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Optical spectra of matrix-isolated palladium atoms. 3. Matrix effects on the electronic structure of Pd atoms

JAIME GARCIA-PRIETO AND OCTAVIO NOVARO*
Instituto de Física, Universidad Nacional Autónoma de México
Apartado postal 20–364, 01000 México, D.F., México

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ABSTRACT. The detailed analysis of the optical spectra (uv-visible absorption and emission and laser-induced luminescence) of palladium atoms isolated in solid argon, kripton and xenon matrices at 12 K reveal that in these environments the Pd atoms are isolated in three main trapping sites. In the two interstitial sites (tetrahedral and octahedral) of a cubic closed-packed (CCP) crystal structure of the inert solid, the Pd atoms preserve the gas-phase electronic ground state configuration $4d^{10}\,{}^1S_0$, but in each one the deactivation of electronic excited states is quite different. In a substitutional site the atom changes the gas-phase electronic ground state configuration $4d^{10}$ to one of $4d^9 5s^1$ electronic configuration, that is the ${}^3D_3$ state becomes the ground state. The broad band luminescence studies reveal that in the Pd/Ar and Pd/Kr systems there exists a very efficient process of population of the very long-lived $4d^9 5s^1\,{}^3D_3$ metastable state from Pd($4d^{10}\,{}^1S_0$) atoms isolated in a interstitial octahedral site. This process also occurs in the Pd/Xe system, but seems less efficient. The occurrence of this process brings as consequence that the optical spectra show more bands than expected. On the other hand, it was found that the pass from Ar to Xe matrices has a deep effect on the allowness of forbidden transitions, this is clearly manifested in the absorption and emission spectra of Pd($4d^{10}\,{}^1S_0$) atoms isolated in an interstitial tetrahedral site of a Xe matrix where unambiguously the bands of these spectra can be assigned. This effect seems absent in the Pd/Ar system, but in Pd/Kr it is only manifested in the more sensible excitation and emission spectra. As consequence of (i) the coexistence of Pd atoms in two electronic ground states, (ii) the fast population of a long-lived metastable state and (iii) the heavy atom effect: the uv-visible absorption spectra of Pd atoms isolated in Ar, Kr and Xe matrices will be a superposition of uv-visible absorption spectra whose contributions from (i) to (iii) will depend of the matrix (Ar, Kr and Xe). This brings as consequence that the net uv-visible absorption spectra of Pd atoms isolated in Ar and Kr matrices looks similar, but is substantially different in a Xe matrix.

RESUMEN. En este trabajo se muestra, a través de un análisis detallado de espectros ópticos (absorción uv-visible y luminiscencia de emisión inducida por láser) de átomos de paladio aislados en matrices sólidas de gases nobles: argón, kriptón y xenón a 12 K, que los átomos Pd están aislados en tres sitios principales de atrapamiento. En dos de esos sitios intersticiales de una estructura cristalina CCP con simetrías tetrahedral y octahedral, respectivamente, los átomos Pd permanecen en su estado base $4d^{10}\,{}^1S_0$, pero la desactivación de los estados excitados es distinta. En un sitio de sustitución el átomo cambia su estado base con configuración $4d^{10}$ a una de las configuraciones excitadas $4d^9 5s^1$, haciendo que el estado más estable sea un estado ${}^3D_3$. Los estudios de luminiscencia de banda ancha revelan que en los sistemas Pd/Ar y Pd/Kr existe un proceso muy eficiente de población del estado metaestable de vida larga $4d^9 5s^1\,{}^3D_3$ a partir del

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*Miembro del Colegio Nacional

estado base Pd($4d^{10}\,{}^1S_0$) de los átomos aislados en un sitio intersticial de simetría octahedral. Este proceso también ocurre en el sistema Pd/Xe, pero aparentemente con menor eficiencia. La existencia de dicho proceso trae como consecuencia que los espectros muestren más bandas de lo esperado. Por otro lado, la sustitución de matrices de Ar por Xe tiene un profundo efecto en facilitar transiciones prohibidas como se evidencia en los espectros de absorción y emisión de átomos Pd($4d^{10}\,{}^1S_0$) aislados en sitios intersticiales de simetría tetrahedral en matrices de Xe, donde las bandas de dichos espectros pueden asociarse unívocamente. Sin embargo, este efecto aparentemente está ausente en el sistema Pd/Ar, mientras que en Pd/Kr se manifiesta sólo para los espectros más sensibles de excitación y emisión. Debido a (i) la coexistencia de átomos de Pd en dos estados base electrónicos distintos, (ii) la rápida población del estado metaestable de vida larga y (iii) el efecto de átomo pesado: el espectro de absorción uv-visible de átomos Pd aislados en matrices de Ar, Kr y Xe será una superposición de espectros de absorción uv-visible cuyas contribuciones de (i), (ii) y (iii) dependerán de la matriz usada (Ar, Kr o Xe). Esto trae como consecuencia que el espectro neto de absorción uv-visible de los átomos de paladio aislados en matrices de kriptón y argón sean muy similares, pero difieran sustancialmente de los obtenidos en matrices de xenón.

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1. INTRODUCTION

The optical spectra of Pd atoms isolated in rare gas matrices (Ne, Ar, Kr and Xe) has been one of the more controversial of all the optical spectra of matrix isolated metal atoms. Mann and Broida made the first report on the uv-visible absorption spectra of Pd atoms isolated in an Ar matrix [1]. They report four bands at 297, 313, 320 and 338 nm assigned to the gas-phase $(4d^9 5p^1)\,{}^1P_1^0,\ {}^3D_1^0, {}^3P_1^0 \leftarrow (4d^{10})^1S_0$ transitions, which occur at 245, 248, 263 and 276 nm, respectively. This was thought at the time to be an odd result as the data implied surprisingly a large red shift from the respective gas-phase value of the order of 6500 cm^{-1}. Klotzbücher and Ozin [2] soon demonstrated that this spectrum corresponds to Pd$(N_2)_x$ complexes and shown that, besides the relatively weak molecular spectrum of this complexes, there is a very intense spectrum bellow 250 nm which passed undetected in Mann and Broida's study. The uv-visible absorption spectra of Pd atoms isolated in neat Ar, Kr, and Xe matrices, at 6–8 K, reported by Klotzbücher and Ozin [2, 3] consisted of a set of bands in the 200–250 nm region in all the matrices. They excluded two broad and weak bands, at 255 and 310 nm, respectively, found in the Pd/Xe system, as part of the spectrum. They interpret their spectra, at least for the Pd/Ar and Pd/Kr systems [3], as due to the superposition of two triplets, each one corresponding to the gas-phase transitions $(4d^9 5s^1)\,{}^1P_1^0,\ {}^3D_1^0,\ {}^3P_1^0 \leftarrow (4d^{10})\,{}^1S_0$ of Pd atoms entraped in two different sites. Their matrix-gas phase spectra correlation established an extremely large blue shift in the anomalous order of Xe > Kr > Ar (average matrix shift: $4980 > 4170 > 3590$ cm^{-1}, respectively). They sustain that the exceptionally large blue shift of the Pd/Xe spectrum is indicative of a substantial and specific metal atom-matrix interaction between the polarizable Pd atom and the most polarizable of the inert gases, as is xenon. A complementary result, that was observed by Grinter and Stern [4, 5] in the Pd/Ar and Pd/Kr systems, at 5 K, is related to the MCD spectra of a long-lived excited state of matrix-isolated Pd atoms. They found that when scanned from larger wavelengths toward shorter no MCD signal can be detected above 250 nm, but if the dichrograph is then returned rapidly to long wavelengths and the MCD spectrum is remeasured, a new, exceptionally strong, and rapid decaying MCD signal is readily observable in the 290–360 nm region. They suggested that the metastable state corresponds to the paramagnetic Pd atom of $4d^8 5s^2\,{}^3F_4$ ground state, which is 25101 cm^{-1} above the gas-phase $4d^{10}\,{}^1S_0$ ground state, and the 290–360 nm MCD spectra correspond to $4d^8 5s^1 5p^1 \leftarrow 4d^8 5s^2({}^3F_4)$ transitions.

More recently, Kolb and co-workers [6] extended the optical spectra analysis of Pd atoms isolated in Ne, Ar, Kr and Xe matrices at 5.5 K. They obtained the absorption, emission and emission yield spectra of Pd atoms isolated in these matrices, and the transient-absorption spectrum from a metastable state of Pd atoms isolated in a Ne matrix. From their thermal annealing experiments they concluded that Pd atoms are isolated, in all the matrices, in only one trapping site. On the other hand, they assume that the 200–260 nm absorption spectra of Pd atoms isolated in all the rare gas matrices, correspond to transitions from the $4d^{10}\,{}^1S_0$ ground state to the twelve $4d^9 5p^1$ derived levels, which will be allowed by matrix interaction. This brought as consequence to assume an average matrix shift of the absorption spectra to the blue in the order Xe > Ne > Ar > Kr (8050 > 6850 > 6050 > 5650 cm^{-1}, respectively) [6, 7]. From their analysis on the average matrix shift and the known diameter (1.10 Å) of the $\mathrm{Pd}(4d^{10}\,{}^1S_0)$ atom, they concluded that in Ne, Ar and Kr matrices the Pd atom is isolated in an octahedral interstitial site, whereas in a Xe matrix this trapping site is the more constricted tetrahedral interstitial site. As Klotzbücher and Ozin, they explicitly exclude the relatively broad absorption bands of the 250–350 nm region of the Pd/Xe system as due to Pd atoms. On the other hand, they report that the emission and emission yield spectra of the Pd/Ar and Pd/Xe systems are similar and show only one broad emission feature around 495 nm whose corresponding emission yield spectra shown maxima in the region of the atomic absorption bands but no specific conclusions could be drawn. Their emission spectra of the Pd/Ne system consisted of a set of relatively narrow bands in the 310–650 nm region; they excluded explicitly some of this bands as due to Pd atoms. Their assignment involve transitions of the type: $4d^8 5s^2 \to 4d^9 5s^1$, $4d^8 5s^2 \to 4d^{10}$ and $4d^9 5p^1 \to 4d^9 5s^1$. Finally, their transient-absorption spectrum from photoliticaly prepared metastable state of Pd atoms isolated in a Ne matrix, was assigned to $4d^9 5p^1 \leftarrow 4d^9 5s^1$ transitions, from the $4d^9 5s^1\,{}^3D_1$ ground state.

At the time that Kolb and co-workers published their optical spectra analysis of matrix isolated Pd atoms Ozin and García-Prieto [8] were finishing their own analysis of the optical spectra of the Pd/Ar system. Much of their results and almost all their conclusions were and are completely different to those reported by Kolb and co-workers. It forced Ozin and García-Prieto to reconsider their analysis and to do complementary experiments on the $\mathrm{Pd/N_2/Ar}$ and $\mathrm{Pd/N_2}$ systems [9]. In papers 1 [8] and 2 [9] of this series they reported these early result. In summary, the results of Ozin and García-Prieto [8, 9] demonstrated that the 200–260 nm absorption spectra of the Pd atoms isolated in an Ar matrix at 12 K are the result of the superposition of ΔJ-allowed transitions from the gas-phase $4d^{10}\,{}^1S_0^1$ ground state and from the $4d^9 5s^1\,{}^3D_3$ metastable state (lifetime of 2.2 min), with gas phase to matrix shift of less than 2400 cm^{-1}. The broad band luminescence data revealed at least two different Pd atom trapping sites where the deactivation of the excited states follow different pathways. In one site, the indirect photolytic population of the $^3D_3$ metastable state from the $^1S_0$ ground state seems to be very efficient. Recognizing this process, the excitation and emission spectra from the $^3D_3$ metastable state were identified and the detailed spectral assignments were given (a matrix shift of less of 1800 cm^{-1} was found in this case). Part of the excitation spectra correspond very well with the previously reported "transient absorption spectra" of Pd atoms isolated in Ne, Ar and Kr matrices [4, 6]. However, the assignment of the correspondent emission spectra contrast with published data [10] in which similar spectra have been ascribed to emission from the $Pd(N_2)_x$ complexes [9]. The other site contains Pd atoms whose emission spectra are characterized by a broad emission band at 486 nm. Finally, laser-induced luminescence revealed, unequivocally, the isolation of permanent $Pd(4d^9 5s^1\,{}^3D_3)$ atoms in a third site of an Ar matrix [9].

