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Luminescence Spectra of Mass-Selected Pt_2 in Argon

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We report on an observation of the luminescence and luminescence excitation spectra of platinum dimers in an argon matrix. Samples were produced by sputtering from a metal target, followed by mass selection of dimer ions and codeposition with electrons and argon on a cold substrate. Emission is induced by pumping into the 800−815 nm region with a titanium−sapphire laser. Five sharp, intense spectral lines are observed, with an average spacing of 197.4 ± 3.3 cm^{-1} and origin at 10 730.5 ± 0.6 cm^{-1}. A much weaker vibrational progression in the emitting state gives $\omega_e' = 179.2 \pm 0.6$ cm^{-1}. Fluorescence excitation profiles were also obtained and are well simulated using data from previous gas-phase measurements. A rather wide separation of the origins of excitation and emission indicates rapid intersystem crossing in the excited state, with the possibility that our emission is not to the dimer ground state.

I. Introduction

The dimer of platinum has been the subject of several recent experimental and theoretical studies. Jansson and Scullman[1] obtained an optical absorption spectrum in rare gas matrices. Photoelectron spectra[2] as well as resonant two-photon ionization spectra[3] have been published, and a complete active space SCF calculation has been carried out by Balasubramanian.[4] Our interest stems from resonance Raman spectral studies of various transition metal dimers such as Co_2,[5] Ni_2,[6] Re_2,[7] Rh_2,[8] and Ru_2.[9] Of particular interest in these studies is the degree to which d-orbitals contribute to bonding. Accurate values for the ground state force constants derived from the Raman frequencies have been invaluable in these determinations. The only previous ground state data for Pt_2 comes from the photoelectron spectra of Ho *et al.*[2] from which a vibrational frequency of 215 (15) cm^{-1} was obtained. In order to enable careful comparisons of force constants across the periodic table, we initiated an attempt to obtain a more accurate value for this parameter by searching for resonance Raman spectra, utilizing our mass-selected ion cluster deposition technique. Although no Raman spectrum was observed, we did obtain a sharp, intense luminescence spectrum, on which we report here.

II. Experimental Section

The CCNY cluster deposition source has been described in detail elsewhere.[10] Briefly, an argon ion beam (typically 15 mA at 25 keV) sputters a cooled, platinum target (Alfa Aesar, 99.9%). The sputtered products are extracted by electrostatic lenses, mass-selected using a Wien filter, bent by 10° to eliminate neutrals, and then guided into the deposition region. Platinum dimer (or atomic) ions were then codeposited with argon gas and electrons onto a ∼14 K substrate, composed of a CaF_2 plate. Ion currents under soft landing conditions could be measured on a Faraday plate in the deposition region and were Pt^+ (48 nA), Pt_2^+ (7 nA), and Pt_3^+ (3 nA). Prior to deposition, the selected ions were simultaneously slowed to 10 eV by a surrounding "Faraday cage". Matrices were grown at about 4−6 μm/h with an Ar:metal ratio of approximately 10^4:1. Emission spectra were recorded using the visible output of an argon ion laser (Spectra Physics model 2045) pumping a titanium−sapphire laser. Scattered light was collected at 90° into a Spex 1877E 0.6 m Triplemate Spectrometer and detected by a liquid nitrogen cooled CCD detector (Spex model "Spectrum One") with DM3000R software.

