

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 L₃-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. This contains 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 ¹S₀ 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 ¹S₀ 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 PdAr₂. 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.

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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 $2000 - 3000 \text{ cm}^{-1}$. 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 33700 cm^{-1} (297 nm, 4.18 eV), 31900 cm^{-1} (313nm, 3.96 eV), 31300 cm^{-1} (320 nm, 3.88 eV) and 29600 cm^{-1} (338 nm, 3.67 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 $\text{Pd}(\text{N}_2)_n$ 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} [2] which were in reasonable agreement with the gas phase values [3] but with relatively large blue-shifts of $3500 - 6300 \text{ cm}^{-1}$. 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 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}) 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 $27800 - 34500\text{ cm}^{-1}$ (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 $40000 - 50000\text{ cm}^{-1}$ (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} (625 – 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 – 125nm, 4 – 10 eV)) made use of the BESSY synchrotron radiation source, whereas the lower energy (16000 – 32000 cm^{-1} (625 – 313 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} 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 $4d^9 5p^1$ 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 distinguished two sets of bands [16], one consisting of several relatively narrow lines in the $16700 - 33300 \text{ cm}^{-1}$ (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 $37000 - 50000 \text{ cm}^{-1}$ (270 – 200 nm, 4.60 – 6.20 eV), which corresponded to the absorption spectra, and a second one from $28600 - 34500 \text{ cm}^{-1}$ (350 – 290 nm, 3.55 – 4.28 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 $28600 - 34500 \text{ cm}^{-1}$ (350 – 290 nm, 3.55 – 4.28 eV) region. From these detailed investigations they concluded that the $38500 - 50000 \text{ cm}^{-1}$ (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) 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 minute 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 experiments on Pd in Kr and Xe matrices. They concluded that there were three distinctive optical spectra implying three distinct trapping environments. Two of these have a 1S_0 ($4d^{10}$) ground state, and one a 3D_3 ($4d^95s^1$) ground state. They used the estimates of the radius of the 1S_0 as 0.55 \AA [15] and 3D_3 state as 1.35 \AA [17], to imply the 1S_0 states would be found in the interstitial tetrahedral (Xe) or interstitial octahedral (Ar, Kr) sites, and the 3D_3 in either a less restricted octahedral site or a substitutional site.

Therefore, from the matrix electronic spectra there are two contradictory positions, one where the absorption peaks are due to a single octahedral interstitial site [14] and one where there are three different sites, with two different electronic configurations [16-18]. Many of these sites are not detected in absorption, but only observed in excitation and emission experiments. However, many of the reports indicate the presence of a photochemically accessible excited state, variously assigned as 3F_4 [12, 13], 3D_1 [14] or 3D_3 [16-18].

Taketsugu et al. have carried out calculations on PdAr, PdAr₂ and PdAr₃ using CCSD(T) with counterpoise corrections and relativistic effects [19], which built on their previous work on PtAr and PtAr₂ [20]. Their results are summarised in Table 1, and from these it is clear that the binding energies for the diargon linear compounds are much higher than for the monoargon compounds, and those for platinum are significantly higher than those for palladium. The bond lengths follow the trend of the binding energies so that those for the monoargon compounds are longer than the diargon compounds, and those for platinum are shorter than those for palladium. PdAr₂ and PtAr₂ were calculated to be linear, and PdAr₃ trigonal planar. The binding mechanism involves s-d_σ hybridisation, which is most effective in linear geometries. In the case of Pt-Ar complexes they showed that the triplet potential energy curves were repulsive, but the singlet state was stabilised giving rise to $^1\Sigma^+$ PtAr and $^1\Sigma_g^+$ PtAr₂, and that the triplet and singlet potential energy curves crossed at some Pt-Ar interatomic distance. No potential energy curve crossings of the singlet and triplet states were found for Pd-Ar complexes and therefore only the 1S_0 state is stabilised by noble gas binding giving rise to $^1\Sigma^+$ PdAr, $^1\Sigma_g^+$ PdAr₂ and $^1A_1'$ PdAr₃. Pt with a $5d^96s^1$ configuration has a 3D_3 ground state, with an 1S_0 excited state 6140 cm^{-1} (0.7613 eV) above this [3]. In contrast, Pd has a $4d^{10}$ configuration with a 1S_0 ground state.

Table 1. Summary of calculated interatomic distances r_e , binding energies BE_e and IR active harmonic wavenumbers ω for palladium and platinum argon compounds [19, 20].

	PdAr	PdAr ₂	PdAr ₃	PtAr	PtAr ₂
$r_e / \text{\AA}$	2.797	2.544	2.901	2.383	2.352
$BE_e / \text{kJ mol}^{-1}$	3.9	16.8	11.6	30.3	82.2
ω / cm^{-1}	53.9	154.0		184.7	233.2

The previously reported experimental data have all used electronic absorption, emission, excitation and laser induced luminescence to investigate the electronic structure of Pd atoms in noble gas matrices. However, the geometrical structure has been implied. One of the few techniques that yields direct structural information from cryogenic matrices is X-ray absorption spectroscopy (XAS) [21]. This is usually divided into X-ray absorption fine structure (XAFS) which covers the whole spectrum, X-ray absorption near edge structure (XANES) which deals with the features around the edge, and extended X-ray absorption fine structure (EXAFS) which describes the oscillations after the edge. Therefore, given the contentious nature and interpretation of the Pd/Ar matrix electronic spectra, we decided to use matrix isolation X-ray absorption spectroscopy as a direct structural probe to investigate the location of Pt and Pd atoms within a solid argon matrix. As X-ray absorption spectroscopy is an averaging technique, it is important to produce only atomic species, rather than mixtures containing higher oligomers. We have shown previously [22, 23] that an Ar⁺ hollow cathode sputtering device is an excellent source of matrix isolated atoms with no appreciable dimer formation, and this was the approach used for the XAS study presented here. Thermal evaporation was used to check the consistency of the Pd UV-vis spectra.

Experimental

The palladium atoms were generated via either thermal evaporation or sputtering. For thermal evaporation palladium wire (0.25 mm 99.99%, Goodfellow) was wound within and around a tantalum support wire (0.5 mm, 99.99% Goodfellow) and heated using *ca.* 40 A at 1 V. A copper disc with a 6 mm hole in it was placed between the filament and deposition window to reduce the heat load, and collimate the beam of atoms. The palladium and platinum atoms generated in a hollow-cathode sputtering device used a design based on that of Green and Reedy [24, 25], and is shown in Figure 1.