The purpose of the present research is to complete our understanding of the optical spectra of Pd atoms isolated in rare gas matrices (Ar, Kr and Ke). This allows to know the place where the Pd atoms reside and the influence of the surroundings on the electronic configuration of the ground and excited states of the metal atom.

2. EXPERIMENT

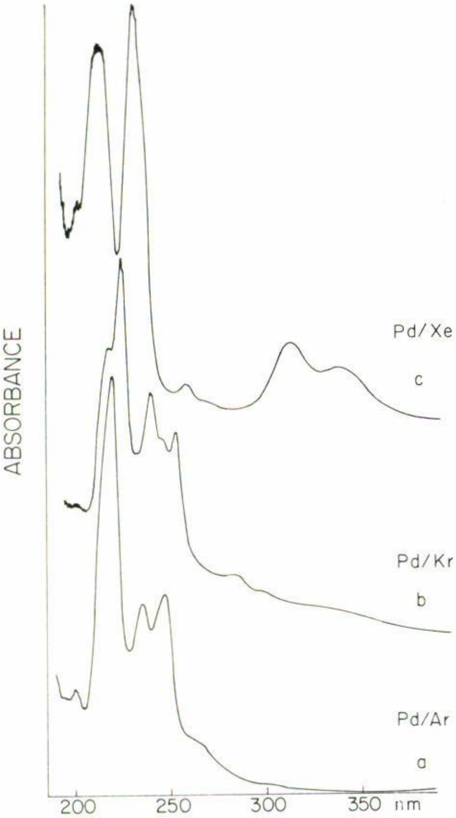
The experimental arrangement and the sample preparation method are essentially the same as those described in paper 1 [8]. In summary, the Pd metal (99.99% supplied by McKay Inc. NY) was resistively evaporated from Pd strips as well as Pd wire wound at the center of a Ta filament. Research grade Ar, Kr and Xe gases were supplied by Matheson of Canada. The temperature of the sample deposition was 12 K and the Pd/Matrix-Gas ratio mass always smaller than $1/10^4$ in order to guarantee the isolation of Pd atomic species. Some samples were annealed in the range of 12–35 K and some were irradiated with monochromatic uv-light by several periods of time.

The absorption spectra were recorded on a Perkin Elmer 330 spectrometer in the range of 195–900 nm, with high ordinate expansion in the region of 270–900 nm. The instrument only permitted scans from long to short wavelengths. Broad band emission and excitation studies were performed on a Perkin Elmer MFP-44B spectrometer in the 200–900 nm region. Spectral scans from short to long wavelengths only were possible with this instrument. Laser-induced luminescence experiments were performed with an Innova 90 series Ar ion laser source (lines at 454.5, 457.9, 465.8, 472.7, 476.5, 488.0, 496.5, 501.7 and 514.5 nm) coupled to 1-m Jobin Yvon Ramanor U-100 double monochromator and interfaced to a Columbia Model 964 microcomputer.

3. RESULTS

3.1. *The Pd/Ar system*

An exhaustive analysis of the uv-visible absorption and emission spectra of Pd atoms isolated in Ar matrices at 12 K has been reported in papers 1 [8] and 2 [9] of this



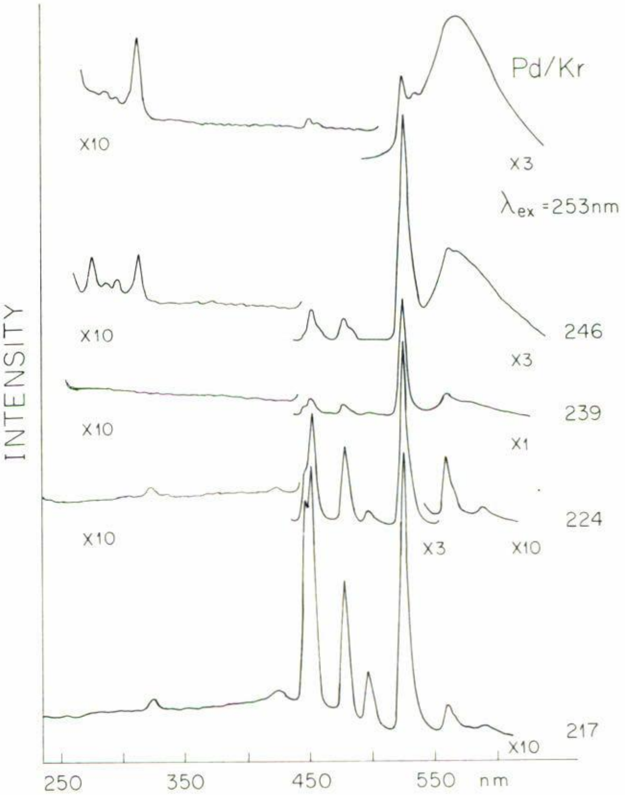


FIGURE 1. (Left) UV-Visible absorption spectra of Pd atoms isolated in (a) Ar, (b) Kr, and (c) Xe matrices at 12 K. Pd/RG $\simeq 1/10^4$. Spectral scanning in from long to short wavelengths.

FIGURE 2. (Right) Emission spectra of Pd atoms isolated in a Kr matrix (Pd/Kr $\simeq 1/10^4$) at 12 K, excited at the wavelengths indicated.

series. From this studies it was inferred that the Pd atoms occupy in an Ar matrix three main trapping sites. In two of them the electronic ground state of the Pd atoms is the same as in gas phase Pd atoms, that is $4d^{10}\,{}^1S_0$, whereas in the third, they have a $4d^9 5s^1\,{}^3D_3$ electronic ground state which is in gas phase 6564 cm^{-1} above the ground state. Additionally, it was found that in one of the trapping sites, which contains Pd(${}^1S_0$) atoms, there is a very efficient process of deactivation of the electronic excited states that end specifically in the long lived $4d^9 5s^1\,{}^3D_3$ metastable state (2.2 min). As consequence of this fact we interpreted the absorption spectra of Fig. 1a as a superposition of absorption spectra coming from Pd atoms in each main trapping site.)

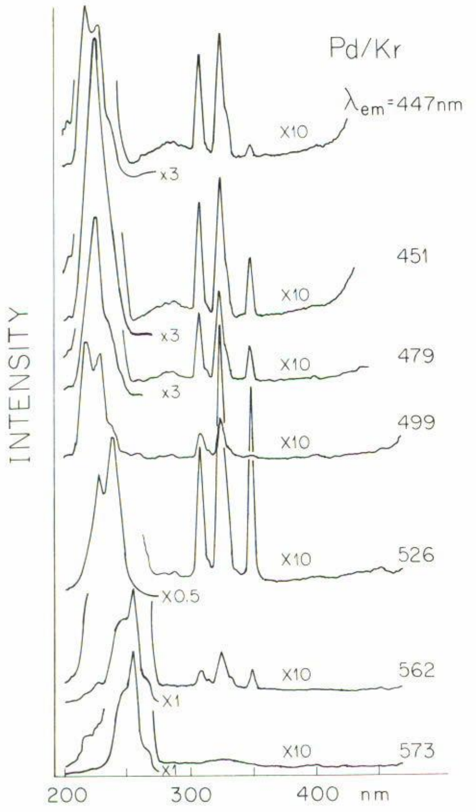
3.2. The Pd/Kr system

The optical spectra of Pd atoms isolated in Kr matrices have been previously investigated by the Ozin [2, 3], Grinter [4, 5] and Kolb [6] groups. As expected, our uv-visible absorption spectrum (Fig. 1b) is virtually identical to those previously reported. On the other hand, the spectrum is quite similar to that of Pd atoms isolated in Ar matrices and, as in this case, it shows more absorption bands than those expected for gas phase Pd atoms [7, 11]. In gas phase the expected transitions in the 200–400 nm range are those corresponding to $(4d^9 5p^1)^1\, {}^1P_1^0,\ {}^3D_1^0,\ {}^3P_1^0 \leftarrow (4d^{10})\, {}^1S_0$, which absorb at 245, 248 and 276 nm, respectively [12]. The fact that there are more bands than expected, has been interpreted by the Ozin [2, 3] and Kolb [6, 7] groups as a matrix effect, where there is an extensive mixture of states, implicating that the transitions from the ground state ${}^1S_0(4d^{10})$ to the twelve excited states with $4d^9 5s^1$ electronic structure (Fig. 8) can be partially allowed. This interpretation implies that the spectra of Pd atoms in a Kr matrix will have a blue shift, with respect to the correspondent gas phase, of almost 6000 cm^{-1}. In the basis of the results here reported, we will give, later on, an alternative interpretation that is substantially different to those given before [2–7].

The emission and excitation spectra of Pd/Kr are quite similar, in shape and behaviour, as of Pd/Ar one. As in the case of Pd/Ar the emission spectra that result from the selective photoexcitation of the Pd atoms at the wavelength correspondent to the maximal absorption, are constituted by two sets of bands in the 400–700 nm range (Fig. 2). The set of narrow bands, siting at 400–600 nm region, is quite similar in shape and position, even when not in intensity, to the Pd/Ar (Fig. 2 of Ref. [8]). As in the Pd/Ar system, the second set is constituted by only one broad band, but red shifted (maximum at 486 nm in Ar and 570 nm in Kr). As in Pd/Ar, the narrow bands emission spectra have their origins from the photoexcitation in all the 200–255 nm absorption region (Fig. 3), whereas the broad band emission has its origins from the photoexcitation in all the 240–255 nm absorption region (Fig. 3). On the other hand, and without counterpart in Pd/Ar, in the Pd/Kr we observe other set of emission bands in the 270–315 nm region and, as in the case of the broad emission band (570 nm), it has its origin from the photoexcitation in all the 240–255 nm absorption region.

As in the Pd/Ar system, the excitation spectra of the correspondent emission bands show two well defined regions (Fig. 3); one at 200–270 nm, which match very well with the absorption spectrum of the matrix isolated Pd atoms (Fig. 1b), and the other in the 300–350 nm, which has no counterpart in the atomic absorption spectra. The excitation spectrum associated with the 570 nm broad emission band does not show any band in the 290–350 nm region (Fig. 3), a comparable situation to Pd/Ar. The excitation spectrum corresponding to the emission of the 270–315 nm region, show a set of bands (Fig. 4), whose positions correspond to those of the excitation spectrum due to the broad emission band.

A detailed analysis of the 300–350 nm excitation spectrum reveal that, as in the Pd/Ar system, its intensity is dependent of the uv-light of the source of excitation of the spectrometer in use (Fig. 5). However, it is important to remark that, at difference of Pd/Ar, the intensity of the excitation spectrum grows, not only when the sample is previously irradiated in the 200–240 nm region, but also (even when in less intensity, 38%) when is irradiated in the 315–340 nm region According with the observed photodependence of the excitation spectrum of the 290–350 nm region, the emission spectrum also shows a dependence with the uv-light. From Fig. 6 we can see that the intensity of the emission spectrum of narrow bands depend if the sample has been previously ir-



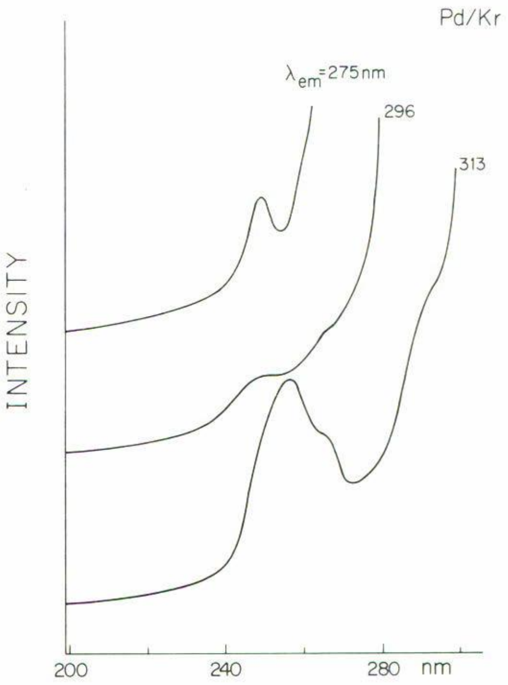


FIGURE 3. (Left) Excitation spectra of Pd atoms isolated in a Kr matrix ($Pd/Kr \simeq 1/10^4$) at 12 K, with the emission monochromator set at the wavelengths indicated. Spectral scanning is from short to long wavelengths.

