁻¹ and $\omega_e x_e = 0.42 \pm 0.03$ cm⁻¹. The vibrational frequency reported for this state lies within the error limits of all of the states reported in the photoelectron study of Pt₂⁻,¹⁵ and therefore no meaningful comparison to the photoelectron study can be made. Likewise, the errors in the vibrational frequencies calculated for Pt₂ in Balasubramanian's study are undoubtedly large enough to prevent the unique identification of this state by a comparison to theory.⁹

In the first gas-phase investigation of Ni₂, which is isovalent with Pt₂, a similar low-energy state remained populated in the jet-cooled molecular beam and was mistakenly assigned as the ground state.¹⁷ In the case of Ni₂, this metastable state was characterized by $\Omega = 4$, while the true ground state was subsequently found to possess either $\Omega = 0_g^+$ or 0_u^- .¹⁸ It was suggested that the large change in Ω between this metastable state and the ground state prevented its relaxation via collisions with helium during the supersonic expansion.¹⁸ It is quite possible that a similar effect is occurring in the case of Pt₂, and that the unquenched electronic state observed in the present dispersed fluorescence studies possesses a value of Ω that differs substantially from that of the ground state. According to the most detailed *ab initio* calculations available, the Pt₂ ground state is of $\Omega = 0_g^+$ symmetry, and the lowest-energy excited state possesses $\Omega = 5_u^-$.⁹ Clearly, one would expect it to be difficult to quench a high angular momentum state with $\Omega = 5_u^-$ to a state of $\Omega = 0_g^+$ symmetry, since this requires the complete reversal of the angular momentum on one of the 5*d*⁹ platinum

cores. If the *ab initio* calculation is correct, the $\Omega = 5_u$ state that is calculated to have a vibrational frequency of 193 cm⁻¹ and to lie 614 cm⁻¹ above the ground $\Omega = 0_g^+$ state⁹ is a strong candidate for this unquenched excited state of Pt₂. Further experiments, particularly rotationally resolved ones, will obviously be required to test this possibility.

V. CONCLUSIONS

Dispersed fluorescence from the $A-X^1\Sigma^+$ system of AgAu has been used to establish the $X^1\Sigma^+$ ground state vibrational constants of $\omega_e'' = 198.22 \pm 0.11$ cm⁻¹, and $\omega_e''x_e'' = 0.5122 \pm 0.0023$ cm⁻¹. This vibrational frequency corresponds to a vibrational force constant of $k = 1.61 \times 10^5$ dynes/cm, almost exactly midway between the force constants of Ag₂ and Au₂. In addition, a Franck-Condon analysis of the fluorescence intensities has provided an estimate of the change in bond length upon electronic excitation of $\Delta r_e = 0.214 \pm 0.005$ Å. This is consistent with our previous assignment of the A state as a mixed configuration consisting of the $4d_{Ag}^{10}5d_{Au}^9\sigma^2\sigma^{*1}$ and $4d_{Ag}^{10}5d_{Au}^{10}\sigma^1\sigma^{*1}$ ion-pair character.

Dispersed fluorescence from four different excitations of Pt₂ has been used to establish the vibrational constants of the Pt₂ ground state as $\omega_e'' = 222.26 \pm 0.31$ cm⁻¹ and $\omega_e''x_e'' = 0.62 \pm 0.02$ cm⁻¹. The increased vibrational frequency of Pt₂ as compared to Au₂ ($\omega_e = 190.9$ cm⁻¹) suggests the possibility of significant 5d orbital contributions to the bonding in diatomic platinum. In addition to the ground state, a low-lying excited state located 2876.8 ± 10.1 cm⁻¹ above the ground state has been characterized by vibrational constants of $\omega_e' = 197.3 \pm 1.8$ and $\omega_e'x_e' = 0.06 \pm 0.22$ cm⁻¹. Finally, another low-energy state of Pt₂ has been identified, with vibrational constants of $\omega_e = 210.85 \pm 0.59$ cm⁻¹ and $\omega_e x_e = 0.42 \pm 0.03$ cm⁻¹. This last state was found to be incompletely quenched in the jet-cooled molecular beam, and its term energy could not be determined in the present set of experiments.

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