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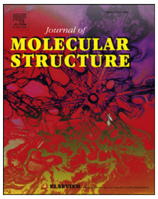

X-ray absorption study of platinum and palladium atoms in argon matrices: Evidence for platinum in a substitutional site and a short Pd–Ar interaction

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ABSTRACT

The Pt L_3-edge X-ray absorption spectrum of Pt atoms generated in a hollow cathode sputtering device and trapped in an Ar matrix yielded a Pt–Ar distance of 3.78(4) Å with a coordination number of ca. 12 which confirms the evidence from electronic absorption spectroscopy that Pt atoms occupy a substitutional site in the Ar lattice. These data also yield a van der Waals radius for Pt atoms of 1.90 Å. The Pd K-edge X-ray absorption spectrum of sputtered Pd atoms trapped in an Ar matrix is radically different to that for Pt atoms. The analysis reveals a much shorter Pd–Ar distance of 2.53(3) Å with a low coordination number close to 1, together with an "atomic" EXAFS like spectrum with no significant oscillations indicating the absence of any well defined nearest neighbours. On annealing to 25 K, the 2.53(3) Å interaction essentially disappears to leave the "atomic" spectrum. The featureless "atomic" spectrum is associated with Pd $^1S_0$ atoms in an argon substitutional site, or other site such as a grain boundary with high disorder. The short Pd–Ar distance of 2.53(3) Å is consistent with Pd atoms with a $^1S_0$ atomic ground state in an interstitial octahedral site, the formation of a $PdAr_n$ exciplex with a short Pd–Ar distance, or the formation of a more formal palladium argon compound such as $PdAr_2$. Although it is not possible to be definitive, the most likely carrier of the short Pd–Ar distance is a $PdAr_n$ exciplex. What is clear is that this work has identified a short Pd–Ar interaction for the first time.

1. Introduction

The electronic absorption spectra of platinum atoms in argon matrices [1,2] are very similar to those of the $^3D_3$ ($5d^96s^1$) ground state in the gas phase [3], apart from consistent blue-shifts of 2000–3000 cm^{-1}. The data from krypton matrices are similar, but there is the possibility of a specific interaction between platinum and xenon [2]. Nickel atoms have a $^3F_4$ ($3d^84s^2$) ground state in the gas phase [3], but are known to co-exist as both $^3D_3$ and $^3F_4$ ground states in noble gas (Ng) matrices, with their relative populations changing on photolysis and annealing [4–9]. The history of palladium atoms in noble gas matrices has been much more chequered and controversial. The initial spectra reported by Mann and Broida [10] with bands at 33690 cm^{-1} (296.8 nm, 4.177 eV), 31950 cm^{-1} (313.0 nm, 3.961 eV), 31270 cm^{-1} (319.8 nm, 3.877 eV) and 29600 cm^{-1} (337.8 nm, 3.670 eV) had large red-shifts of *ca.* 6500 cm^{-1} from the gas phase data [3]. This was thought to be odd at the time as it is much more usual for matrix atomic data to be blue-shifted from the gas phase data due to the repulsive interaction between the metal atom and the matrix host. Klotzbücher and Ozin [2] subsequently showed that the spectral features identified by Mann and Broida [10] were in fact due to $Pd(N_2)_n$ complexes. Whilst the presence of nitrogen might be due to an air leak, Klotzbücher and Ozin thought it was much more likely to be due to chemisorbed impurities on the metal films which required careful outgassing, and we have observed similar phenomena in our experiments as well. The genuine spectra of Pd atoms in argon and krypton matrices had intense features between 40000 and 50000 cm^{-1} (250–200 nm, 4.96–6.20 eV) [2] which were in reasonable agreement with the gas phase values [3] but with relatively large blue-shifts of 3500–6300 cm^{-1} (0.43–0.78 eV). As for platinum atoms, the xenon data were subtly different and could indicate an interaction between Pd and Xe. Klotzbücher and Ozin [11] reinvestigated the palladium atom noble gas systems as whilst

