# The Role of Hydrogen in Formation of Pd XANES in Pd-Nanoparticles

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**Abstract.** The effects of hydrogen in Pd nanoparticles on the features of Pd K-edge X-ray absorption near edge structure (XANES) are studied. Simulations indicate a linear dependence of the intensities of XANES maxima upon the concentration of hydrogen in the bulk of Pd clusters at low H-concentrations and stepwise increase of the first near edge peak at high concentrations. The effects of the diffusion of H atoms over the interstitial sites are considered. The application of the obtained results to the experimental spectra measured in PdH nanoparticles of sizes from 1.3nm to 10.5nm indicates low H-concentrations and high mobility of H-atoms in the bulk of the nanoparticles.

## 1. Introduction

Palladium is well known for its hydrogen absorption ability [1] and has been extensively studied as a hydrogen storage material for many decades [2-4]. Palladium nanoparticles are of great interest because of their large active surface area. The lattice parameter for fcc palladium increases after hydride absorption [5]. For bulk palladium hydride different phases are presented depending on the hydrogen concentration and these phases correspond to different lattice parameters [6, 7]. However, one should use the term "phase" very carefully when speaking about nanoparticles. Numerous studies observe lattice expansion for $PdH_x$ nanoparticles [8-13], but numerical values of the lattice parameter changes differ from that of bulk samples.

X-ray absorption spectroscopy (XAS) [14] is a powerful technique for obtaining structural information of nanostructured samples and it was applied to Pd clusters in numerous works [8, 10, 12, 13]. Lattice expansion was commonly observed from Pd K-edge extended X-ray absorption fine structure (EXAFS) data analysis, however no direct information on hydrogen presence, its concentration and positions in fcc of metallic Pd nanoparticles was obtained. Significant changes in Pd L3-edge XANES for bulk and nanostructured PdH were analyzed in [13, 15].

In this work we found hydrogen effects on Pd K-edge X-ray absorption near edge structure (XANES). The performed calculations show a very strong sensitivity of the first near

edge peaks relative intensity on hydrogen presence, total H concentration and positions occupied by H atoms in fcc. of palladium, which must be taken into consideration for a correct theoretical description of experimental data. A significant increase of the first peak in the theoretical spectrum calculated for a simple model of a PdH cluster is observed. Calculations show a linear dependence of that XANES peak on the hydrogen concentration in the Pd cluster. Changes in Pd K-edge XANES caused by H migration from octahedral to tetrahedral interstitial sites were analyzed. Results of analysis indicated a very high probability of hydrogen diffusion through the bulk of Pd nanoparticles of different sizes in the experiment made by our coauthors [13], and also explain changes in XANES for previous experimental works [8, 10].

## 2. Pd K-edge XANES calculation

### 2.1. General description

Theoretical Pd K-edge XANES spectra were calculated for small (135 Pd atoms) nanoclusters of bare Pd and Pd-hydride. The Pd local structure used for spectra modeling was taken as in the fcc lattice of Pd-foil. The fcc-like local structure of Pd-nanoparticles was confirmed by the Fourier Transform of experimental [13] Pd K-edge EXAFS for nanoparticles of the sizes from 1.3 nm to 10.5 nm [16]. Small clusters of 19 Pd atoms were used for hydrogen migration effects calculation.
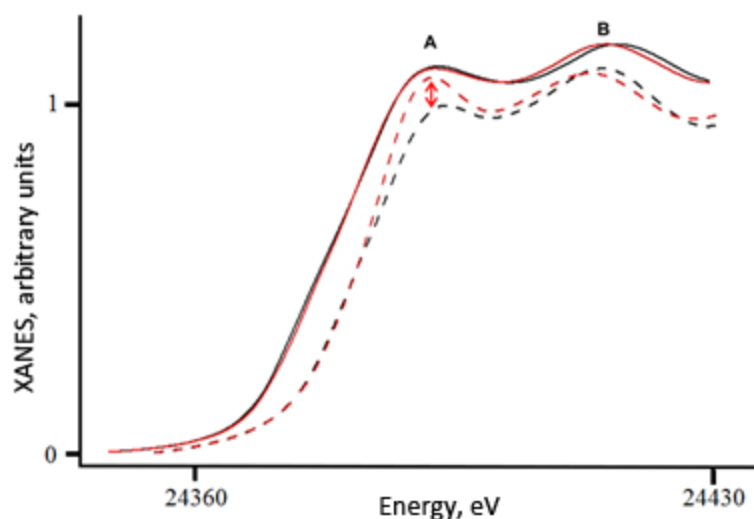


**Figure 1.** Experimental (solid) and theoretical (dash) Pd K-edge XANES for bare (black) and hydride (red) palladium nanoparticles.