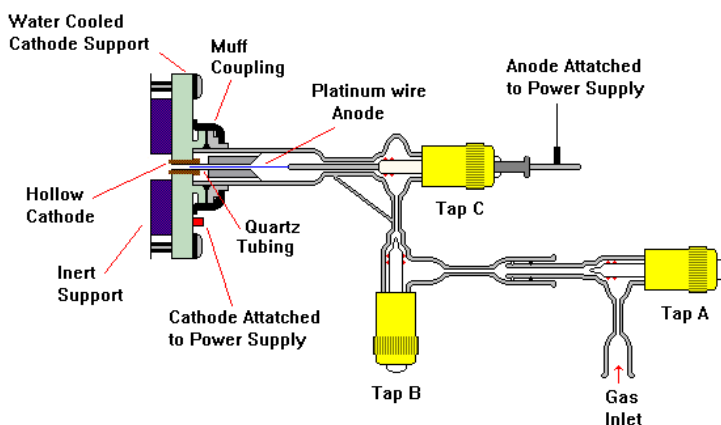


Figure 1. Hollow cathode sputtering device.

The hollow cathode consisted of a copper screw (Goodfellow, 99.95% OFHC) with a 2.5 mm hole machined through the centre and the whole assembly was mounted in a water cooled and electrically isolated metal flange to which the glass vacuum jacket containing the anode and gas inlet system was connected via a muff coupling. To convert this to a palladium or platinum hollow cathode, a tube of the appropriate metal was made by rolling a 25 mm x 25 mm x 0.025 mm foil (Goodfellow, 99.99%) and inserting this inside the hollow copper screw. This resulted in a liner approximately 0.1 mm thick. The platinum anode (0.4 mm

Goodfellow, 99.99%) was mounted on an adjustable drive (Tap C) (modified Young's PTFE tap) and held centrally in the platinum cathode by a thin quartz tube. The flow rate of the discharge gas through the sputtering device was controlled by PTFE capillary (Young's) valves Tap A and B and the flow was sufficient for it to act as the matrix gas as well. The sputtering device was operated at *ca.* 600 – 700 V and 15 mA by an Ion-Tech DC power supply. With pressures in the vacuum chamber of the order 1×10^{-7} mbar, a gas flow producing a chamber pressure of around 2×10^{-5} mbar was found to be required to sustain the gas discharge. Deposition times were generally 2 – 5 minutes for the UV-Vis-NIR experiments. The relatively large volumes of gas required to sustain the discharge meant that for the UV-Vis-NIR experiments deposition times longer than around 10 minutes had a deleterious effect on the quality of the spectra with significant scattering at short wavelengths. For the XAFS experiments the deposition time was 10 – 15 min for Pt and 20 – 25 min for Pd.

The UV-Vis-NIR spectra were recorded using a Varian Cary 5E spectrometer with a vacuum shroud equipped with CaF₂ windows and a APD DE204SL Displex closed cycle helium cryostat (base temperature of *ca.* 10 K) with a CaF₂ deposition window. The X-ray absorption spectra were collected at the Daresbury Laboratory SRS operating at 2 GeV with circulating currents of *ca.* 200 mA using the same cryostat but with a vacuum chamber equipped with beryllium windows. The Pt L₃-edge X-ray absorption spectra were collected in fluorescence mode (Canberra 13 element SSD detector) on station 9.2 using a Si(220) double crystal monochromator detuned by *ca.* 50 % to remove harmonic contamination. The Pd K-edge spectra were collected in fluorescence mode (Canberra 30 element SSD) on station 16.5 using a Si(311) double crystal monochromator, with harmonic rejection achieved by mirrors. Between eight and fourteen one hour spectra were collected for each matrix sample, averaged

and calibrated using the first maximum in the first derivative of the Pt L₃-edge of Pt foil (11564.0 eV) or Pd K-edge of Pd foil (24350.0 eV) [26]. Background subtraction was carried out using PAXAS [27] by fitting the pre-edge region to a quadratic polynomial, subtracting this from the data and approximating the atomic component of the post-edge region with a high (typically sixth) order polynomial. This approximation was optimized in order to minimize the low-*r* features in the Fourier transforms by an iterative process, although it should be noted that atomic XAFS features may be expected in this part of the FT especially in the case of platinum [28]. Fitting of the experimental data was carried out with EXCURV98 [29] making use of single and multiple scattering curved wave theory, a von-Barth ground state and a Hedin-Lundqvist exchange potential.

Results and Discussion

Platinum atoms in solid argon

The electronic absorption spectrum of the products of sputtering a platinum hollow cathode with argon, and trapped in solid argon is shown in Figure 2.

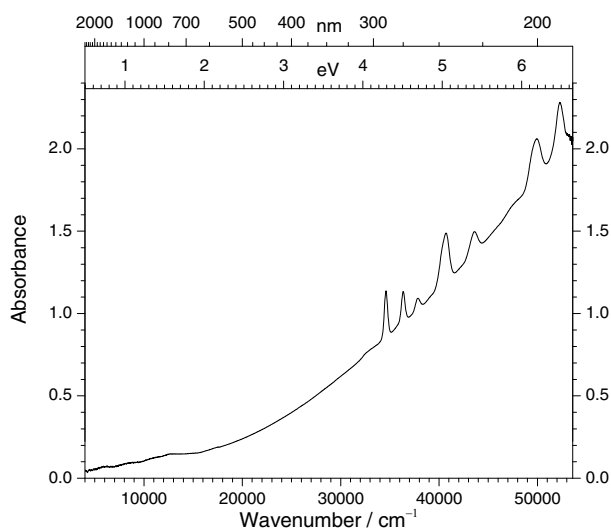


Figure 2. Electronic absorption spectrum of platinum atoms in solid argon produced by Ar⁺ sputtering of platinum hollow cathode.

Other than the steeply rising baseline, which is a consequence of the amount of gas required to sustain the discharge in the sputtering device, this spectrum is essentially identical to that published for Pt atoms previously [1, 2] and shows no evidence for Pt₂ [30]. The peak positions, and previous assignments are given in Table 2. Therefore, as noted previously, the hollow cathode sputtering source is an excellent source of platinum atoms [22].

Table 2. Peak positions (cm⁻¹) and assignments for Pt atoms in an argon matrix.

Pt atoms produced by sputtering ^(a)	Pt atoms produced by thermally evaporation ^(b)	Excited state configuration (based on a 5d ⁹ 6s ¹ , ³ D ₃ ground state) ^{(b)(c)}
34610	34722	5d ⁹ 6p ¹
36360	36496	5d ⁹ 6p ¹

37860	38022	5d ⁸ 6s ¹ 6p ¹
40300 (sh)		
40720	40983	5d ⁹ 6p ¹
43610	43859	5d ⁸ 6s ¹ 6p ¹
49940	50251	5d ⁹ 6p ¹
52290	52083	5d ⁸ 6s ¹ 6p ¹

(a) this work, (b) reference [2], (c) the terms and levels are not given for all of these states in the original atomic data compilation [3].