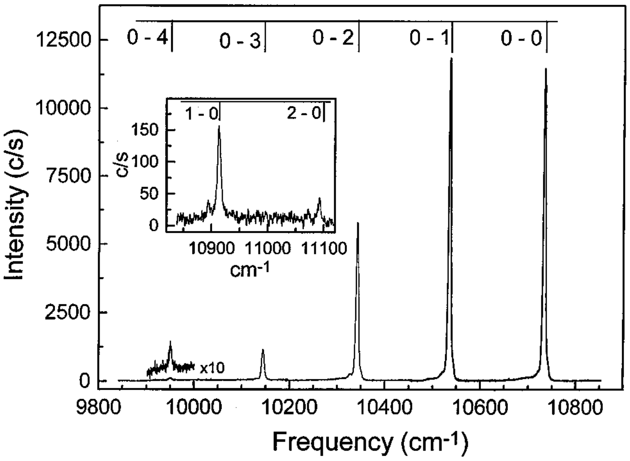

Figure 1. Laser fluorescence spectrum of Pt_2 in an argon matrix (sample content 45 nA-h) showing progressions in the lower state ($v' = 0 \rightarrow v''$) and (inset) in the emitting state ($v' \rightarrow v'' = 0$). The excitation wavelength is 815.4 nm for both spectra.

III. Results and Analysis

No absorption features, useful as a guide for finding *resonance* Raman (or other) spectra, were observed. However, earlier work by Jansson and Scullman[1] and by Taylor *et al.*[3] indicated that Pt_2 absorbs in the 800−900 nm region, thus providing a starting point in a search for spectra. Although no Raman transitions were observed, we found several sharp fluorescence features (see Figure 1) when pumping in the 800−815 nm region. The measured fluorescence frequencies are given in Table 1 and were obtained by averaging data at 38 different excitation wavelengths (22 in the case of the 0−4 transition). The Figure 1 spectrum consists of a fairly strong progression ($v' = 0 \rightarrow v''$) in the lower state vibrational frequency (average $\omega_e'' = 197.4 \pm 3.3$ cm^{-1}) and (see inset) a much weaker progression ($v' \rightarrow v'' = 0$) in the emitting state

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TABLE 1: Measured Transition Frequencies for Pt_2 in Argon, with Estimated Uncertainties (1 standard deviation) in Parentheses

assignment ($v'-v''$)	frequency (vacuum cm^{-1})	$\Delta G(v'' + {}^1/_2)$	assignment ($v'-v''$)	frequency (vacuum cm^{-1})	$\Delta G(v' + {}^1/_2)$
0−0	10 730.5(6)	198.3(1)	0−0	10 730.5(6)	179.6(7)
0−1	10 532.2(6)	201.6(16)	1−0	10 910.1(4)	178.8(6)
0−2	10 330.6(19)	195.3(2)	2−0	11 088.9(4)	
0−3	10 135.3(18)	194.4(11)			
0−4	9 940.9(6)				

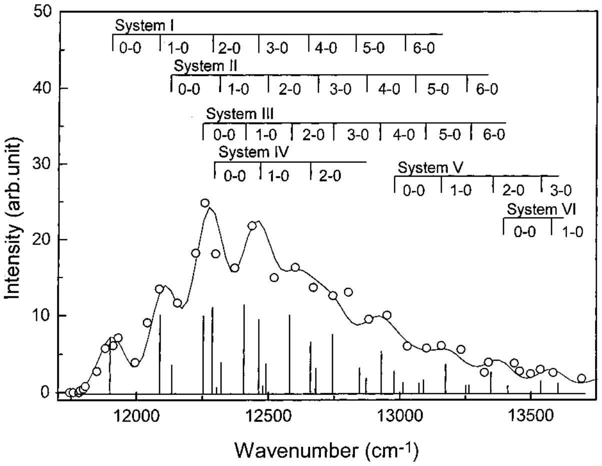

Figure 2. Emission excitation profile (filled circles) of the 0−0 band of Pt_2 in argon. Also shown is a fit to the matrix profile (solid line) using gas-phase data (shifted by 503 cm^{-1}, see text) from ref 3. Each transition was given a Gaussian line shape with a width of 103 cm^{-1} and an intensity as shown in the stick spectrum.