XANES spectra were calculated using two different approaches: the multiple scattering technique (FEFF9) within muffin-tin approach [17, 18] and the finite difference method (FDMNES) with full potential [19]. Analysis of calculated spectra showed that first

near edge peaks are very sensitive to hydrogen presence and its location in the lattice. A model of Pd cluster with H atoms located in octahedral interstitial site gives an increase of peak A (fig.1). These results are in contradiction with experimental data [13] where these changes are negligible, which should indicate low hydrogen concentration in the bulk of experimentally observed nanoparticles. As both muffin-tin and full potential approaches indicate this effect, less time-consuming FEFF calculations were chosen for further investigation.

Relative intensity of peak A $(I_A/I_B)$ was taken as a numerical description of observed changes. This value showed stability to the changes in cluster size, interatomic distances and FEFF parameters: region of self-consistent potential (SCF), full multiple scattering area (FMS), type of exchange-correlation potential. The following structural changes were then studied: total hydrogen concentration in Pd cluster, hydrogen migration from octahedral to tetrahedral interstitial site near the absorbing Pd atom. Calculations showed that the value of $I_A/I_B$ is significantly affected only by H atoms presence in the nearest coordination shell. Dependence on the further hydrogen is negligible and $I_A/I_B$ tends to its value in the bare Pd cluster. Therefore only nearest shell hydrogen atoms modifications were involved in our study.


## 2.2. Hydrogen concentration effects

A strong dependence of the relative intensity $I_A/I_B$ on the H-atoms' concentration was observed. The number of hydrogen atoms in the octahedral interstitial sites of the nearest to absorbing Pd atom coordination shell was varied from 0 to 6. Further shells were not affected for the reasons mentioned above. For each configuration Pd K-edge XANES spectra were calculated. Different configurations of hydrogen atoms in 6 octahedral interstitial sites possible for models containing 2-4 H atoms were taken into consideration: XANES spectra for non-equivalent configurations were calculated and summed using corresponding weight coefficients. Calculated relative intensities $I_A/I_B$ are shown in fig.2.

A linear dependence of $I_A/I_B$ on the number of H atoms is observed for small H concentration. When the number of H atoms corresponds to a β-phase concentration (>60%) a non-linear increase occurs. Linear dependence of intensity increase is observed due to the fact that at low concentrations H-atoms do not interact with each other and contribute to Pd K-edge XANES independently. We suppose that a non-linear increase for high concentrations indicates the presence of inter-hydrogen correlations which is consistent with strain field effects responsible for the well-known difficulty in obtaining high loaded PdH samples [20].

According to the obtained results hydrogen concentration in the bulk of a palladium clusters must be considered for theoretical XANES calculation. However, a determination of hydrogen concentration from an experimental XANES without any complementary knowledge appears to be a difficult problem as concentration is not the only parameter responsible for peak A intensity changes.
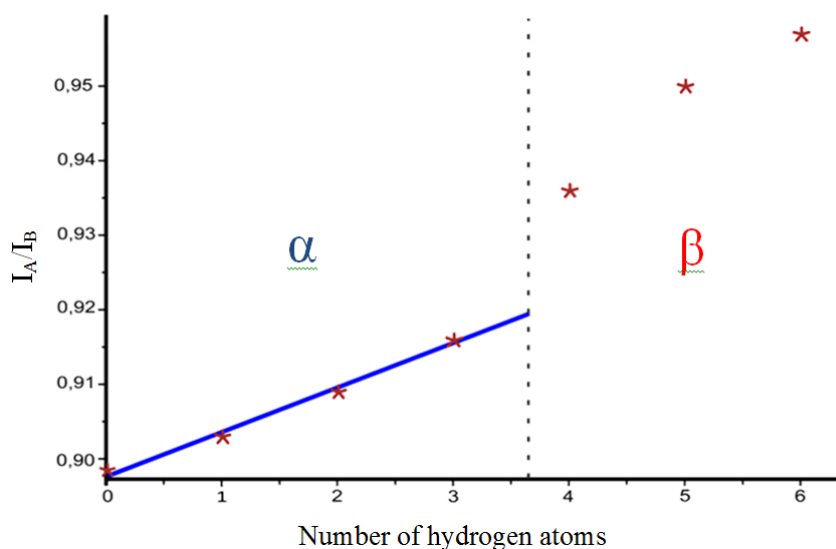
**Figure 2.** Increase of the relative intensity of the first peak of calculated Pd K-edge XANES with the increase of number of H-atoms in the nearest octahedral interstitial sites (stars) and linear approximation for intensity behavior at low concentrations.