The Pt L₃-edge EXAFS and FT of the products from the hollow cathode sputtering of platinum are shown in Figure 3(a). The data is noisy as it was only possible to run the discharge/deposition for 10 – 15 minutes, whereas in the conventional matrix EXAFS experiments deposition times of several hours are often required. As a result of this the data set is also relatively short. Despite these limitations, which give rise to relatively high R factors, it is clear from the FT that the data are dominated by an interaction at just under 4 Å, which is best fit by *ca.* 12 argon atoms at 3.78(4) Å (see Table 3 for refinement details). The 2σ² mean square displacement term in the Debye-Waller factor, which describes the extent of the thermal and static disorder, is relatively large (0.039 Å²) for this shell, but is similar to that observed for Kr in solid Ar [31], but slightly larger than for Hg atoms in solid Ar [32]. For solid argon the fcc lattice parameter of 5.3118 Å indicates an argon-argon interatomic distance of 3.756 Å with a radius of 1.878 Å [33]. The commonly quoted van der Waals radius values of Ar are 1.88 Å [34] or 1.89 Å [35]. The Pt-Ar distance of 3.78(4) Å determined in this work, combined with an occupation number of 12 is excellent evidence that the Pt atom is located in a substitutional site in the argon lattice. The Pt-Ar distance of 3.78(4) Å is very similar to the Ar-Ar distance and assuming an argon radius of 1.878 Å, indicates a hard sphere radius of Pt atoms of *ca.* 1.90 Å, which is larger than the 1.5 Å normally quoted based on HF calculations [15] or the standard van der Waals radius value of 1.72 or 1.75 Å [34]. The 1.72 Å value is based on a non-bonding platinum-platinum distance

of 3.44 Å in tetrahedral tetramethylplatinum [36], although a value of 3.73 Å for chloro(trimethyl)platinum is also reported in the same article. The value of 1.90 Å determined in this work is closer to this latter value (1.87 Å) and is therefore a potentially more accurate value of the van der Waals radius of Pt. Whilst there is some evidence in the FT in Figure 3(a) for the more distant Pt...Ar shells in the fcc lattice at $\sqrt{2}r$, $\sqrt{3}r$ and $\sqrt{4}r$, the quality of the data means that it was not possible to fit them reliably. This may also be a result of the Pt-Ar distance being slightly greater than the ideal Ar-Ar distance indicating some distortion of the lattice.

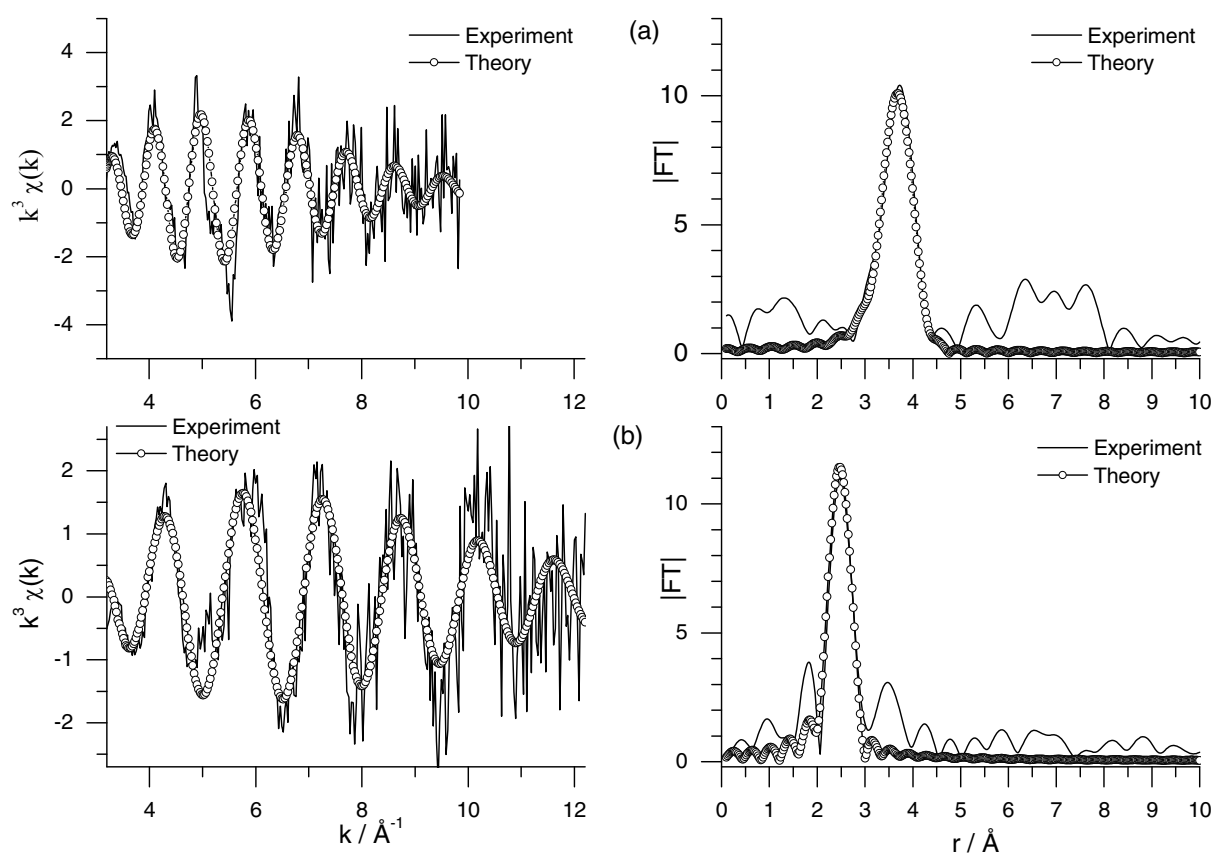


Figure 3. (a) Pt L_3 -edge EXAFS (left) and FT (right) for Pt atoms produced by Ar^+ sputtering of a platinum hollow cathode. (b) Pd K-edge EXAFS (left) and FT (right) for Pd atoms produced by Ar^+ sputtering of a palladium hollow cathode.

Therefore, both the electronic absorption and the X-ray absorption data confirm that the Pt atoms are located within substitutional sites in solid argon.