FIGURE 4. (Right) Excitation spectra of Pd atoms isolated in a Kr matrix ($Pd/Kr \simeq 1/10^4$) at 12 K, with the emission monochromator set at the wavelengths indicated. Spectral scanning is from short to long wavelengths.

radiated with 240 nm-light. However, it is important to remark, as is suggested by the excitation spectra of Fig. 5 (traces 1 to 4) that the emission spectra of narrow bands before 240 nm-light irradiation (Fig. 6, traces a and c) might correspond to an emission spectrum that result from a metastable state that is simultaneously prepared with the same light excitation. This situation contrasts with the apparent absence of absorption bands (Fig. 1b) in the 290–350 nm region of the uv-visible absorption spectrum of this system. In fact the uv-visible absorption spectrum of Pd atoms isolated in a Xe matrix, which later on will be considered (Fig. 1c), shows clearly the presence of absorption bands in this spectral region.

A systematic study on the concentration of Pd atoms and contaminant molecules (as N_2 or O_2) in the sample, has demonstrated without any doubts that the isolated species are Pd atoms [8, 9]. Under this premise we can interpret the photosensitive spectra of the Pd/Ar and Pd/Kr systems as those corresponding to Pd atoms where the electronic tran-

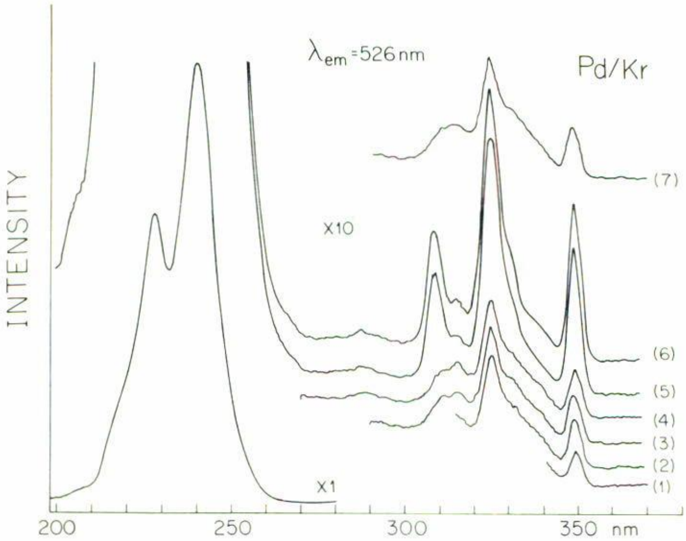


FIGURE 5. Excitation spectra of Pd atoms isolated in a Kr matrix (Pd/Kr $\simeq 1/10^4$) at 12 K, with the emission monochromator set at 526 nm. Spectral scanning is from short to long wavelengths starting at: (1) 340 nm, (2) 315 nm, (3) 290 nm, (4) 270 nm, (5) 240 nm, (6) 200 nm, and (7) 290 nm. The sample was kept in the dark for 15 min between each scan.

sitions are originated from a specific metastable state. The fact that the narrow emission bands are also generated when the Pd atoms are photoexcited in the 200–260 nm region, corresponding to the expected transitions [11, 12] $(4d^9 5p^1)\,{}^1P_1^0,\ {}^3D_1^0,\ {}^2P_1^0 \leftarrow (4d^{10})\,{}^1S_0$, suggest the occurrence of a intersystem crossing from singlet to triplet states. The similarity of the emission spectra that result from the photoexcitation in the atomic absorption region (220–260 nm) and the other that result from the photoexcitation in the 290–350 nm spectral region after photolysis by uv-light (215–250 nm) implicate that the same electronic states, from the triplet state manifold, are involved in these transitions. An exception to this are the emission bands at 486 nm for Pd/Ar and 270–315 nm and 570 nm for Pd/Kr system, which only appear following the excitation in the 245–255 nm absorption region and apparently do not show any uv-light dependence. In fact the 486 nm emission band has been interpreted as due to Pd atoms whose deactivation process is different to that which shows a spectra of narrow emission bands uv-light dependent [8, 9].

A detailed correlation of all observed bands (of excitation and emission) in the Pd/Ar system with those electronic energy levels of Pd atoms has allowed to establish that the metastable state which is reponsible of the observed photosensitive spectra, should be the $4d^9 5s^1\,{}^3D_3$ state, which is 6564 cm^{-1} above the $4d^{10}\,{}^1S_0$ ground state of gas phase Pd atoms [12]. In view of the similarities of the photosensitive spectra of the Pd/Ar and Pd/Kr systems, we must conclude that the metastable state is the same in both cases and that in both systems operate the same mechanisms that provoke the observed spectra. In agreement with this assignment is the estimated lifetime of the ${}^3D_3$ metastable state, which is 2.2 and 1.2 min in Ar and Kr matrices, respectively. We must point out that

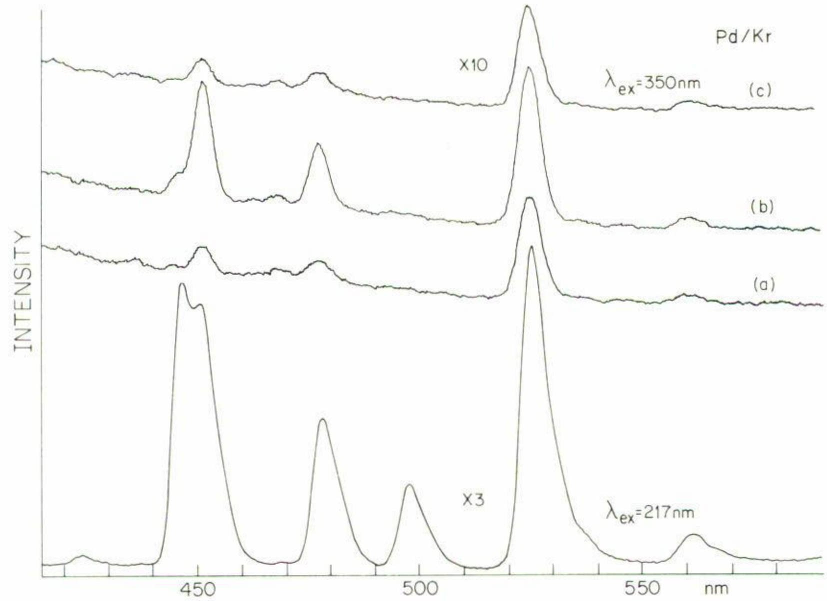


FIGURE 6. Emission spectra of Pd atoms isolated in a Kr matrix (Pd/Kr $\simeq 1/10^4$) at 12 K, excited at 350 nm: (a) after 30 min in the dark, (b) immediately after 240 nm photolysis for 5 min, and (c) after 15 min in the dark. For comparison purposes the emission spectra excited by 215 nm monochromatic light has been included.

this lifetimes have been determinated indirectly, measuring the rate of decaying of the 340 nm excitation band in Ar and its correspondent at 349 nm in Kr matrices (Fig. 7). In paper 1 [8] the details of the procedure followed in order to get this lifetimes, are given.

A summary of the mechanism that operates in the formation of the photosensitive spectra of the Pd/Ar and Pd/Kr systems, is given in Fig. 8; in Table I is given the assignment of the observed bands. Fig. 8 suggests that after photoexcitation of the Pd${}^1S_0$ atoms, isolated in an Ar or Kr matrix, to their first ΔJ-allowed excited states (${}^1P_1^0$, ${}^3D_1^0$ and ${}^3P_1^0$) [12], a fast (roughly picosecond) nonradiative relaxation process [13, 14] populates lower exited states in the triplet manifold which subsequently relax by radiative and nonradiative process to the ${}^3D_3$ metastable state. Once in the ${}^3D_3$ state, the Pd atoms are sufficiently long lived to suffer excitations to states inaccessible from the ${}^1S_0$ ground state. Once prepared in these excited states, the Pd atoms are again able to relax radiatively and nonradiatively to lower excited states within the manifold of the ${}^3D_3$ metastable state. This cycle will be perpetuated until the Pd(${}^3D_3$) atoms population is depleted through relaxation to one ${}^1S_0$ ground state. It is noteworthy that the excited Pd atoms can potentially also escape from the triplet manifold by the spin-forbidden transitions ${}^1D_2 \leftarrow {}^3F_3$ (see Table I and Fig. 8). From this state the Pd atom could reenter to the triplet manifold by a nonradiative process or relax to the ${}^1S_0$ ground state. In view of the ΔJ-forbidden nature of the ${}^1D_2 \rightarrow {}^1S_0$ transition, the large energy gap between these two electronic levels, and the facility of the repopulation of the ${}^3D_3$ state through the ${}^1D_3$ and ${}^3D_2$ states, it is expected that the depopulation of the triplet manifold via the latter

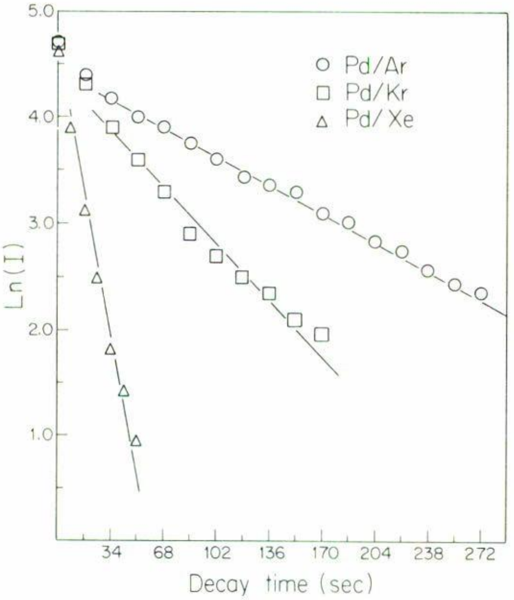


FIGURE 7. Lifetime plot of the $^3D_3$ metastable state of the Pd atoms isolated in Ar, Kr and Xe matrices, and measured through the decay of the excitation band at 340, 349 and 363 nm (for Ar, Kr and Xe, respectively), and with the emission monochromator set at 526, 525 and 529 nm, respectively.

mechanism will be minor as compared to the direct deactivation from the $^3D_3$ state.

Returning to the absorption spectra of the Fig. 1, it is now reasonable to propose that for the Pd/Ar and Pd/Kr systems their spectra are the result of the superposition of ΔJ-allowed transitions from the $^1S_0$ ground state and those from the $^3D_3$ metastable state. The efficient and rapid population of the $^3D_3$ metastable state, together with the relatively fast response of the uv-visible spectrometer compared to the long lifetime (2.2 and 1.2 min in Ar and Kr, respectively) of this state, creates the interesting situation that the ΔJ-allowed transitions $(4d^96s^1)\,^3D_2,\,^3D_3 \leftarrow (4d^95s^1)\,^3D_3$ and two $4d^85s^1(\ )5p^1 \leftarrow (4d^95s^1)\,^3D_3$ occur during the spectral scanning period (normally 20 nm/min). As it can be derived from Fig. 8, the first two transitions are expected to fall around the same spectral region as the ΔJ-allowed transitions $(4d^95p^1)\,^1P_1^0,\,^3D_1^0,\,^3P_1^0 \leftarrow (4d^{10})\,^1S_0$, whereas the last two are expected to be at slightly higher energy. A more precise indentification of these band will be given latter on in the Pd/Xe system.