with an average frequency of $\omega_e' = 179.2 \pm 0.6$ cm^{-1}. No sequence features were observed.[11] Isotope effects were not observed, as (predicted) splittings in the fluorescent spectra are only about 0.5 cm^{-1}, i.e., much less than the approximately 5 cm^{-1} half-widths of these lines. Annealing of samples to 25 K led to no change in the observed spectra. One further emission occurs at 10 852 (2) cm^{-1}, but this is largely excited between 12 500 and 13 000 cm^{-1}, which is an entirely different fluorescence excitation profile from that (see below) of the transitions shown in Figure 1. The average lower state frequency is $\omega_e'' = 197.4 \pm 3.3$ cm^{-1}, which is within experimental error of the ground state frequency (215 ± 15 cm^{-1}) reported by Ho *et al.*[2] Our lower state vibrational separations do not fall off monotonically, but rather $\Delta G(v'' + {}^1/_2)$ *increases* between $v'' = 1$ and 2 before decreasing for $v'' = 3$ and 4. Although this effect is small (and might be argued to arise from measurement errors), this pattern of vibrational energy separations is quite robust, persisting in all of the several methods that we used for analyzing the data. Accordingly, it seems likely that the lower state vibrational levels are perturbed by a nearby state, which is not too surprising for, as pointed out by Taylor *et al.*,[3] "with 157 molecular states present within 0.2 eV of the lowest dissociation threshold, it is likely that perturbations between these states will be significant." The Table 1 data suggest a perturbing state with origin near $v'' = 2$ (i.e., at approximately 400 cm^{-1}) and a vibrational frequency close to that of the perturbed state.

Figure 2 shows the measured (filled circles) fluorescence excitation profile (emission intensity *vs* excitation wavelength) for the 0−0 band of Pt_2. Excitation profiles for the 0−1 through 0−3 transitions are essentially identical to the Figure 2 result. Sufficient detail is observed to indicate a vibrational progression, but the spacing is slightly uneven indicating a possible overlap of several electronic transitions. This is consistent with the high-resolution gas-phase absorption spectrum of Pt_2,[3] where several overlapping systems (denoted I, II, etc.) were observed in a region corresponding to our matrix spectrum. In order to compare our results with those in the gas phase, we carried out a simulation of the matrix excitation spectra using the data for systems I−VI given in Table 1 of ref 3. Since the lowest gas-phase transition (the 0−0 band of system I) occurs at 11 426 cm^{-1}, whereas our observed origin is 11 929 cm^{-1} (i.e., 503 cm^{-1} to the blue), all the ref 3 transitions were shifted by a constant 503 cm^{-1}, but the ω_e and $\omega_e x_e$ values determined from the high-resolution spectra were maintained. Each line was given a Gaussian profile with a width of 103 cm^{-1}, as determined from the lowest frequency line of the matrix spectrum, which is relatively isolated from the rest. The relative intensities of the first few transitions *within* each of systems I−IV were kept the same as those in the gas-phase spectrum (Figure 1 of ref 3), but it was found necessary to adjust the relative intensities *among* each of these systems. Thus, we found the best fit with system III most intense, rather than I or II as observed in the gas phase.[12] The stick spectrum in Figure 2 gives the best fit intensities for each of the contributing lines, and the solid line is the overall result of our simulation. The correspondence between the two data sets is surprisingly good, indicating the possibility that the absorption spectrum in the matrix arises from the same transitions as are observed in the gas phase. However, we have made the rather questionable assumption of a constant matrix shift for the electronic origins of each of the six systems involved. Given the relatively broad line widths and the fact that these systems have roughly comparable vibrational spacings, other fits with varying matrix shifts are also possible.

IV. Discussion

The origin of absorption (excitation) differs from that of emission by nearly 1200 cm^{-1}, which indicates that the first excited state in absorption is not the same as that responsible for emission. The fact that ω_e' for our emitting state (179.2 cm^{-1}) does not obviously correspond to any of the ω_e' of systems I−VI in the gas-phase analysis[3] supports this idea. Since no absorption from the ground state to the emitting state is observed, it is most likely that this process is formally forbidden. The lack of direct emission in the matrix from the states of systems I−VI indicates that radiationless processes depopulating these states is rapid by comparison with emission lifetimes.