Table 3. EXAFS refined parameters for sputtered Pt and Pd atoms in argon matrices

Bond type (occupation number)	$r / \text{\AA}^{(a)(b)}$	$2\sigma^2 / \text{\AA}^2^{(c)}$	$E_f^{(d)}$	$R^{(e)}$
Pt-Ar (12)	3.778(20)	0.0385(31)	-14.8(13)	61.5
Pd-Ar (1.2)	2.529(12)	0.0099(32)	-3.3(19)	51.2

^(a) Refinement standard deviation in parentheses; ^(b) estimated systematic errors in EXAFS bond lengths are $\pm 1.5\%$ for well-defined co-ordination shells; ^(c) $2\sigma^2$ is the mean square displacement term in the Debye-Waller factor; ^(d) E_f is a single refined parameter to reflect differences in the theoretical and experimental Fermi levels;

$$^{(e)} R = \left[\int |\chi^T - \chi^E| k^3 dk / \int |\chi^E| k^3 dk \right] \times 100\%$$

Palladium atoms in solid argon

The electronic absorption spectrum of palladium atoms in an argon matrix produced by Ar^+ sputtering is shown in Figure 4 (a). During the deposition a blue/green emission was observed from the matrix, which persisted for a short time once deposition was complete. In order to confirm that the spectrum was representative of palladium atoms, the spectrum of thermally evaporated palladium atoms in an argon matrix was also recorded and this is shown in Figure 4(b), where no emission was observed. Apart from the rising background in the sputtered sample (as also observed for Pt atoms) the two spectra are very similar to each other, and to those published previously [2, 11, 12, 14, 16-18], with no evidence for Pd_2 [11] or $\text{Pd}(\text{N}_2)_n$ [2, 37]. The shoulders to high energy of the most intense peak at 45350 cm^{-1} are not so pronounced in our work as in some of the previous reports [2, 11, 14]. The position of the three bands at 40320 cm^{-1} (248.0 nm, 4.999 eV), 42110 cm^{-1} (237.5 nm, 5.221 eV) and 45350 cm^{-1} (220.5 nm, 5.623 eV) in Figure 4(a) correspond to the Site B bands at 40300 cm^{-1} (248 nm, 5.00 eV), 42400 cm^{-1} (236 nm, 5.26 eV) and 45500 cm^{-1} (220 nm, 5.64 eV) observed after deposition at 10 – 12 K in Klotzbücher and Ozin's work [11]. After deposition at 20 – 25 K they observed a second triplet, labelled site A, at lower energies (39500 cm^{-1}

(253 nm, 4.90 eV), 40800 cm⁻¹ (245 nm, 5.06 eV) and 44100 cm⁻¹ (227 nm, 5.47 eV). The three site B transitions have been assigned slightly differently between the two papers of Klotzbücher and Ozin [2, 11] and the ones from the later paper [11] are given in Table 4. Although there has been a significant amount of work subsequently, including the proposal of three different sites and two electronic states (¹S₀ and ³D₃) for Pd atoms in Ar, none of the later papers provide an alternative definitive assignment of these features in Ar matrices, despite the stated presence of both ³D₃ and ¹S₀ states. This is almost certainly due to the breakdown of the AMCOR approach as a result of the extensive mixing of the states.

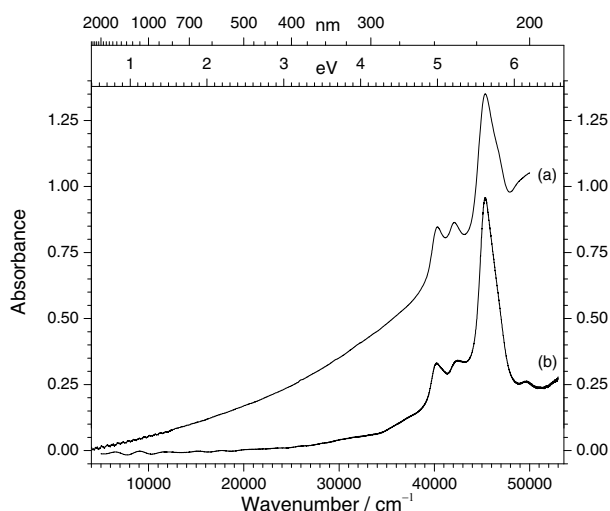


Figure 4. Electronic absorption spectra of palladium atoms in argon matrices, (a) produced by Ar⁺ sputtering of Pd hollow cathode, (b) produced by thermal evaporation.

Table 4. Electronic absorption data (cm⁻¹) for palladium atoms in argon matrices.

Ar ⁺ sputtering ^(a)	thermal evaporation ^(a)	thermal evaporation ^(b)	Assignment ^(b)
40320	40220	40300	³ P ₁ ← ¹ S ₀
42110	42450	42400	³ D ₁ ← ¹ S ₀
45350	45340	45500	¹ P ₁ ← ¹ S ₀
	49650		

(a) this work, (b) reference [11].

The Pd K-edge EXAFS and FT for sputtered Pd atoms in solid Ar are shown in Figure 3(b). From these it is immediately clear that palladium atoms and platinum atoms have very different structural characteristics in argon matrices. The frequency of the EXAFS oscillations is much lower in the Pd K-edge data (Figure 3(b)) compared to the Pt L₃-edge data (Figure 3(a)). This indicates a shorter interatomic interaction in the case of Pd than Pt and as a result the first peak in the FT of the Pd K-edge data is at a much shorter distance (ca. 2.5 Å) than the first peak at 3.78(4) Å in the FT of the Pt L₃-edge data. The main peak in the FT of the Pd K-edge data is best fit by a Pd-Ar interaction of 2.53(3) Å, with a small coordination number of 1.2 (see Table 3). When Pd-Pd interactions were modelled, the fit was considerably worse both in terms of the R factor and also the match of the phase and intensity of the oscillations in the EXAFS, therefore confirming that this is a short Pd-Ar distance. There was no change in the ten spectra averaged over the data acquisition time of 10 – 12 hours for the data in Fig 3(b).

When the matrix was warmed to 25 K in the absence of X-rays and only in low level ambient light, a blue/green emission was observed similar to that on deposition, indicating that it is thermoluminescence rather than photon induced. On cooling to 10 K and after the emission had disappeared, there was a significant change in the X-ray absorption spectrum as shown in Figure 5. As in the case of the initial Pd K-edge data, there were no changes in the eight spectra collected over 8 – 9 hours and averaged together. Figure 5 shows the raw absorption data, and the lack of any significant change in the edge height (the spectra have been offset slightly for clarity) indicates that there is the same amount of palladium present in both spectra. However, there is a significant reduction in the intensity of the EXAFS oscillations after the edge following annealing to 25 K (Figure 5(b)) compared to deposition (Figure

5(a)). As a consequence of this there is little information content in the EXAFS region as there are effectively no oscillations to model once the data has been background subtracted.