A detailed analysis of the narrow band excitation spectrum (290–350 nm) of the Pd/Ar system (Fig. 4 of Ref. [8]) revealed the existence of a stable atomic specie of palladium which coexist with the Pd($^1S_0$) atoms [8, 9]. This was evident when we analyzed in detail the emission spectra that result from the 340 nm photoexcitation without previous uv-light photolysis (Fig. 5 of Ref. [8]). The resultant spectrum is quite similar, even when in much less intensity, than the photosensitive spectrum. In view that the profile of the emission and excitation spectra for both species are almost identical (Figs. 4 and 5 of Ref. [8]), this has been interpreted as evidence of the coexistence, in an Ar matrix at 12 K, of Pd atoms isolated in two stable electronic states: the $4d^{10}\,^1S_0$ and the $4d^95s^1\,^3D_3$. A

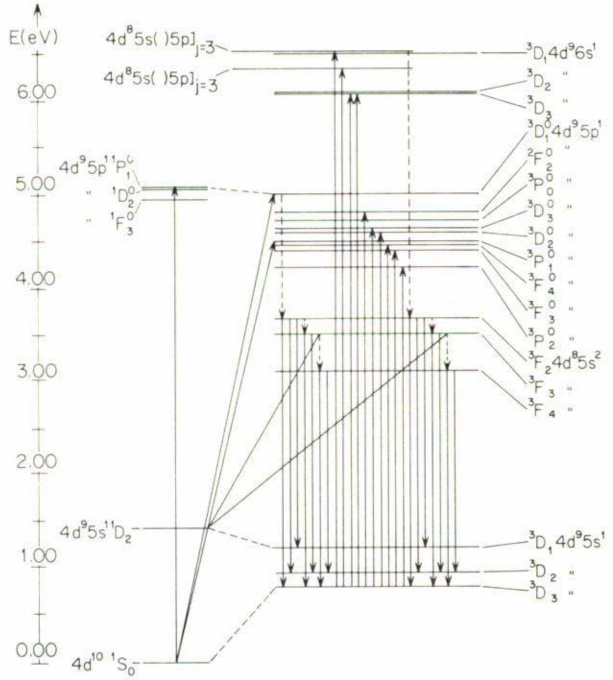


FIGURE 8. Atomic gas-phase Pd energy level diagram depicting the $J \to J$ allowed transitions ($\rightarrow$) and nonradiative transitions ($\dashrightarrow$). Gas-phase data were taken from C.E. Moore, Natl. Bur. Stand (US) Circ. 467 (1958), where it is noted that no information is given about the terms and multiplicities of the $4d^8 5s(\ )5p$ states.

definitive confirmation of this proposal was given from a systematic study of laser-induced luminescence [9], where the sample was photoexcited in the spectral region correspondent to the electronic transitions $4d^8 5s^2\,{}^3F_4 \leftarrow 4d^9 5s^1\,{}^3D_3$ and $4d^8 5s^2\,{}^3F_3 \leftarrow 4d^9 5s^1\,{}^3D_3$. The resulting emission spectra (Fig. 11 of Ref. [9]) are constituted by a set of bands, which are completely indentified with transitions from the ${}^3F_4$ and ${}^3F_3$ excited states to lower excited states and the ${}^3D_3$ ground state (Fig. 14 of Ref. [9]).

A similar situation to that described for the Pd/Ar system was observed in the Pd/Kr system, but now with the notable difference that in this system the excitation spectra of the 300–360 nm region is apparently photosensitive to the light of this spectral region. This is manifested in the 349 nm excitation band where we observe an increasing of 38% when the sample is 315–345 nm irradiated with the spectrometer light source (Fig. 5). An explanation of this fact can be found in the diagram of energy levels of Fig. 8 assuming that those originally forbidden transitions from the $4d^{10}\,{}^1S_0$ state are now (by the heavy atom effect [15] of Kr atoms) allowed, which provoke that the cycle that was before described for the photosensitive spectra here is applied again. A confirmation of this proposal is found in the Pd/Xe system where the heavy atom effect is even stronger (see later on).

With this observations we could question the stabilization of the Pd(${}^3D_3$) atoms coexisting with those Pd(${}^1S_0$) atoms in a Kr matrix at 12 K. However our study of laser-

TABLE I. Position (λ, nm) and assignment of some excitation (absorption) and emission bands of Pd atoms isolated in Ar, Kr and Xe matrices at 12 K. The spectral shift is with respect to gas phase Pd atoms. (cm^{-1}).

Matrix			Gas phase	Assignment	Spectral shift		
Ar	Kr	Xe			Ar	Kr	Xe
299	309	321	310	$4d^95p^1\,{}^3F_2^0 \leftarrow 4d^95s^1\,{}^3D_3$	+1187	+104	−1105
			324	$4d^95p^1\,{}^3D_3^0 \leftarrow 4d^95s^1\,{}^3D_3$			
316	326	338	329	$4d^95p^1\,{}^3D_2^0 \leftarrow 4d^95s^1\,{}^3D_3$	+1250	+280	−809
323	331	342	341	$4d^95p^1\,{}^3F_4^0 \leftarrow 4d^95s^1\,{}^3D_3$	+1634	+886	−86
			346	$4d^95p^1\,{}^3F_3^0 \leftarrow 4d^95s^1\,{}^3D_3$			
341	350	361	364	$4d^95p^1\,{}^3P_2^0 \leftarrow 4d^95s^1\,{}^3D_3$	+1853	+1099	+228
424	424	425	432	$4d^85s^2\,{}^3F_2 \rightarrow 4d^95s^1\,{}^3D_3$	+437	+437	+381
445	447	449	455	$4d^85s^2\,{}^3F_2 \rightarrow 4d^95s^1\,{}^3D_2$	+494	+393	+294
451	451	454	462	$4d^85s^2\,{}^3F_3 \rightarrow 4d^95s^1\,{}^3D_3$	+528	+528	−381
478	478	481	489	$4d^85s^2\,{}^3F_3 \rightarrow 4d^95s^1\,{}^3D_2$	+471	+471	+340
500	498	500	510	$4d^85s^2\,{}^3F_2 \rightarrow 4d^95s^1\,{}^3D_1$	+392	+472	+392
526	525	529	539	$4d^85s^2\,{}^3F_4 \rightarrow 4d^95s^1\,{}^3D_3$	+459	+495	+351
562	560	565	577	$4d^85s^2\,{}^3F_4 \rightarrow 4d^95s^1\,{}^3D_2$	+463	+526	+368
592	590	593	606	$4d^85s^2\,{}^3F_3 \rightarrow 4d^95s^1\,{}^1D_2$	+390	+448	+362

induced luminescence, analogous to those of the Pd/Ar system [9], that are summarized in Fig. 9 confirm that, as in Pd/Ar system, the photoexcitation in the spectral region of the ${}^3F_4$, ${}^3F_3 \leftarrow {}^3D_3$ transitions produce an emission spectrum that only is compatible with Pd atoms stabilized in the ${}^3D_3$ ground state. Table II gives the position and assignment of the emission bands observed in our study of laser-induced luminescence of the Pd/Ar and Pd/Kr systems in the spectral range allowed by our instruments (454.5–773.0 nm).

A complete justification of the assignments given in Table II is given in paper 2 [9] for the Pd/Ar system, here we only put in evidence the differences with respect to the Pd/Kr system. First, we must remark the differences in energy that we observe in Tables I and II for the same transitions. This is more notorious for the ${}^3F_3 \rightarrow {}^3D_3$, ${}^3D_2$, ${}^1D_2$ emissions, with a difference of almost 435 cm^{-1}. Assuming that in both cases the assignment is correct, the origin of the differences should be in the differences of the rearrangements of the Pd atom-crystal lattice system that follow the excitation or, and maybe more probably, in the excitation of Pd atoms in secondary sites by the narrow band laser-light source (compared to the broad band arc-xenon light source) with emissions to different wavelengths of that of Pd atoms in the main trapping site. With respect to this last point, we observe that the emission bands at 535 and 574 nm (this last absent in the Pd/Kr system) that follow to the 457.9 nm excitation correspond to the satellite bands joined to the main 526 and 560 nm emission bands that follow the excitation at 514.5 nm (Fig. 11 of Ref. [9] and Fig. 9 of the present report). Their behaviour and expected absence of

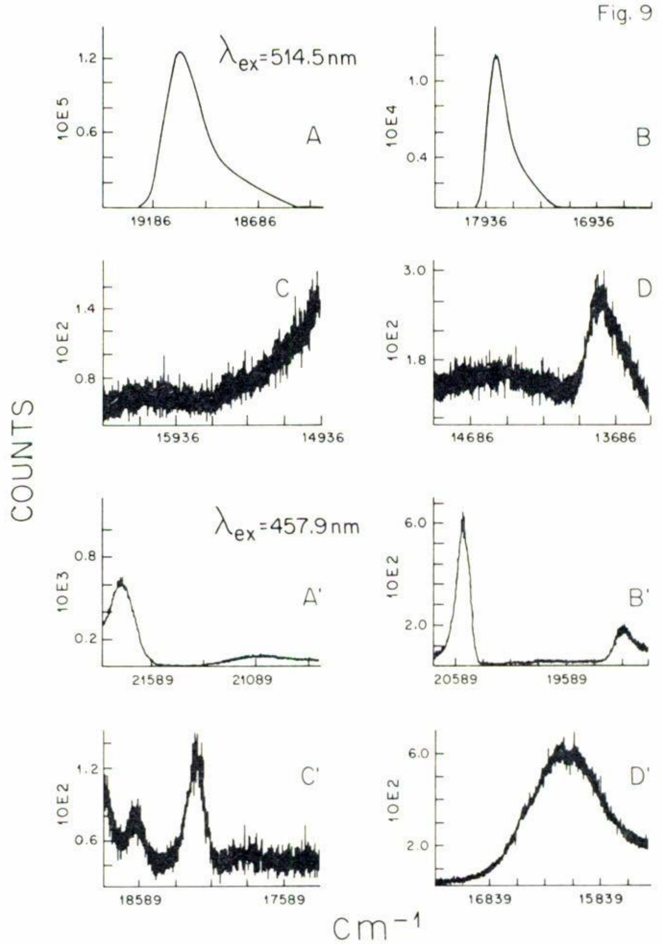


FIGURE 9. Laser-induced emission spectra of Pd/Kr at 12 K, excited (A)–(D) at 514.5 nm and (A′)–(D′) at 457.9 nm. Laser power for (A) and (B) 30 mW, for (C) and (D) 200 mW, and for (A′)–(D′) 100 mW.

emission bands in these spectral regions for free Pd atoms, suggest that they should correspond to Pd($^3D_3$) atoms isolated in secondary trapping sites. Their presence after 457.9 nm excitation should correspond to the internal relaxation from the $^3F_3$ state to the lower $^3F_4$. On the other hand, we must remark that in laser induced luminescence the $4d^8 5s^2\,{}^3F_3$ state is reached directly by photoexcitation from the $4d^9 5s^1\,{}^3D_3$ state (Fig. 9), whereas in the broad band arc xenon excitation (Fig. 2) this state is reached from higher energy states having a $4d^9 5p^1$ electronic configuration.

Here is notorious the absence of the emission bands, induced by laser excitation, corresponding to the $^3F_4 \rightarrow {}^3D_1$ and $^3F_3 \rightarrow {}^1D_2$ transitions in the Pd/Kr systems. However, they are the more weaker in the Pd/Ar system (Fig. 11 of Ref. [9]) and probably in the Pd/Kr system they are out of the detection levels of our instrument or, perhaps more probable, efficient non-radiative process that inhibit this radiative transitions [13], became active.