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the peak positions were in reasonable agreement with the atomic data and could be assigned to transitions from the $^1S_0$ ($4d^{10}$) ground state to the $^1P_1$, $^3D_1$, $^3F_2$ and $^3P_1$ excited states arising from the $4d^95p^1$ configuration, the intensities were more complex than expected. In particular, the spectra consisted of relatively intense high energy triplets, despite two of these transitions being spin-forbidden with low gas-phase oscillator strengths [3]. In Kr matrices, the doublet of triplets observed on deposition was replaced by just one triplet after annealing to 25 K, implying the loss of one unstable matrix site. Differential population of the two matrix sites was also observed for palladium atoms in argon when deposited at 10–12 K and 20–25 K. A new weak feature at lower energy (37700 cm^{-1} (265 nm, 4.68 eV)) due to Pd_2 was also observed either after annealing or after deposition at higher temperatures.

Grinter and Stern [12,13] observed very similar absorption spectra for palladium atoms in argon to those of Klotzbücher and Ozin [2,11]. When they recorded MCD spectra for Pd atoms with scanning from long to short wavelengths, no MCD signal was detected below 40000 cm^{-1} (250 nm, 4.96 eV). However, if the instrument was returned rapidly to lower energy (*ca.* 26700 cm^{-1} (375 nm, 3.31 eV) and the MCD spectrum remeasured, a new very strong and rapidly decaying (half-life of the order of seconds) MCD signal was observed in the 27800–34500 cm^{-1} (360–290 nm, 3.44–4.28 eV) region. This process could be repeated, with only minor changes in the spectrum. The process was also observed after photolysis with other 40000–50000 cm^{-1} (250–200 nm, 4.96–6.20 eV) sources. As the process could be regenerated many times, it was interpreted to be due to a long-lived excited state of Pd, rather than a photochemically generated aggregate or complex. Attempts to identify absorption bands associated with the transient state were unsuccessful. The strength of the post photolysis MCD signal indicated that the species responsible for it was paramagnetic, and Grinter and Stern thought that the most likely state for the transient MCD signal was $^3F_4$ ($4d^85s^2$) which lies *ca.* 25000 cm^{-1} (400 nm, 3.10 eV) above the $^1S_0$ ground state in the gas phase [12,13].

Schrittenlacher et al. carried out absorption, emission and emission-yield experiments in the 16000–80000 cm^{-1} (620–125 nm, 2–10 eV) energy range on Pd atoms isolated in Ne, Ar, Kr and Xe matrices [14]. The high energy experiments (32000–80000 cm^{-1} (313 nm–125 nm, 4–10 eV)) made use of the BESSY synchrotron radiation source, whereas the lower energy (16000–32000 cm^{-1} (620–310 nm, 2–4 eV)) experiments were laboratory based. In Ne matrices, the absorption spectrum remained very similar on annealing up to 9 K, however in Ar matrices the simultaneous decrease of all of the lines at 15 K and 20 K, and their almost complete loss by 28 K, indicated that there was only one trapping site, which was in contradiction to the work of Klotzbücher and Ozin who had proposed two sites [2,11]. The loss of the atomic signals on annealing was believed to be associated with the production of thermally induced aggregates, but no specific absorption bands were identified. Fluorescence and emission yield spectra were also investigated for Ne, Ar, Kr and Xe matrices. For Ne matrices, excitation was carried out at 40800 cm^{-1} (245 nm, 5.06 eV), 41700 cm^{-1} (240 nm, 5.17 eV) and 47200 cm^{-1} (212 nm, 5.85 eV) with the same spectrum being observed for the last two. In Ne matrices strong, sharp emission lines at 27400 cm^{-1} (365 nm, 3.40 eV), 28600 cm^{-1} (350 nm, 3.55 nm) and 30200 cm^{-1} (331 nm, 3.75 eV) were observed (the latter was very weak with 40800 cm^{-1} (245 nm, 5.06 eV) excitation), whereas in Ar, Kr and Xe only broad emission features around 20000 cm^{-1} (500 nm, 2.5 eV) were observed. When the absorption spectrum was recorded during irradiation at 40800 cm^{-1} (245 nm, 5.06 eV) at least five new lines were observed, which disappeared once the light source was turned off. From these experiments, it was concluded that the spectra were due to Pd atoms in uniform trapping sites. The large blue-shift (from gas to matrix) was taken to indicate a strong repulsive interaction between the matrix and the Pd excited states. As a result of extensive mixing of the states, all 12 of the transitions from the $4d^{10}$ ground state to the $4d^95p^1$ levels become allowed by matrix interactions, thus explaining the complexity of the spectra observed, and making assignments using the usual AMCOR (atom to matrix correlation) approach impossible. They interpreted the transient absorption features observed in Ne matrices as being due to a long lived excited state of the Pd atom, most likely to be $^3D_1$ so the observed transitions are from $4d^95s^1$ to the triplet levels of $4d^95p^1$. On the basis of all of their results, and that the radius of Pd is only 0.55 Å in its $^1S_0$ ground state [15], they concluded that Pd atoms were located in interstitial octahedral sites in Ne, Ar and Kr and in interstitial tetrahedral sites in Xe. The interstitial locations explained the large blue-shifts due to the increased repulsion, as well as the unusually high thermal mobility of the atoms.