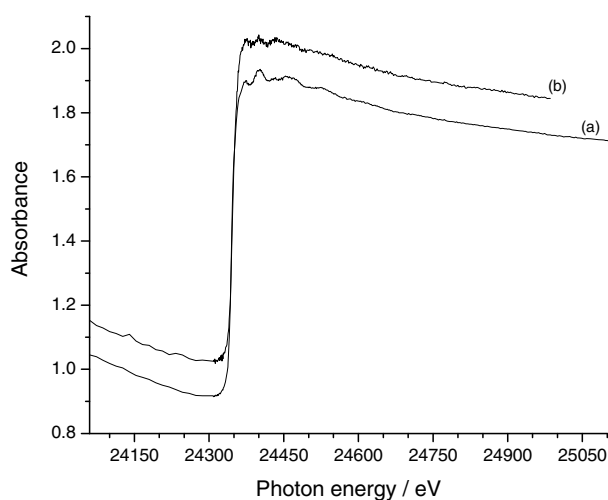


Figure 5. Pd K-edge X-ray absorption spectra of Ar^+ sputtered Pd atoms in solid Ar (a) on deposition at *ca.* 10 K, (b) after annealing to 25 K and recooling to 10 K. (Offset for clarity)

It is clear from these data that the intensity of the oscillation associated with the $2.53(3) \text{ \AA}$ Pd-Ar shell has reduced significantly on annealing, to leave a spectrum that looks almost “atomic” in nature, such as that observed for gas or liquid phase Kr [21] with no well defined nearest neighbours. It is significant that after annealing to 25 K there is no evidence for palladium atom clustering, which would be indicated by clear oscillations. It was not possible to acquire UV-vis data at the same time as the XAFS data, therefore offline UV-vis experiments were carried out and indicated similar behaviour for the sputtered sample on annealing to that seen previously in the thermal evaporation experiments, where the UV signals all decrease in intensity on annealing [2, 11, 14, 16].

The blue/green emission observed both on deposition and annealing may correspond to that observed by Grinter and Stern [12, 13], Schrittenlacher et al. [14] and Ozin and Garcia-Prieto [16, 17] after irradiation at $40000 - 50000 \text{ cm}^{-1}$ (250 – 200 nm, 4.96 – 6.20 eV).

What is clear from the Pd K-edge data is that on condensation of sputtered Pd atoms in solid argon, a short Pd-Ar interaction of 2.53(3) Å with a low occupation number is observed, and this is in stark contrast to the analogous Pt data. On annealing to 25 K, the 2.53(3) Å interaction reduces considerably. Taketsugu et al. [19] comment that a Pd-Ar van der Waals distance should be of the order of 3.51 Å, based on the van der Waals radii of 1.88 Å and 1.63 Å for Ar and Pd, respectively. However, this analysis ignores the very small 0.55 Å radius of 1S_0 Pd [15], which would bring the value down to 2.43 Å. In contrast a covalent interaction would be of the order of 2.33 Å, based on covalent radius values of 0.98 Å and 1.353 Å for Ar and Pd, respectively [19].

These intriguing observations can be interpreted in a number of ways including: the location of the palladium in the argon fcc lattice; the formation of excited state species such as exciplexes; or the formation of distinct palladium argon complexes. These will be considered in turn.

The unit cell of fcc Ar is 5.3118 Å [33] and Table 5 displays the site diameters and distances from the site centre to the nearest argon atom for the substitutional and interstitial sites in solid argon. The diameter of the 1S_0 state of Pd is reported as 1.1 Å [15], and that of the 3D_3 state has been estimated as 2.7 Å [17].

Table 5. Values of site diameters in solid argon and Pd-Ar distances for different sites assuming an argon lattice parameter of 5.3118 Å.

	coordination number	Site diameter / Å	distance from centre of site to nearest neighbour in Ar lattice / Å
substitutional site	12	3.756 (d)	3.756 (d)
octahedral interstitial site	6	1.556 ($\sqrt{2} - 1$) d	2.656 ($\sqrt{1/2}$) d
tetrahedral interstitial site	4	0.844 ($\sqrt{3/2} - 1$) d	2.300 ($\sqrt{3/8}$) d

Therefore, the 1S_0 state with a 1.1 Å diameter can fit easily into an octahedral interstitial site, but would be constrained within a tetrahedral interstitial site, and would potentially rattle around, or be poorly defined in a substitutional site. The 3D_3 state with a 2.7 Å diameter only fits comfortably into a substitutional site, being very constrained in an octahedral interstitial site. Using these data, it is possible to estimate that the nearest Pd-Ar distance for the 1S_0 state is 2.43 Å, whilst that for the 3D_3 state is 3.23 Å. Therefore, the Pd-Ar distance of 2.53(3) Å obtained from the Pd K-edge XAFS data is consistent with the 1S_0 state in an octahedral interstitial site. Assuming an Ar van der Waals radius of 1.878 Å suggests a value of 0.65 Å for the radius of the 1S_0 state of Pd atoms, in good agreement with the HF calculated value of 0.55 Å [15]. The low coordination number is intriguing, as it would be expected to be six for an octahedral interstitial site, but it should be remembered that XAFS is an averaging technique.

The X-ray absorption data after annealing to 25 K has lost most of the intensity of the oscillations due to the 2.53(3) Å Pd-Ar interaction, and this has been replaced by a largely featureless spectrum, much more reminiscent of the spectra obtained for atomic samples such as gas phase krypton, with no well defined nearest neighbours. If the palladium was

clustering this would be expected to give rise to observable oscillations in the EXAFS spectrum. As the amount of Pd remains the same before and after annealing, the best interpretation for the lack of EXAFS oscillations after annealing is that there are a large number of different Pd-Ar interactions present, which result in a spread of distances. This results in large Debye-Waller factors which effectively cancel or wash out various distances to yield what looks like an “atomic” spectrum with no well defined interactions. This also explains the relatively low occupation number in the as-deposited data, as there is a mixture of Pd atoms present, one set with a well defined Pd-Ar distance of 2.53(3) Å, and a second set with a wide range of Pd-Ar distances, and that on annealing the first is converted to the second, accompanied by the emission of blue/green light.

As the 1S_0 Pd atoms fit well into the octahedral site, this could be the source of the 2.53(3) Å interaction, and the “atomic” like signal which is present in both the as-deposited and after annealing spectra arises from 1S_0 Pd atoms in the substitutional holes or other sites such as grain boundaries [38] where a large number of different, or rapidly changing, interactions are possible. In the context of the electronic spectra, Schrittenlacher et al. have commented that the small size of the Pd atom might result in it feeling very little of the matrix cage and hence gas phase like spectra should emerge [14]. In this model the change on annealing would arise from the 1S_0 Pd atoms migrating from the octahedral interstitial sites to the substitutional sites or grain boundaries, but it is not clear why this should be associated with radiative emission.