For molecules with weak spin−orbit coupling, where spin may be regarded as a good quantum number, we would presume that the multiplicity of the emitting state (populated by intersystem crossing) differs from that of the ground state and from any of the excited states involved in absorption. However, for Pt_2 spin−orbit coupling is expected to be very large, and only Ω ($=\Lambda + \Sigma$) is a good angular momentum quantum number. Although the assignment of Ω for the dimer ground state is not certain, calculations by Balasubramanian[4] predict this to be ${}^3\Sigma_g^-(0_g^+)$ arising largely from two δ_u^2 configurations (total weight 62%) plus two δ_g^2 configurations (total weight 32%). If this is correct, then our results can only be explained by the existence of a manifold of states to which spectroscopic transitions are forbidden from the ground state, but which are accessible by means of rapid radiationless transitions. Balasubramanian predicts a low lying state 5_u, which is only 614 cm^{-1} above the ground state (predicted vibrational frequency: 193 cm^{-1}), and another state of symmetry 4_u at 1074 cm^{-1} (predicted vibrational frequency: 240 cm^{-1}). Both these states are candidates for assignment as our lower state, although the 5_u is more likely due to its proximity to the predicted ground state and the fact that the predicted vibrational frequency more closely matches ours. If either 4_u or 5_u corresponds to our lower state, then the matrix-mediated intersystem crossing would involve a rather significant change in Ω.

Recently Pinegar *et al.*[13] have reported on the gas-phase fluorescence of jet-cooled Pt dimers. These authors found a ground state vibrational frequency of 222.5(7) cm^{-1}, and a nearby excited state at 2884(3) cm^{-1} whose vibrational frequency is 197.0(3) cm^{-1}. In addition they discovered a metastable state with a vibrational frequency of 210.9(8) cm^{-1} but were unable to determine the position of this state with respect to the ground state. Their ground state vibrational frequency differs by 25 cm^{-1} from that of our lower state, a shift too large to be explained by matrix effects. There are several possible explanations for this discrepancy. One is that we are not observing emission to the ground state but only to the lowest state in a different manifold, which then rapidly converts to the actual ground state by radiationless transitions. In this case, our lower state must lie within 1200 cm^{-1} of the ground state. Another possibility is that Pinegar *et al*. are not observing emission to the ground state. Since their studies are carried out in the gas phase at low pressures, there is a possibility that their initial sample is in a metastable state (which should be plentiful in this molecule) as opposed to the true ground state. Indeed a metastable state was observed when exciting close to the expansion source, and even though their apparent ground state was seen to remain much farther downstream, this does not rule out the existence of an even longer lived metastable state. The third possibility is that Pinegar *et al*. are indeed observing the true ground state, but the dimer ground state in an argon matrix is different from that in the gas phase. Although our measured frequency is almost identical to that of the gas-phase excited state at 2884 cm^{-1}, this is not the most probable candidate for our lower state as this would imply that matrix effects cause an energy decrease of at least 1683 cm^{-1}, which is unlikely. Furthermore, transitions from the manifold of systems I−VI to the 2884 cm^{-1} state are clearly allowed in the gas phase, while they are forbidden to the state which we observe. It is conceivable that our lowest state coincides with the metastable state observed by Pinegar *et al*., but the electronic origin of this state is unknown. In any case, there is still not sufficient experimental evidence to distinguish which of the above explanations for the discrepancy between the gas-phase and matrix results is most probable.

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(11) The 0−0 through 0−2 transitions show a weak, but relatively sharp feature (most evident for 0−2, see Figure 1) displaced to the red of the principal band by a constant 11 ± 2 cm^{-1}, plus a broader (and still weaker) emission displaced (also to the red) by 34 ± 4 cm^{-1}. These features are not consistent (as predicted by the Table 1 data) with either sequence structure or matrix site effects (which should be displaced proportional to v''). Likely assignments are a librational mode and a phonon side band (see also ref 9) for the 11 and 34 cm^{-1} features, respectively.

(12) System II of the gas-phase spectrum (ref 3) may, in fact, be a vibrational hot band: M. Morse, private communication.

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