TABLE II. Position and assignment of the laser-induced emission bands (λ_{ex} = 457.9 and 514.5 nm) of the Pd/Ar and Pd/Kr systems at 12 K. The spectral is with respect to gas phase Pd atoms

Matrix				Gas phase		Assignment	Spectral Shift (cm^{-1})	
Ar		Kr					Ar	Kr
nm	cm^{-1}	nm	cm^{-1}	nm	cm^{-1}			
460	21739	460	21739	462	21645	$4d^85s^2\,{}^3F_3 \to 4d^95s^1\,{}^3D_3$	+94	+94
—		475	21053					
488	20492	487	20534	489	20450	$4d^85s^2\,{}^3F_3 \to 4d^95s^1\,{}^3D_2$	+42	+84
525	19048	525	19048	539	18553	$4d^85s^2\,{}^3F_4 \to 4d^95s^1\,{}^3D_3$	+495	+495
538	18587	537	18622					
550	18182	549	18215	552	18116	$4d^85s^2\,{}^3F_3 \to 4d^95s^1\,{}^3D_1$	+66	+99
560	17857	561	17825	577	17331	$4d^85s^2\,{}^3F_4 \to 4d^95s^1\,{}^3D_2$	+526	+494
575	17391	—	—					
605	16529	—	—	606	16502	$4d^85s^2\,{}^3F_3 \to 4d^95s^1\,{}^1D_2$	+27	—
—	—	619	16155					
644	15528	—	—	666	15015	$4d^85s^2\,{}^3F_4 \to 4d^95s^1\,{}^3D_1$	+513	—
—	—	689	14514					
725	13793	725	13793	747	13387	$4d^85s^2\,{}^3F_4 \to 4d^95s^1\,{}^1D_2$	+406	+406

Another thing that reveals the laser-induced luminescence studies is the presence of the relative broad band at 619 nm (16155 cm^{-1}) that appears as consequence of the 457.9 nm excitation in the Pd/Kr system. As we can see from the diagram of energy levels of the Pd atom (Fig. 8), the number of possible transitions from the $4d^85s^2\,{}^3F_4$ to the lower energy levels of $4d^95s^1$ configuration are only four of which has been fully identified (Table II). With respect to the $4d^85s^2\,{}^2F_3$ excited state, we also expect the same four transitions, as result of the non-radiative relaxation ${}^3F_3 \rightsquigarrow {}^3F_4$, and four more transitions, corresponding to ${}^3F_3 \to {}^1D_2\,{}^3D_1\,{}^3D_2\,{}^3D_3$; this last have been also identified (Table II). Assuming that the 619 nm band correspond to Pd atoms, this necessarily should correspond to whatever of the two possible transitions (energetically speaking): ${}^3F_3 \to {}^1S_0$ or ${}^3F_4 \to {}^1S_0$. The first corresponds to a displacement of the $4d^{10}\,{}^1S_0$ state above the levels of $4d^95s^1$ configurations, whereas in the second this level should be in between ${}^3D_2$ and ${}^3D_1$ levels of $4d^95s^1$ configuration. In the first we could expect a shift of 1.45 eV, whereas in the second it could be of 0.96 eV, both above their values in the gas phase. Finally, the very weak and very broad emission bands at 475 and 689 nm of the laser-induced luminescence of the Pd/Kr system could be of palladium complexes formed with impurities in the sample [9].

In summary, we can say that in the Pd/Kr system, as in the Pd/Ar system [8, 9], the Pd atoms reside in three different trapping sites. In two of them the Pd atom is

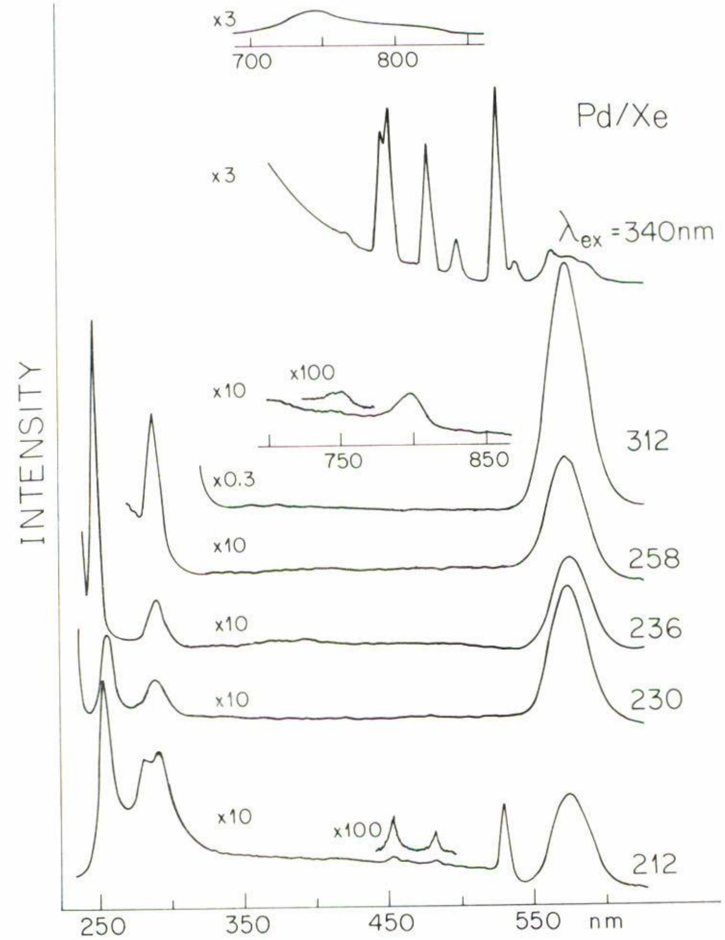


FIGURE 10. Emission spectra of Pd atoms isolated in a Xe matrix (Pd/Xe $\simeq 1/10^4$) at 12 K, excited at the wavelengths indicated.

stabilized in the $4d^{10}\,{}^1S_0$ state whereas in the third in the $4d^9 5s^1\,{}^3D_3$ state. The differences in the structure of the trapping sites for the first two is manifested in differences in the mechanism of deactivation of electronically excited Pd atoms. In one of them the crossing to triplet sites is quite efficient and produces emission and excitation spectra which are photosensitive. In the other, it seems that the combination of radiative and non-radiative mechanisms are operative and lead directly to the $4d^{10}\,{}^1S_0$ ground state. On this respect the results of the Pd/Xe system are much more informative and, therefore, we postpone the discussion on the nature of this sites for later on. The third site is much more peculiar, its effect is such that change the ground state electronic configuration of the Pd atoms, from $4d^{10}\,{}^1S_0$ to $4d^9 5s^1\,{}^3D_3$. It is important to remark that, even when there is a substantial interaction energy, $\Delta E({}^3D_3 - {}^1S_0) \simeq 0.81$ eV, that is developed between the entrapped atom and the matrix lattice, in this third trapping site the relative energies between the distinct electronic levels are almost unaffected.

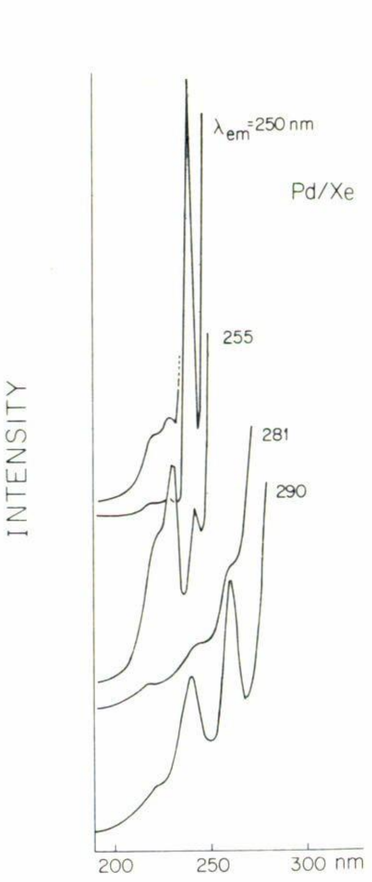
3.3. The Pd/Xe system

The uv-visible absorption spectrum of the Pd atoms isolated in a Xe matrix at 12 K is shown in Fig. 1c. As expected this spectrum is virtually identical to those reported by Kolb [6] and Ozin [2, 3] groups at 5.5 K and 6–8 K, respectively. It is important to point out that the absorption bands observed in the 290–370 nm region seems to have no counterpart in the absorption spectra of the Pd/Ar and Pd/Kr systems (Fig. 1a and 1b, respectively). This bands together with those observed in the 250–290 nm region, have been excluded by Kolb and co-workers [6] as originated by Pd atoms.

Annealing experiments to different temperatures (12–40 K) show substantial changes in the intensity and profile of the spectrum. This changes are similar to those observed in Ar and Kr matrices [3, 6], which have been interpreted as a consequence of the trapping site distribution and agglomeration of the Pd atoms to high temperatures [6]. Contrary to this thermic effects, the photoexcitation in distinct absorption regions, by periods of more than one hour, do not induce any substantial change in the spectrum. It is important to remark that the 250–370 nm absorption spectrum under thermic and photolytic treatment, follow similar behaviour as that of the 200–250 nm absorption spectrum.

The emission spectra, that follow the selective photoexcitation of the Pd/Xe sample, is shown in Fig. 10. A direct comparison of this emission spectra with those of the Pd/Ar (Fig. 2 of Ref. [8]) and Pd/Kr (Fig. 2) reveal certain similitudes and notable differences. The three systems show a broad and intense emission band (maximal at 485, 573 and 577 nm in Ar, Kr and Xe, respectively) and also a narrow band spectrum in the 400–600 nm region, which are very similar in shape and position (Fig. 2 of Ref. [8] and Fig. 2 and 10, respectively). In the differences lies the fact that in Ar and Kr matrices the broad emission band is only produced under photoexcitation in the 245–255 nm region, whereas that in Xe matrix is produced under photoexcitation in any part of the 210–340 nm spectral region. In the Pd/Ar and Pd/Kr systems the emission spectrum is dominated by the narrow band spectrum (420–600 nm), whereas that in Xe matrix this spectrum is only produced under photoexcitation at 212 and 340 nm. As in the Pd/Kr system, in the Pd/Xe system there are emission bands in the high energy region (short wavelengths), however, they differ in shape and position in the first case they are in the 270–315 nm region, in the second in the 245–300 nm. Finally, at the more sensitive level of detection in the Pd/Xe system were also observed emission bands in the 700–850 nm region.

The excitation spectra, corresponding to the emission bands of the Pd/Xe system, are shown in Figs. 11, 12 and 13. The excitation spectra corresponding to the 425, 500, 540 and 590 nm emission bands, not shown in these figures, are quite similar in shape and position as those corresponding to the 481 and 528 nm emission bands, respectively. In contrast with the excitation spectra of the Pd/Ar and Pd/Kr systems those of the Pd/Xe look more complicated but, however, we can still find some similitudes. As in the Pd/Kr system the excitation spectra correspondent to the high energy emission bands (245–300 nm, Fig. 11) show a set of bands localized at the same region of the main absorption spectrum (210–265 nm, Fig. 1c). In this excitation spectra we can distinguish clearly the 229 nm ($\lambda_{\mathrm{em}} = 255$ nm) and 260 nm ($\lambda_{\mathrm{em}} = 290$ nm) bands that correspond in position to those observed in the absorption spectrum (Fig. 1c) at 230–238 and 259 nm,



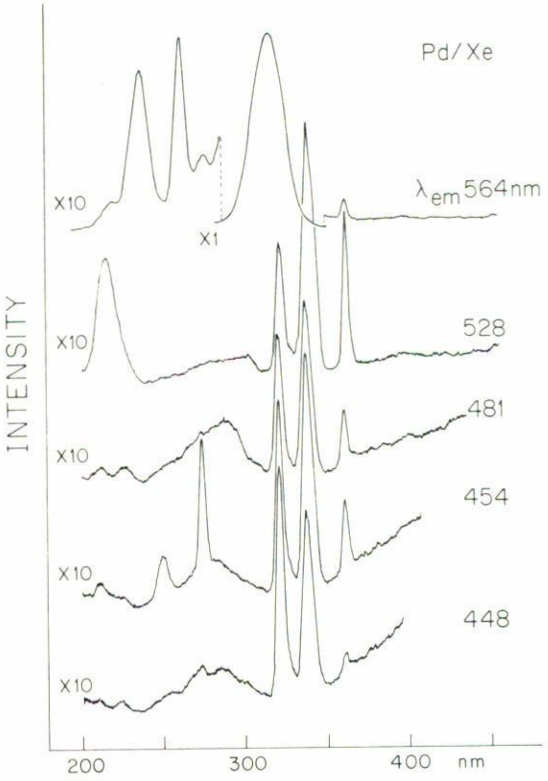
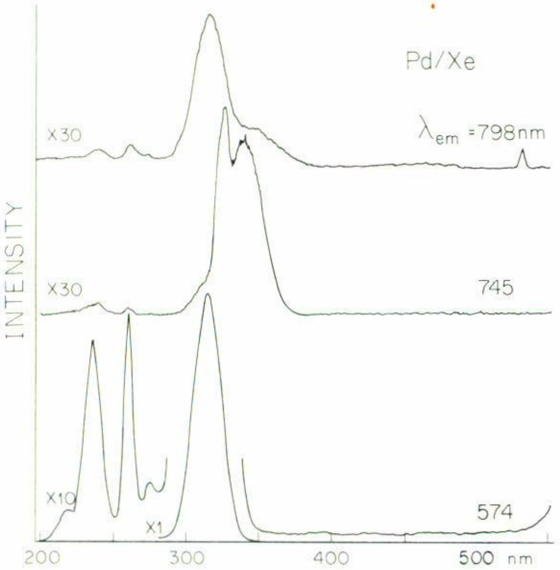


FIGURE 11. (Left) Excitation spectra of Pd atoms isolated in a Xe matrix (Pd/Xe $\simeq 1/10^4$) at 12 K, with the emission monochromator set at the wavelengths indicated. Spectral scanning is from short to long wavelengths.