As the blue/green emission was observed during deposition, it is most likely that the Pd atoms are being pumped by the Ar^+ discharge which has components throughout the visible and ultraviolet regions as well as the vacuum ultraviolet, and that there is further relaxation of the excited state on annealing. Grinter and Stern observed the effects of photolysis by 40000

– 50000 cm⁻¹ (250 – 200 nm, 4.96 – 6.20 eV) in their MCD spectra and assigned the excited state as ³F₄ [12, 13]. Schrittenlacher et al. observed broad emission in Ar at ca. 20000 cm⁻¹ (500 nm, 2.48 eV) and the better resolved emission in Ne matrices was assigned as originating from a ³D₁ state [14]. Ozin and Garcia-Prieto [16, 17] and Garcia-Prieto and Novaro [18] have observed emission in the 17500 – 25000 cm⁻¹ (570 – 400 nm, 2.18 – 3.10 eV) range with excitation at 46500 cm⁻¹ (215 nm, 5.77 eV), 42700 cm⁻¹ (234 nm, 5.30 eV) and 40000 cm⁻¹ (250 nm, 4.96 eV) and assigned the excited state as ³D₃. They also commented that the photochemical population of this ³D₃ state from the ¹S₀ ground state seemed to be very efficient. Therefore, the 2.53(3) Å Pd-Ar distance observed on deposition and which decays on annealing could arise from this excited state. However, the Pd-Ar distance is not consistent with a ³D₃ state which has an estimated diameter of 2.7 Å [17], as this would result in a Pd-Ar interaction of the order of 3.2 – 3.3 Å. However, if the excited state is a palladium argon exciplex species, then a shorter Pd-Ar interaction would be expected. For example the calculated minimum in the Hg-Ar potential energy surface for the gas-phase HgAr₂ van der Waals cluster reduced from 3.98 Å to 3.34 Å on going from the ¹S₀ ground state to the A ³P₁ excited state, but increased to 4.66 Å for the B excited state [39]. These potential energy data have subsequently been used to study mercury noble gas exciplexes in solid matrices using the Molecular Dynamics with Quantum Transitions (MDQT) methodology [40, 41]. For an Hg atom in a box of 499 Ar atoms the Hg-Ar bond length in the Ar-Hg*-Ar exciplex embedded in the solid argon was found to be 3.44 Å, and in the Ar-Hg*-Xe exciplex it was 3.55 Å, compared to 3.83 Å in the ground state. There was no evidence for complex formation with ground state ¹S₀ Hg for either Ar or Xe, and the interaction in the B excited state was much weaker, especially in the case of argon. These mercury noble gas exciplexes were of the form of linear triatomics, similar to ground state PdAr₂ [19], although bent geometries with similar interatomic distances were also found for

Ar-Hg*-Xe and Xe-Hg*-Xe exciplexes in solid argon. Therefore, an alternative explanation is that on deposition there is a mixture of 1S_0 Pd atoms in substitutional or other sites with high disorder such as grain boundaries giving rise to the “atomic” EXAFS spectrum, with a palladium exciplex species giving rise to the 2.53(3) Å Pd-Ar distance, and that on annealing the exciplex decays to 1S_0 Pd in substitutional sites or grain boundaries, with blue/green emission. As a result of the mixture of species present it is not possible to identify the Pd-Ar coordination number in the proposed PdAr_n exciplex.

If the Pd-Ar distance of 2.53(3) Å is not the result of an interaction between 1S_0 Pd atoms and argon in an octahedral interstitial site, or the formation of an exciplex, then it could be due to the formation of a Pd-Ar bond in a ground state compound. The computational work of Taketsugu et al. [19] predicted a Pd-Ar bond length for linear PdAr₂ of 2.554 Å which is very close to the Pd-Ar distance of 2.53(3) Å observed in these Pd K-edge experiments. PdAr₂ was the most stable of PdAr, PdAr₂ and PdAr₃ (Table 1) and the bonding of the Pd and Ar atoms is due to s-d_σ hybridisation due to the mixing of the 4d¹⁰ and 4d⁹5s¹ configurations. They also noted that it is only the 1S_0 state that is stabilised by binding with the argon, and this may explain why the short distance and emission was only observed for Pd with a 1S_0 ground term (4d¹⁰) and not Pt with a 3D_3 ground term (5d⁹6s¹), even though the binding energy is much greater for PtAr₂. Within this explanation, there is a mixture of 1S_0 Pd atoms in substitutional sites (or grain boundaries) and PdAr₂ on deposition, and that on annealing PdAr₂ decays with blue/green emission and the formation of 1S_0 Pd atoms in a substitutional site (or grain boundary). Direct experimental data on noble gas – metal distances are sparse, particularly for those involving argon, but Gerry and co-workers have reported gas phase Ar – Cu distances of 2.2 – 2.3 Å for ArCuX [42], Ar – Ag distances of 2.5 – 2.6 Å in ArAgX [43] and

Ar – Au distances of 2.4 – 2.5 Å for ArAuX [44, 45] (X = F, Cl, Br). The 2.53(3) Å Pd-Ar value determined in this work is consistent with these values.

In all three of the possible explanations of the Pd K-edge data, the “atomic” like component is due to the presence of 1S_0 Pd atoms in a substitutional site, or other sites such as grain boundaries with high disorder. As annealing to 25 K is accompanied by emission, this would indicate that the 2.53(3) Å Pd-Ar feature is due an excited or unstable state which decays on annealing, and that this could either be a PdAr_n exciplex or PdAr₂. As similar emission has been observed for Pd/Ar systems before [12-14, 16-18], this favours the exciplex explanation. The lack of a short Pt-Ar distance in the Pt L₃-edge data rules out the formation of PtAr₂, which according to the calculations [19] has a binding energy almost five times that of PdAr₂. Although it should be noted that there was no complex formation between the 3D_3 ground state and Ar in the computational work, so that the Pt 1S_0 excited state would need to be appreciably populated for it to form.

Therefore, whilst the current data does not allow for an unambiguous assignment of the 2.53(3) Å Pd-Ar interaction, and it would be attractive to assign it to PdAr₂, we think the most likely explanation is that it is due to the formation of a PdAr_n exciplex species. Whether the Pd-Ar distance of 2.53(3) Å is due to Pd-Ar interactions with the matrix host, or the formation of exciplexes or more formal complexes, it should be noted that this appears to be the first report of a short palladium-argon distance, and is only ca. 0.2 Å longer than the Pd-Cl bond length in [PdCl₄]²⁻ [46-48].

Conclusions

The electronic absorption spectrum and Pt L₃-edge XAFS data for Pt atoms in solid argon produced by sputtering are entirely consistent with Pt atoms being located in a substitutional site within the Ar fcc lattice, with a Pt-Ar distance of 3.78(4) Å and a coordination number of *ca.* 12. These data give an estimate of the van der Waals radius for Pt of 1.90 Å.