Ozin and Garcia-Prieto subsequently published two papers [16,17] which came to a radically different conclusion to that of Schrittenlacher et al. [14]. The absorption spectra of Ozin and Garcia-Prieto [16] were essentially the same as those observed in the previous studies [2,11,12,14], and as observed previously [14] annealing to 12–25 K resulted in significant reduction in the intensity of the peaks in the spectrum. Their emission spectra of Pd atoms in solid argon using excitation at 39500 - 46500 cm^{-1} (253 - 215 nm, 4.90 - 5.77 eV) distinguished two sets of bands [16], one consisting of several relatively narrow lines in the 16700–33300 cm^{-1} (600–300 nm, 2.07–4.13 eV) region, and a second set consisting of only one broad band at 20600 cm^{-1} (486 nm, 2.55 eV). The excitation spectra [16] consisted of two regions, one from 37000 to 50000 cm^{-1} (270–200 nm, 4.59–6.20 eV), which corresponded to the absorption spectra, and a second one from 28600 to 34500 cm^{-1} (350–290 nm, 3.54–4.27 eV), which did not have a counterpart in the absorption spectrum (apart from a very weak band around 33300 cm^{-1} (300 nm, 4.13 eV)). The excitation spectra associated with the 20600 cm^{-1} (486 nm, 2.55 eV) emission band was the only one which did not show excitation bands in the 28600–34500 cm^{-1} (350–290 nm, 3.55–4.28 eV) region. From these detailed investigations they concluded that the 38500–50000 cm^{-1} (260–200 nm, 4.77–6.20 eV) absorption spectrum of Pd atoms in an Ar matrix is the result of the superposition of the ΔJ allowed transitions from the $^1S_0$ ground state found in the gas phase, together with a $^3D_3$ metastable state with a relatively long lifetime that is populated during spectral acquisition. Luminescence data indicated the presence of at least two different Pd atom environments, with different deactivation pathways. One of these sites contains the $^3D_3$ metastable state generated indirectly by efficient photolysis of the $^1S_0$ ground state. The other site contains Pd atoms with a broad 20600 cm^{-1} (486 nm, 2.55 eV) emission band. In addition, laser induced luminescence provided evidence for permanent $^3D_3$ ($4d^95s^1$) atoms in a third site [16].

Garcia-Prieto and Novaro [18] then built on the earlier work of Ozin and Garcia-Prieto [16,17] which they summarised as inferring that the Pd atoms in solid argon matrices occupy three main trapping sites. Two of these contain Pd atoms with the same $^1S_0$ ($4d^{10}$) electronic ground state as gas-phase Pd atoms, and the third site contains Pd in a $^3D_3$ ($4d^95s^1$) electronic state, that is 6564 cm^{-1} (0.8138 eV) above the $^1S_0$ state in the gas phase. For one of the sites that contains $^1S_0$ Pd, there was a very efficient deactivation process that yielded a $^3D_3$ ($4d^95s^1$) metastable state with a 2.2 min lifetime. Garcia-Prieto and Novaro [18] used the earlier Ar matrix work of Ozin and Garcia-Prieto [16,17] and carried out complementary absorption, emission, excitation and laser induced luminescence

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