FIGURE 12. (Right) Excitation spectra of Pd atoms isolated in a Xe matrix (Pd/Xe $\simeq 1/10^4$) at 12 K, with the emission monochromator set at the wavelengths indicated. Spectral scanning is from short to long wavelengths.

respectively. On the other hand, the set of narrow emission bands (420–600 nm) show an excitation spectrum quite similar to those of Pd/Ar and Pd/Kr systems in the 290–365 nm region (Fig. 3 of Ref. [8] for Pd/Ar, Fig. 3 for Pd/Kr and Fig. 12 for Pd/Xe), however, only in the Pd/Xe system specific excitation bands in the high energy region (210–226, 249 and 273 nm) are observed. Particularly important is the 215 nm excitation band (Fig. 12, $\lambda_{\text{em}} = 528$ nm) because it corresponds in shape and position to the 212 nm absorption band (Fig. 1c).

As in the Pd/Ar and Pd/Kr systems, the excitation spectrum related to the 574 nm broad emission band does not show narrow excitation bands in the 300–365 nm region (Fig. 13) but shows a broad band at 315 nm, which corresponds in shape and position to the 313 nm absorption band (Fig. 1c). Moreover, the excitation spectra show also a set of bands at 275, 260, 235 (broad) and, less intense, at 210–220 nm. It is important to remark that the excitation bands at 275, 260 and 235 nm correspond in position, but



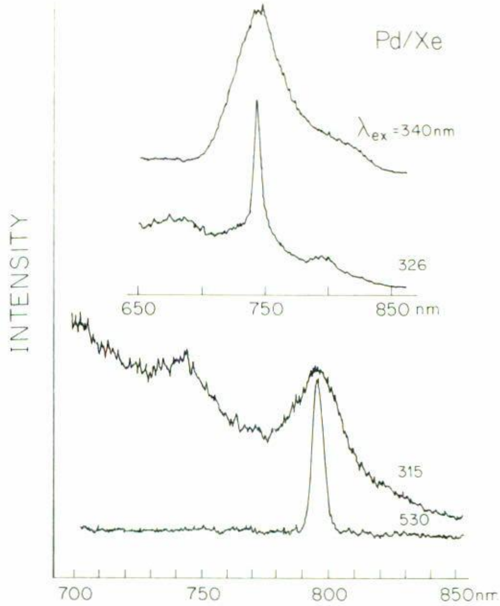


FIGURE 13. (Left) Excitation spectra of Pd atoms isolated in a Xe matrix (Pd/Xe $\simeq 1/10^4$) at 12 K, with the emission monochromator set at the wavelengths indicated. Spectral scanning is from short to long wavelengths.

FIGURE 14. (Right) Emission spectra of Pd atoms isolated in a Xe matrix (Pd/Xe $\simeq 1/10^4$), excited at the wavelengths indicated.

not in intensity, to those observed in the uv-visible absorption spectrum (Fig. 1c) to 270, 259 and 230–238 nm, respectively.

The excitation spectra related to the emission bands at 745 and 798 nm (Fig. 13) show a set of bands that are the same as those related to the 574 nm broad emission band but much less intense (bands at 235, 260, 275 and 315 nm). However, at difference of the excitation spectra related to the 574 nm broad emission band, the excitation spectra related to the 745 and 798 nm emission bands show also a set of unique bands: one broad in the 340 nm region, common to both, and other narrow, one at 376 nm related to the 745 nm emission band and the other at 530 nm due to the 798 nm emission band. The emission spectra that result from the 326 and 530 nm photoexcitation show a very interesting situation. Exciting them at 326 nm produce an emission spectra quite similar to that produced by excitation at 340 nm, but with the notable difference that in this case the 746 nm emission band is much more narrow (Fig. 14). Exciting at 530 nm only one narrow emission band results and coincides in position with the 797 nm broad emission band that results from the photoexcitation at 315 nm (Fig. 14).

As in Pd/Ar and Pd/Kr, the 315–365 nm excitation spectra related to the narrow emission bands of the Pd/Xe system show a clear dependence with the uv-light. Figure 15 shows in detail this effect for the excitation spectrum related to the 529 nm emission band (similar results were obtained for the other narrow emission bands of the 420–600 nm region). As it was established in the Pd/Ar and Pd/Kr systems, these spectra reveal

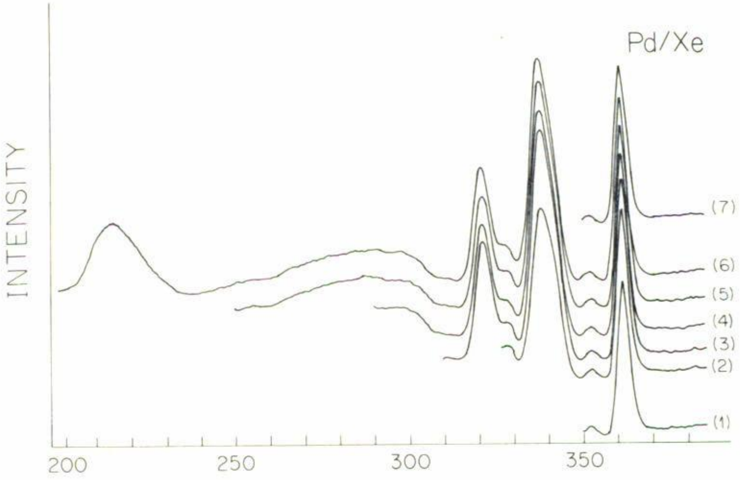


FIGURE 15. Excitation spectra of Pd atoms isolated in a Xe matrix (Pd/Xe $\simeq 1/10^4$) at 12 K, with the emission monochromator set at 529 nm. Spectral scanning is from short to long wavelengths starting at: (1) 350 nm, (2) 327 nm, (3) 310 nm, (4) 290 nm, (5) 250 nm, (6) 200 nm, and (7) 350 nm. The sample was kept in the dark for 15 min between each scan.

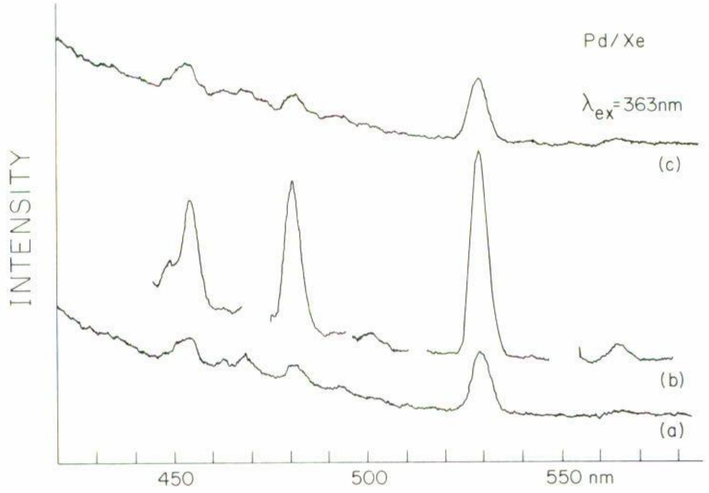


FIGURE 16. Emission spectra of Pd atoms isolated in a Xe matrix (Pd/Xe $\simeq 1/10^4$) at 12 K, excited at 350 nm: (a) after 30 min in the dark, (b) immediately after 315 nm photolysis by 1 min (with a spectral scanning rate of 60 nm/min in each spectral range indicated), and (c) after 5 min in the dark.

that their intensity will depend of the previous absorption of uv-light. As in the Pd/Kr system, but not in the Pd/Ar system, the intensity of the 315–365 nm excitation spectra will depend of the 315–350 nm light absorption (in the case of the Fig. 15 we observe an increase of 18 and 28% in the 362 and 337 nm excitation bands, respectively). It is very important to remark that the substantial increase in the intensity of the narrow bands 290–360 nm excitation spectra of Pd/Ar (∼800%) and Pd/Kr (∼350%) systems will occur when the samples are previously irradiated with 210–250 nm light, this is not the case for the Pd/Xe system where their excitation spectra do not change in intensity when the sample is irradiated with 210–250 nm light.

According with this photosensitive behaviour of the narrow bands 315–365 nm excitation spectra are the photosensitive behaviour of their related emission spectra. An example of this is given in Fig. 16 for the 363 nm excitation (The other lines show the same behaviour): first, keeping the sample in the dark for 30 min after deposition and latter on photoexciting at 315 nm by 1 min periods and taking immediately the emission spectrum in the indicated spectral region; finally, after 10 min of keeping the sample in the dark. The fast decay in the intensity of the emission band is indicative of the shorter lifetime of the metastable state in this matrix than in Ar or Kr matrix.

The decay of the 363 nm excitation band, monitored through the 529 nm emission band, was measured and the resulting lifetime was of 0.2 min (Fig. 7). With the exception of the first seconds, where the decay is very fast and not exponential, the decay is of first order. As in the Pd/Ar and Pd/Kr systems we investigated the laser-induced luminescence at wavelengths of the 454.5–514.5 nm region. Surprisingly, given the results in Pd/Ar and Pd/Kr, there was not detected any emission band in the 454.5–773.0 nm spectral range.

4. DISCUSSION

4.1. Main trapping sites

4.1.1. First trapping site

It was pointed out that the optical spectra of the Pd/Xe system show many similarities with those of the Pd/Ar and Pd/Kr systems, but also show notable differences. The similarity of the narrow band emission spectra and their related excitation expectra (at least in the 300–360 nm region), and their common photodependence, suggest that in the three matrices exist trapping sites of the Pd($4d^{10}\ {}^1S_0$) atoms, in which the ${}^3D_3$ metastable state is the reference state from which occur many of the observed transitions following a mechanism as that summarized in Fig. 8. However, and at difference of that observed in the Pd/Ar and Pd/Kr systems, in the Pd/Xe system this mechanism seems to be not predominant. This is manifested in the excitation spectra where it is observed that only certain regions of these spectra (205–230, 250–300 and 310–365 nm regions, in Fig. 12) are able to produce the narrow bands emission spectra, which contrast with those observed in the Pd/Ar and Pd/Kr systems where this emission spectra are produced by excitation in almost all the absorption region (Fig. 1a and Fig. 3 of Ref. [8] and Figs. 1b and 3, respectively). As consequence we can interpret the differences in the absorption spectra of Fig. 1c for Pd/Xe with respect to those of Pd/Ar and Pd/Kr systems (which are quite similar, Figs. 1a and 1b) as due in this two last cases to a spectral superposition with comparable contributions of the absorption spectra coming from the expected gas phase

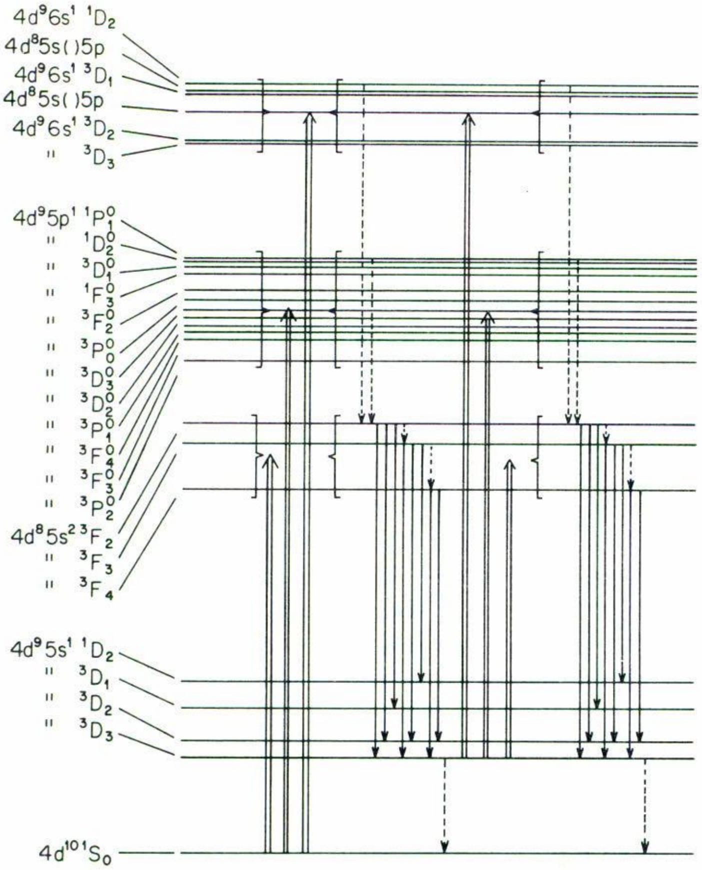
TABLE III. Position (λ, nm) and assignment of the absorption bands, in the 300–365 nm region, of the Pd/Xe system at 12 K. The spectral shift is with respect to gas phase Pd atoms. (cm^{-1}).