The Pd K-edge data are radically different indicating a very different structural environment. The as-deposited data contains a short Pd-Ar distance of 2.53(3) Å, with a low coordination number, together with what appears to be an “atomic” EXAFS spectrum as a result of a lack of well defined nearest neighbours. On annealing to 25 K, the short distance disappears, indicating the instability of this species, and all that is left is the “atomic” like spectrum. In all three of the possible explanations the “atomic” spectrum before and after annealing is associated with the small ¹S₀ Pd atoms (1.1 Å diameter) in either substitutional sites in the argon fcc lattice (3.76 Å diameter), or in sites with high disorder such as grain boundaries. The Pd-Ar distance of 2.53(3) Å is remarkably short and is potentially consistent with: the ¹S₀ state of Pd atoms trapped in an octahedral interstitial site in the argon fcc lattice; the presence of PdAr_n exciplexes with a short Pd-Ar interaction; or the formation of PdAr₂ complexes. At the present time it is not possible to say with certainty which of these is correct, but we believe that the best explanation is either the formation of PdAr_n exciplexes or PdAr₂ complexes. Whilst it would be attractive to opt for PdAr₂, we believe that the formation of PdAr_n exciplexes in the argon lattice caused by photolysis during the sputtering process is probably the best explanation for the short Pd-Ar distance. What is clear is that we have directly observed a short Pd-Ar interaction for the first time, albeit in a very unstable species.

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References

- [1] D.W.H. Carstens, W. Brashear, D.R. Eslinger, D.M. Gruen, Correlation between gaseous atomic spectra and the absorption spectra of atoms isolated in noble gas matrices, *Appl. Spectrosc.*, 26 (1972) 184-217.
- [2] W.E. Klotzbücher, G.A. Ozin, Reinvestigation of the optical spectra of nickel, palladium and platinum atoms in noble gas matrices, *Inorg. Chem.*, 15 (1976) 292-295.
- [3] C.E. Moore, Atomic Energy Levels, Volume III (Molybdenum through Lanthanum and Hafnium through Actinium), Circular of the National Bureau of Standards 467 (Reprinted as NSRDS-NBS 35 Volume III, 1971), (1958).
- [4] C.P. Barrett, R.G. Graham, R. Grinter, The electronic ground-state of matrix-isolated nickel atoms, *Chem. Phys.*, 86 (1984) 199-204.
- [5] T.A. Cellucci, E.R. Nixon, Study of low-lying electronic states of Ni atoms in solid inert gas matrices, *J. Chem. Phys.*, 81 (1984) 1174-1177.
- [6] W. Schrittenlacher, W. Schroeder, H.H. Rotermund, D.M. Kolb, Fluorescence-spectra of matrix-isolated Ni atoms, *Chem. Phys. Lett.*, 109 (1984) 7-12.
- [7] W. Schroeder, R. Grinter, W. Schrittenlacher, H.H. Rotermund, D.M. Kolb, The electronic-spectra of matrix-isolated nickel atoms - the coexistence of the 3D_3 and 3F_4 ground-states in Ar, Kr, and Xe, *J. Chem. Phys.*, 82 (1985) 1623-1630.
- [8] M. Vala, M. Eyring, J. Pyka, J.C. Rivoal, C. Grisolia, Electronic states of matrix-isolated Ni atoms - a magnetic circular and linear dichroism study, *J. Chem. Phys.*, 83 (1985) 969-974.
- [9] G.H. Jeong, K.J. Klabunde, Matrix induced frequency-shifts of transition-metal atoms in Ar, Kr, and Xe matrices at 10 K, *J. Chem. Phys.*, 91 (1989) 1958-1971.
- [10] D.M. Mann, H.P. Broida, Ultraviolet absorption spectra of transition metal atoms in rare gas matrices, *J. Chem. Phys.*, 55 (1971) 84-94.
- [11] W.E. Klotzbücher, G.A. Ozin, Optical spectra of hafnium, tungsten, rhenium, and ruthenium, atoms and other heavy transition metal atoms and clusters ($Zr_{1,2}$, $Pd_{1,2}$, $Au_{1,2,3}$) in noble gas matrices, *Inorg. Chem.*, 19 (1980) 3767-3776.
- [12] R. Grinter, D.R. Stern, Detection by magnetic circular-dichroism of a long-lived excited-state of matrix-isolated palladium atoms, *J. Chem. Soc., Chem. Comm.*, (1982) 40-41.
- [13] R. Grinter, D.R. Stern, Magnetic circular-dichroism studies of matrix-isolated metal atoms, *J. Mol. Struct.*, 80 (1982) 147-150.
- [14] W. Schrittenlacher, H.H. Rotermund, D.M. Kolb, Optical-spectra of matrix-isolated palladium atoms, *J. Chem. Phys.*, 83 (1985) 6145-6149.
- [15] S. Fraga, J. Karwowski, K.M.S. Saxena, *Handbook of Atomic Data*, Elsevier, Amsterdam, 1976.