## 2.3. Hydrogen migration

Numerous works have studied a quantum delocalization and diffusion of hydrogen in bulk metal samples [21-23]. One should expect that light hydrogen atoms are in permanent motion in palladium nanoclusters and are able to diffuse through different interstitial sites in fcc of palladium. We studied an effect of hydrogen diffusion on Pd K-edge XANES in a simple model of a 19 atom Pd cluster with one H atom migrating from one octahedral interstitial site to another via neighboring tetrahedral one.

Fig.3. illustrates peak A intensity dependence on the hydrogen position during H atom migration from octahedral to tetrahedral sites. Calculation of the relative intensity for the bare 19 atom Pd cluster was also performed and is plotted as a red dashed line. The maximum increase of peak A was observed when H atom was located in octahedral position; tetrahedral position also corresponds to a local maximum but with much weaker intensity changes. According to ab initio calculations for hydrogen migration in Pd lattice [24] potential energy has minima at both of these interstitial sites. When the H atom was located on a triangle face connecting an octahedron and a tetrahedron, which is a saddle position, opposing changes of peak A intensity were achieved.

Such dependence means that intensity changes should become more negligible with the higher mobility of hydrogen. According to the results reported by our coauthors [13] interatomic distances in supported Pd hydride nanoparticles were bigger than distances in bulk palladium hydride which should decrease energy barriers between the neighboring interstitial sites and should favor more intense diffusion.
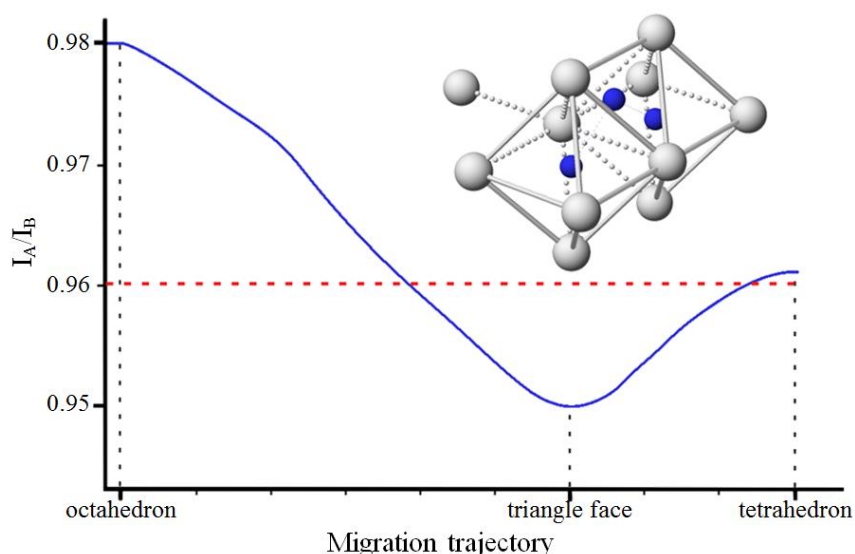
**Figure 3.** Dependence of the relative intensity of peak A upon the position occupied by the hydrogen atom. On the horizontal axis the generalized coordinate for hydrogen migration from octahedron to tetrahedron is plotted. The red dashed line is a relative intensity value for the model with no hydrogen. Plotted cluster geometry illustrates two neighboring octahedral interstates connected via a tetrahedron.

## 3. Summary and conclusion

Calculation showed that the hydrogen concentration and the effect of hydrogen diffusion must be reflected in Pd K-edge XANES. These results compared with experimental data [13] indicate both low hydrogen concentration in the bulk of Pd nanoparticles and high mobility of hydrogen atoms. It should be mentioned that in works [8, 10] an increase of peak A is observed.

However these parameters should correlate with each other. A probability of existence of an unoccupied interstate near the existing H atom decreases with an increase of hydrogen concentration and should prevent diffusion. On the other hand diffusion magnitude increases with an increase of interatomic distances which also depend on hydrogen concentration. All these relations should make the process of determination of described parameters more complicated. Thereby Pd K-edge XANES data for $PdH_x$ nanoparticles may be used to give complementary information on EXAFS analysis, Pd $L_3$-edge XANES, X-ray diffraction data and other techniques.

## 4. Acknowledgements

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