Xe	Gas phase	Assignment	Spectral shift
315	337	$4d^8 5s^2\, {}^3F_2 \leftarrow 4d^{10}\, {}^1S_0$	~ +2802
	354	$4d^8 5s^2\, {}^3F_3 \leftarrow 4d^{10}\, {}^1S_0$	
340	398	$4d^8 5s^2\, {}^3F_4 \leftarrow 4d^{10}\, {}^1S_0$	+4286

transitions, $(4d^9 5s^1)\, {}^1P_1^0,\ {}^3D_1^0,\ {}^3P_1^0 \leftarrow (4d^{10})\, {}^1S_0$, and that generate from the $4d^9 5s^1\, {}^3D_3$ metastable state; in the first it is also due to the spectral superposition but now with different weight in their contributions.

On this last point we must consider the "heavy atom effect" [15], which facilitates the occurrence of originally forbidden electronic transitions to be allowed, when we go from matrices of light Ar atoms to matrices of heavy Xe atoms. This effect actually has been clearly manifested in the shortening of the lifetime of the ${}^3D_3$ metastable state (Fig. 7) of the Pd atoms isolated in Ar matrices (2.2 min), in Kr matrices (1.2 min) and in Xe matrices (0.2 min), in Kr matrices (1.2 min) and in Xe matrices (0.2 min). Another manifestation of the "heavy atom effect" is found in the photodependence of the narrow bands emission spectra of the Pd/Kr and Pd/Xe systems when they are photoexcited in the 300–370 nm region (Fig. 5 and 15, respectively). As it was pointed out for the Pd/Kr systems, the fact that we observe a photodependence of the narrow bands emission spectra when the sample is photoexcited in the 300–360 nm, obeyed the occurrence of electronic transitions in this region from the ground state ${}^1S_0$, which are originally forbidden for gas phase Pd atoms [11]. According with the diagram of energy levels of Fig. 8 the expected transitions in this spectral region, which by the heavy atom effect should be manifested, are the corresponding to $(4d^8 5s^2)^3F_2,\ {}^3F_3,\ {}^3F_4 \leftarrow (4d^{10})\, {}^1S_0$, which in case that they occur in gas phase should be at 337, 354 and 398 nm, respectively. We must remark that only the Pd/Xe system shows absorption bands in this spectral region, which is in agreement with the major effect of the heavy Xe atoms which allow the mixing of configurations that make possible that these electronic transitions occur [15]. In the Pd/Kr system this transitions are only manifested in the excitation spectra (Fig. 5) which are more sensitive that the absorption spectra [16], and in the Pd/Ar system they are absent even in the excitation spectra (Fig. 4 of Ref. [8]) which is in agreement with the almost null effect of the light Ar atoms on the mixing of configurations necessary to allow these transitions. In Table III and Fig. 17 are given tentative assignments of the 300–360 nm absorption bands of the Pd/Xe system. The assignment should be seen with caution because the spectrum only shows two substantially broad bands (Fig. 1c), when the expected transitions are three, ${}^3F_2,\ {}^3F_3,\ {}^3F_4 \leftarrow {}^1S_0$. The apparent absence of one of the absorption bands might be that is weak or is strongly overlapped with the others and, therefore, can not be resolved by the instrument.

In view of the important effect of the Xe atoms on the allowness of the forbidden transitions, we expect more than one group of transitions. The Fig. 17 shows this set of



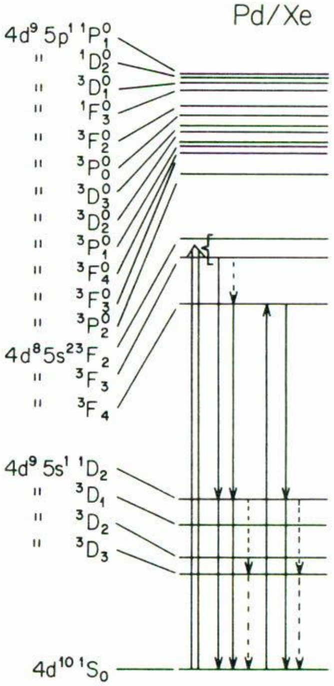


FIGURE 17. (Left) Schematiced representation of the electronic transitions (200–600 nm) of the Pd atoms isolated in Kr and Xe matrices.

FIGURE 18. (Right) Schematiced representation of the electronic transitions (300–900 nm) of the Pd atoms isolated in a Xe matrix.

possibilities. The group of transitions that we expect to observe with our spectrometer are those that implicate the change in the electronic configuration from the $4d^{10}$ ground state to the $4d^8 5s^2$, $4d^9 5p^1$, $4d^8 5s^1 5p_1$ and $4d^9 6s^1$ excited states, being the two last groups very near in energy (Fig. 17). The group of transitions $4d^8 5s^2 \leftarrow 4d^{10}$ already have been identified and correspond in the Pd/Xe system to the absorption broad bands of the 300–360 nm region (Fig. 1c). In the group of transitions $4d^9 5p^1 \leftarrow 4d^{10}$ are implicit those observed in gas phase $(4d^9 5p^1)\,^1P_1^0,\ ^3D_1^0,\ ^3P_1^0 \leftarrow (4d^{10}\,^1S_0$ and it is expected that they appear in the three matrices in the 220–275 nm spectral range. On the other hand, in the Pd/Kr and Pd/Xe systems we observe in the excitation spectra (Fig. 3 and 12, respectively), a broad structureless band of low intensity in the 250–300 nm region which could involve several of the $4d^9 5p^1 \leftarrow 4d^{10}$ transitions. Finally,the group of transitions $4d^8 5s^1 5p^1 \leftarrow 4d^{10}$ and $4d^9 6s^1 \leftarrow 4d^{10}$ should occur at very high energies (> 220 nm) and, therefore, they could be responsible for the very weak band observed at 200–220 nm in the three matrices.

4.1.2. Second trapping sites

The Pd/Ar and PdKr systems have manifested a second trapping site where the $4d^9 5s^1\ ^3D_3$ state is stabilized permanently. On this respect the laser-induced luminescence of these systems are definitive proof of this stabilization because the observed excitation and emission transitions (Fig. 11 of Ref. [9] and Fig. 9 and Table II) are only congruent with the energy levels of Pd atoms when we assume a $^3D_3$ ground state. The absence of an emission spectrum by laser excitation in the Pd/Xe system could suggest that in this system do not exist similar trapping sites that allow the $^3D_3$ stabilization, or that there exist different deactivation channels to those of Pd($^3D_3$)/Ar and Pd($^3D_3$)/Kr systems. The fact that even in neat nitrogen matrices exists a site where the $^3D_3$ state is stabilizated [9] support more the idea that in Pd/Xe system there exist another deactivation channel by which the electronically excited Pd($^3D_3$) atom can be deactivated.

The presence of the 532 nm band in the excitation spectra of Fig. 13, for $\lambda_{\text{em}} =$ 798 nm, of the Pd/Xe system point out that in fact there is a different deactivation channel for the electronically excited Pd($^3D_3$) atoms. It has been suggested (Table II) that the 530 nm excitation band correspond to the $4d^8 5s^2\ ^3F_4 \leftarrow 4d^9 5s^1\ ^3D_3$ transition. The emission spectra that result of the 530 nm photoexcitation, consist of a unique narrow band (Fig. 14) at 797 nm. The fact that we can not observe this band in the laser-induced luminescence study, could be the limitations imposed in our spectrometer that only allowed scanning until 773.0 nm. The assignment of this emission band to an especific electronic transition is not simple, because as we have seen (Tables I and III) the spectral shift (with respect to the gas phase) in a Xe matrix do not follow a well defined pattern and, therefore, we can not use this parameter as a guide to specify the involved transition. This seems more complicated if we consider that now the ground state is the $4d^9 5s^1\ ^3D_3$ and the $4d^{10}\ ^1S_0$ state is above of the first one. This brings as consequence the possibility that the 797 nm emission band correspond to the $^3F_4 \rightarrow {}^1S_0$ transition.

On the other hand, it is interesting (Fig. 14) that the 797 nm narrow emission band coincides in position with a broad band that result of the 315 nm photoexcitation. It has been pointed out that the excitation around 315 nm (Fig. 10, $\lambda_{\text{ex}} = 312$ nm) produce, moreover of the 746 and 799 nm broad emission bands, a very intense and broad band at 575 nm which are similar to the 490 and 570 nm emission bands observed in Pd/Ar and Pd/Kr systems, respectively, which have been attributed to Pd atoms isolated in a third trapping site (see later on). The coincidence of the narrow and broad emission bands at 797 nm could suggest that they are related to the same transition but due to Pd atoms entrapped in different sites. By the assignments of the other bands given latter on we exclude this possibility and, in this particular case, me consider a fortuitous coincidence of the narrow and broad bands at 797 nm which correspond to different electronic transitions.

A similar situation results for the emission band at 746 nm (Fig. 14), which result of the 326 or 340 nm photoexcitation, with the notable difference that the first is narrow and the second broad. By their appearance and position we can assume that the narrow excitation band at 326 nm, and its associated 746 nm emission band, correspond to Pd atoms isolated in trapping sites where there is a great affinity for the $^3D_3$ stabilization, already stable or transitory. By their position this narrow band should correspond re-

TABLE IV. Position (λ, nm) and assignment of some excitation (absorption) and emission bands of Pd atoms isolated in Ar, Kr and Xe matrices at 12 K. The spectral shift is with respect to gas phase Pd atoms. (cm^{-1}).

Matrix			Gas phase	Assignment	Spectral shift		
Ar	Kr	Xe			Ar	Kr	Xe
—	—	232	245	$4d^9 5p^1\ {}^1P_1^0 \leftarrow 4d^{10}\ {}^1S_0$	—	—	$\sim +2536$
			248	$4d^9 5p^1\ {}^3D_1^0 \leftarrow 4d^{10}\ {}^1S_0$			
—	—	260	276	$4d^9 5p^1\ {}^3P_1^0 \leftarrow 4d^{10}\ {}^1S_0$	—	—	+2230
—	—	275	294	$4d^9 5p^1\ {}^3P_2^0 \leftarrow 4d^{10}\ {}^1S_0$	—	—	+2350
486	—	—	510	$4d^8 5s^2\ {}^3F_2 \rightarrow 4d^9 5s^1\ {}^3D_1$	+968	—	—
—	570	575	606	$4d^8 5s^2\ {}^3F_3 \rightarrow 4d^9 5s^1\ {}^1D_2$	—	+1042	+890
—	—	746	747	$4d^8 5s^2\ {}^3F_4 \rightarrow 4d^9 5s^1\ {}^1D_2$	—	—	+18
—	—	797	853	$4d^9 5s^1\ {}^1D_2 \rightarrow 4d^{10}\ {}^1S_0$	—	—	+824

spectively to the transition $4d^9 5p^1\ {}^3D_3 \leftarrow 4d^9 5s^1\ {}^3D_3$ and $4d^8 5s^2\ {}^3F_4 \leftarrow 4d^9 5s^1\ {}^1D_2$, having a spectral shift of −189 and +18 cm^{-1} with respect to the gas phase.