- [16] G.A. Ozin, J. Garcia-Prieto, Optical-spectra of matrix-isolated palladium atoms .1. the absorption and emission-spectra and the decay kinetics of the 3D_3 metastable state of Pd in Ar matrices, *J. Phys. Chem.*, 92 (1988) 318-324.
- [17] G.A. Ozin, J. Garcia-Prieto, Optical-spectra of coexisting 1S_0 and 3D_3 palladium atoms and $^1\Sigma^+ \ ^3\Sigma^+$ Pd(N₂) binary palladium dinitrogen molecules isolated in argon matrices - a study by UV-visible absorption, broad-band and laser-induced fluorescence, and infrared and Raman spectroscopies, *J. Phys. Chem.*, 92 (1988) 325-337.
- [18] J. Garcia-Prieto, O. Novaro, Optical spectra of matrix-isolated palladium atoms .3. Matrix effects on the electronic structure of Pd atoms, *Rev. Mex. Fis.*, 43 (1997) 130-158.
- [19] Y. Taketsugu, T. Taketsugu, T. Noro, Theoretical prediction of noble-gas compounds: Ng-Pd-Ng and Ng-Pt-Ng, *J. Chem. Phys.*, 125 (2006) 154308.
- [20] Y. Ono, T. Taketsugu, T. Noro, Theoretical study of Pt-Ng and Ng-Pt-Ng (Ng=Ar, Kr, Xe), *J. Chem. Phys.*, 123 (2005) 204321.
- [21] N.A. Young, The application of synchrotron radiation and in particular X-ray absorption spectroscopy to matrix isolated species, *Coord. Chem. Rev.*, 277 (2014) 224-274.
- [22] A.J. Bridgeman, G. Cavigliasso, N. Harris, N.A. Young, A matrix isolation and DFT study of the generation and characterization of monomeric vapour phase platinum chlorides, *Chem. Phys. Lett.*, 351 (2002) 319-326.
- [23] I.J. Blackmore, A.J. Bridgeman, N. Harris, M.A. Holdaway, J.F. Rooms, E.L. Thompson, N.A. Young, Experimental evidence for a Jahn-Teller distortion in AuCl₃, *Angew. Chem. Int. Ed.*, 44 (2005) 6746-6750.
- [24] D.W. Green, G.T. Reedy, Infrared-spectra of matrix isolated plutonium oxides, *J. Chem. Phys.*, 69 (1978) 544-551.
- [25] I.R. Beattie, P.J. Jones, K.R. Millington, A.D. Willson, The infrared spectra of matrix isolated thorium and uranium tetrachlorides. Change of shape with matrix gas, *J. Chem. Soc., Dalton Trans.*, (1988) 2759-2762.
- [26] A.C. Thompson, D. Vaughan, D.T. Attwood, E.M. Gullikson, M.R. Howells, J.B. Kortright, A.L. Robinson, J.H. Underwood, K.J. Kim, J. Kirz, I. Lindau, P. Pianetta, H. Winick, G.P. Williams, J.H. Scofield, Center for X-ray Optics and Advanced Light Source X-ray Data Booklet, 2nd ed., Lawrence Berkeley National Laboratory, University of California, Berkeley, California, USA, 2001.
- [27] N. Binsted, PAXAS, Program for the analysis of X-ray absorption spectra, University of Southampton, U.K., (1988).
- [28] W.E. O'Grady, X. Qian, D.E. Ramaker, Systematic chemical effects observed in "Atomic" X-ray absorption fine structure, *J. Phys. Chem. B*, 101 (1997) 5624-5626.
- [29] N. Binsted, EXCURV98, CCLRC Daresbury Laboratory Computer Program, CCLRC, Daresbury Laboratory, U.K., (1998).
- [30] K. Jansson, R. Scullman, Optical absorption spectra of PtO and Pt₂ in rare gas matrices, *J. Mol. Spectrosc.*, 61 (1976) 299-312.
- [31] I.R. Beattie, N. Binsted, W. Levason, J.S. Ogden, M.D. Spicer, N.A. Young, EXAFS, matrix isolation, and high temperature chemistry, *High Temp. Sci.*, 26 (1989) 71-86.
- [32] J.F. Rooms, A.V. Wilson, I. Harvey, A.J. Bridgeman, N.A. Young, Mercury-fluorine interactions: a matrix isolation investigation of Hg...F₂, HgF₂ and HgF₄ in argon matrices, *Phys. Chem. Chem. Phys.*, 10 (2008) 4594-4605.
- [33] C.S. Barrett, L. Meyer, X-ray diffraction study of solid argon, *J. Chem. Phys.*, 41 (1964) 1078-1081.
- [34] A. Bondi, van der Waals volumes and radii, *J. Phys. Chem.*, 68 (1964) 441-451.
- [35] M. Mantina, A.C. Chamberlin, R. Valero, C.J. Cramer, D.G. Truhlar, Consistent van der Waals radii for the whole main group, *J. Phys. Chem. A*, 113 (2009) 5806-5812.

- [36] R.E. Rundle, J.H. Sturdivant, The crystal structures of trimethylplatinumchloride and tetramethylplatinum, *J. Am. Chem. Soc.*, 69 (1947) 1561-1567.
- [37] W. Schrittenlacher, W. Schroeder, H.H. Rotermund, H. Wiggenhauser, R. Grinter, D.M. Kolb, The optical-spectra of matrix-isolated palladium-nitrogen complexes: An investigation by absorption, emission, and photoelectron spectroscopy, *J. Chem. Phys.*, 85 (1986) 1348-1354.
- [38] E. Jacquet, D. Zanuttini, J. Douady, E. Giglio, B. Gervais, Spectroscopic properties of alkali atoms embedded in Ar matrix, *J. Chem. Phys.*, 135 (2011) 174503.
- [39] J. Zúñiga, A. Bastida, A. Requena, N. Halberstadt, J.A. Beswick, A theoretical study of the $\text{HgAr}_2(^3\text{P}_1 \leftarrow ^1\text{S}_0)$ vibronic spectrum, *J. Chem. Phys.*, 98 (1993) 1007-1017.
- [40] G. Rojas-Lorenzo, J. Rubayo-Soneira, S.F. Alberti, Dynamics of exciplex formation in rare gas media, *Chem. Phys.*, 362 (2009) 34-40.
- [41] R. Lozada-García, G. Rojas-Lorenzo, C. Crépin, M. Ryan, J.G. McCaffrey, Hg-Xe exciplex formation in mixed Xe/Ar matrices: molecular dynamics and luminescence study, *J. Phys. Chem. A*, 119 (2015) 2307-2317.
- [42] C.J. Evans, M.C.L. Gerry, Noble gas-metal chemical bonding? The microwave spectra, structures, and hyperfine constants of Ar-CuX (X = F, Cl, Br), *J. Chem. Phys.*, 112 (2000) 9363-9374.
- [43] C.J. Evans, M.C.L. Gerry, The microwave spectra and structures of Ar-AgX (X = F, Cl, Br), *J. Chem. Phys.*, 112 (2000) 1321-1329.
- [44] C.J. Evans, D.S. Rubinoff, M.C.L. Gerry, Noble gas-metal chemical bonding: The microwave spectra, structures and hyperfine constants of Ar-AuF and Ar-AuBr, *Phys. Chem. Chem. Phys.*, 2 (2000) 3943-3948.
- [45] C.J. Evans, A. Lesarri, M.C.L. Gerry, Noble gas-metal chemical bonds. Microwave spectra, geometries, and nuclear quadrupole coupling constants of Ar-AuCl and Kr-AuCl, *J. Am. Chem. Soc.*, 122 (2000) 6100-6105.
- [46] B. Schüpp, L. Schröder, H. Schulte, C. Bähz, N. Mattern, H.-L. Keller, $\text{Cs}_2[\text{PdCl}_4]$ — neue Ergebnisse zu einer „altbekanntem“ Verbindung, *Z. anorg. allg. Chem.*, 628 (2002) 1708-1714.
- [47] A. Assoud, G. Meyer, Ein neues Chloropalladat(II): BaPdCl_4 , *Z. anorg. allg. Chem.*, 628 (2002) 1246-1247.
- [48] J.R. Hester, E.N. Maslen, N. Spadaccini, N. Ishizawa, Y. Satow, Electron density in potassium tetrachloropalladate (K_2PdCl_4) from synchrotron radiation data, *Acta. Crystallogr. B*, 49 (1993) 842-846.
- [49] D.A. Fletcher, R.F. McMeeking, D. Parkin, The United Kingdom Chemical Database Service, *J. Chem. Inf. Comput. Sci.*, 36 (1996) 746-749.