4.1.3. Third trapping site

From Figs. 10 and 14 is evident that in the Pd/Xe system exist a third trapping site where the photoexcited Pd atoms produce, in the 500–850 nm region, a broad band emission spectra. The 575 nm broad band of much more intensity that all observed, has an appearance and position similar to those observed in the Pd/Ar (486 nm) and Pd/Kr (570 nm). On the other hand, the apparent minor intensity of the broad emission bands at 746 and 797 nm can be due to part to the lower sensitivity of the instrument in this spectral region (see experimental section) and the possible non-radiative mechanisms that now are influenced by the nature of the trapping site [13]. The absence of the two last bands (746 and 797 nm) in the emission spectra of the Pd/Ar and Pd/Kr systems suggest that in these cases the non-radiative mechanisms of deactivation should be dominant.

In view that now we have more information on the broad emission bands, we can try the assignment in a more confident manner, at least for the Pd/Xe. Assuming that the Pd atoms responsible of this emission spectra are atoms in its $4d^{10}\ {}^1S_0$ ground state, then the broad absorption (excitation) bands at 300–360 nm of the Pd/Xe system (Figs. 1c, 12 and 13) should be assigned, as suggested before (Fig. 17 and Table III) to $(4d^8 5s^2)\ {}^3F_2,\ {}^3F_3,\ {}^3F_4 \leftarrow (4d^{10})\ {}^1S_0$.

Having stabilished some excited states in this third trapping site we can follow the deactivation. Fig. 18 shows the possible channels of this process. According to this scheme the broad emission bands at 575, 746 and 797 nm of the Pd/Xe system, should correspond to the following transitions (Table IV): $(4d^8 5s^2)\ {}^3F_3,\ {}^3F_4 \rightarrow (4d^9 5s^1)\ {}^1D_2$ and $(4d^9 5s^1)\ {}^1D_2 \rightarrow (4d^{10})\ {}^1S_0$, respectively.

It has been pointed out that in the Pd/Kr system only one broad emission band at 570 has been observed. Its appearance and position suggest that it should correspond to the $4d^85s^2\,{}^3F_3 \rightarrow 4d^95s^1\,{}^1D_2$, transition observed at 575 nm in the Pd/Xe system, the small blue shift (153 cm^{-1}) when passing from Xe to Kr matrix is a common shifting observed in other systems [11]. The 486 nm broad emission band of the Pd/Ar system seems, however, not to adjust to this transition, because that might imply an anomalous 4075 cm^{-1} blue shift. A better option could be its assignment to the $4d^85s^2\,{}^3F_2 \rightarrow 4d^95s^1\,{}^3D_1$ transition, which imply a 968 cm^{-1} blue shift (Table IV) and, therefore, comparable to that observed in the ${}^3F_3 \rightarrow {}^1D_2$ transition of the Pd/Kr and Pd/Xe systems. In fact this assignment is in agreement with the minor effect of the heavy atom that we expect in an Ar matrix, which is a requirement to observe the crossing from the triplet to the singlet mainfold.

A detailed examination of the excitation spectra which appear as consequence of the 574 nm photoexcitation (Fig. 13) revealed a set of bands in the high energy region (205–280 nm). As it was anticipated, this is the spectral region where the gas-phase like atomic transition [11], that is the $(4d^95p^1)\,{}^1P_1^0,\ {}^3D_1^0,\ {}^3P_1^0 \leftarrow 4d^{10})\,{}^1S_0$, which in gas phase absorb to 245, 248 and 276 nm, respectively (Table IV) occur. Assuming that this are the dominant transitions in the 205–280 nm region of the Pd/Xe system, then the relatively broad band at 232 nm of the Fig. 13a should contain the ${}^1P_1^0,\ {}^3D_1^0 \leftarrow {}^1S_0$ transitions and the 260 nm should correspond to the ${}^3P_1^0 \leftarrow {}^1S_0$. As it was pointed out the identification of this transition in the Pd/Ar and Pd/Kr systems is obstructed by the dominant overlapping of spectra from Pd atoms isolated in those trapping sites where occur an efficient photoconversion to the $4d^95s^1\,{}^3D_3$ metastable state. On the other hand, the assignment of the 275 and 210–220 nm excitation bands (Fig. 13) do not result easy because there are several possibilities in a Xe matrix where the heavy atom effect is very important. According to the blue shifting observed in other transitions, the 275 nm excitation band might correspond to the $4d^95p^1\,{}^3P_2^0 \leftarrow 4d^{10}\,{}^1S_0$ transition, whereas the set of bands at 210–220 nm might correspond to transitions from the $4d^{10}\,{}^1S_0$ ground state to the $4d^96s^1\,{}^3D_{3,2,1}$ and $4d^85s(\;)5p$ excited states which are near in energy [12].

Finally, the assignment of the emission bands localized in the high energy region of the Pd/Kr and Pd/Xe spectra (Figs. 2 and 10, respectively) is not simple. However, at least for the Pd/Kr system they seem to be generated in this third trapping site. It has been pointed out, that the emission spectrum of the 300–315 nm region appear together with the 570 nm broad emission band and, as this band, only appear by 245–265 nm photoexcitation (Fig. 2) and do not show signals of uv-photodependence. Unfortunately, with the available information is difficult to give a reliable assignment of this emission bands.

4.2. Structure of the trapping sites

Given the physical conditions by which the samples are formed (see experimental section) we expect that they have a policrystaline structure, where the Pd atoms should reside preferentially inside of the microcrystals that form the matrix [17, 18]. The crystal structure of the inert gas solids (Ar, Kr and Xe) bellow the 20 K is preferentially CCP (cubic close-packed structure) [19]. In this structure we distinguish three sites in the crystal array (Fig. 19): the substitutional, with twelve neighbor atoms; the octahedral interstitial,

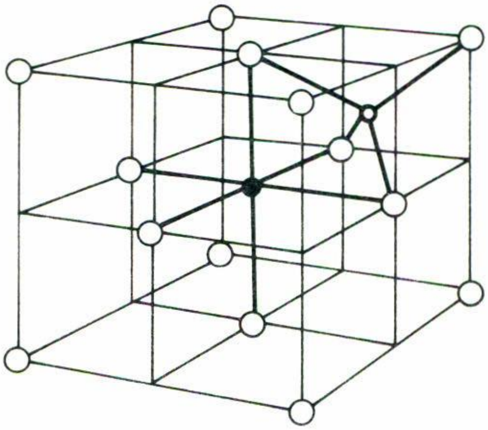


FIGURE 19. Illustration of the trapping sites in a crystal array of a cubic close-packet (CCP). ○: substitutional site; •: octahedral site; ∘; tetrahedral site.

with six neighbor atoms; and the tetrahedral interstitial with four neighbor atoms. In each site we can define a spherical cavity whose dimensions occupy the maximal volume without disturbing the crystal array [19]: Table V gives the diameter of such spherical cavities for each matrix gas that we used [19]. On the other hand, a detailed analysis of the crystal as a whole show that for each substitional site there is one octahedral interstitial and two tetrahedral interstitial sites.

Given the efficient thermal diffusion of the Pd atoms in the inert matrices, it has been suggested [6] that this should be isolated in interstitial sites. Moreover, before of our Pd/Rare-Gas studies [3, 6], it was assumed that the Pd atoms are isolated in their gas phaselike $4d^{10}\,{}^1S_0$ ground state, which possess a 1.1 Å average diameter [20]. With this diameter the octahedral interstitial site could be the most indicated to contain the Pd atoms, as is suggested from the data of Table V.

Recent theoretical calculations on the interaction energy of a Pd($4d^{10}$) atom with a He($1s^2$) atom (The less polarizable of the inert gases) [21] and Pd($4d^{10}$) with a $H_2(\sigma^2)$ molecule [22], have shown a clear attractive interaction with a 3.3 and 1.8 Å equilibrium distance, respectively. With this precedents we expect a notorious stabilization interaction energy between the Pd atom and the atoms of the Ar, Kr or Xe lattices. On the other hand, the fact that the stabilization of a metal atom in certain sites depend not only of the dimensions of this sites but also of a delicate balance of repulsive and attractive interactions of this atom with the highborn atoms of the crystal lattice, give the possibility that even in the more constricted (the tetrahedral interstitial site), might reside the Pd($4d^{10}$) atoms. Given the major abundance of this site, this might be, from the statistical point of view, more favorable to retain the Pd($4d^{10}$) atoms.

A rough estimation of the atomic diameter of the Pd($4d^9 5s^1\,{}^3D_3$) atoms, can be obtained from the atomic diameter of the Ni($3d^8 4s^2\,{}^3F_4$) of 2.4 Å and of the Pt($5d^9 6s^1\,{}^3D_3$) of 3.0 Å [20]. The average value of 2.7 Å as an estimation of the atomic diameter of Pd($4d^9 5s^1\,{}^3D_3$) is near to 2.8 Å for the Ag($4d^{10} 5s^1\,{}^2S_{1/2}$), that is neighbor to Pd in the periodic table. In view of this estimated value we can suggest that the Pd($4d^9 5s^1\,{}^3D_3$)

TABLE V. Diameter (Å) of the spherical cavities of maximal volume, of the main sites of a CCP crystal array of Ar, Kr and Xe rare gas solids [19].

Matrix	Site		
	Substitutional	Interstitial Octahedral	Interstitial Tetrahedral
Ar	3.76	1.56	0.85
Kr	3.99	1.65	0.90
Xe	4.34	1.80	0.97

atoms will be isolated in a less restricted octahedral interstitial site or, surely in a more favorable site as is the substitutional (Table V).

From our analysis we expect that the Pd atoms will reside in the three more stable sites of the crystal array of an Ar, Kr or Xe matrix and, moreover, that their optical spectra will depend of the degree of interaction of these atoms with their neighbor of the lattice. With respect to this last point we have seen that, in general terms, there are three distinctive optical spectra: two that are originated from Pd atoms in a $4d^{10}\ {}^1S_0$ ground state, and another whose Pd atoms have a $4d^9 5s^1\ {}^3D_3$ ground state. A distinctive aspect of this spectra is the linewidth of the emission bands. In the Pd($^3D_3$) atoms isolated in substitutional sites, the half-width of the emission bands is smaller than the corresponding to the same bands but generated by Pd($^1S_0$) atoms, isolated in octahedral interstitial sites, via the $^3D_3$ metastable state. This is clearly manifested in the Ar matrices where we observe a difference of about 30% in the half-width of the narrow emission bands; this effect is reduced substantially in a Kr matrix where we observe a difference of almost 10%, whereas in a Xe matrix this difference is negligible. This difference should be related with the degree of interaction of the Pd atom with the atoms of the lattice. For large cavities (as in a Xe matrix) the effect should be minor that for small cavities (as in an Ar matrix). It is important to point out that this effect, the correspondent to the half-width of the bands, are effects that depend of the shape of the interaction potential surfaces of the Pd atoms (in their involved electronic states) and the neighbor atoms of the lattice [23, 24], whereas the stabilization of the $4d^9 5s^1\ {}^3D_3$ state should be a collective effect that necessarily involves more than the nearest neighbor atoms of the lattice.

Finally, the substantial width of the absorption and emission bands observed in the Xe matrix, and corresponding to the $4d^{10}\ {}^1S_0$ atoms isolated in tetrahedral interstitial sites, are another example of the substantial vibronic coupling of the Pd atoms with the neighbor atoms of the lattice, which is reinforced by the narrow space where the Pd atoms reside (Table V) [25].

5. CONCLUSION

The noble-gas matrix (Ar, Kr or Xe) has a deep effect on the electronic structure of the Pd atoms isolated in its entrails. This effects are manifested as an efficient mechanism of conversion of singlet to triplet states and in the stabilization of the excited states $4d^9 5s^1\ {}^3D_3$, in such degree that in certain sites this result to be the electronic ground state of the Pd atoms.

In the three matrices we identified three main trapping sites, and they seem to coincide with the three main sites of the crystal array of a cubic closed-packed (CCP) crystal structure: the substitutional, with twelve neighbor atoms; the octahedral interstitial, with six neighbor atoms; and the tetrahedral interstitial, with four neighbor atoms. The photophysical behaviour of the Pd atoms isolated in these three trapping sites show notable differences. Particularly, this is manifested in the absorption spectra, where the one corresponding to the Pd/Xe system shows a substantial difference to those of the Pd/Ar and Pd/Kr systems.

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