

# Observation of Optical Phonon in Palladium Hydrides Using Raman Spectroscopy

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## Abstract

The techniques of hydrogen loading in Pd are developed by many workers. And the states of hydrogen in Pd attract many interests because they might be related to the nuclear reactions. In this study, we have tried to observe optical phonon induced by hydrogen-hydrogen interactions in Pd using Raman spectroscopy. This measurement can be done for the sample completely sealed in a glass tube cutting off the influence of the external air, because glass materials are Raman inactive. In the measurement chamber of spectroscopy device, scattered waves of the incident laser beam from the hydrogen storage Pd are detected and Raman shifts including the information about the optical phonon in the sample are derived.

If the large changes in Raman spectra are found, they will help explain the nuclear effects in condensed states of palladium hydride. So far, we have not found large changes, but the peaks of Raman shift at 56 meV both for PdH<sub>x</sub> and PdD<sub>x</sub> are detected. The peaks for PdH<sub>x</sub> are consistent with the data of Sherman *et al.* at 58.5 meV. However, the peaks for PdD<sub>x</sub> are inconsistent with Sherman's result at 39.7 meV.

## 1. Introduction

In order to detect nuclear reactions in solids, calorimetry to measure the heat from the nuclear reaction has been used in many cases. However, it is not easy to measure heat only from nuclear reactions, because heat of formation of the hydrogen storage process is also generated in these systems. Mass spectroscopy also has been used for analyzing the nuclear products. However, it is not easy to do in-situ measurement. In this study, we have tried to develop the third way to detect the nuclear reaction in palladium hydrides, using Raman spectroscopy.

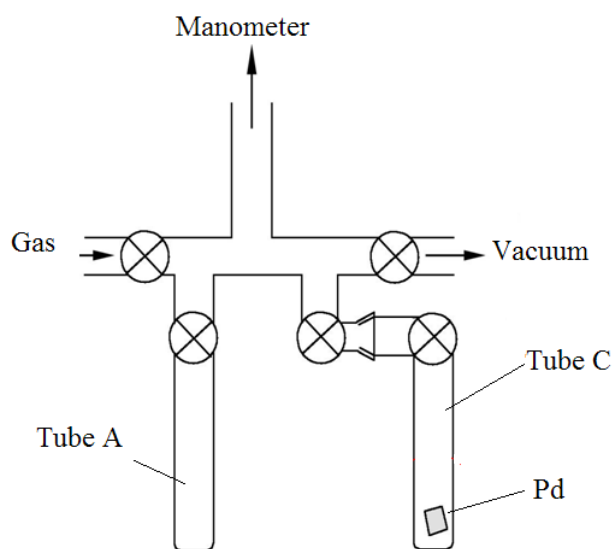
Raman spectroscopy is the method used to observe optical phonon in the molecular vibration or lattice vibration. When laser light is scattered from lattice vibration, most photons are elastically scattered. This is called Rayleigh scattering. However, a small fraction of scattered wave has different frequency from incident waves. In this case, the frequency shift  $\Delta\nu$  is called Raman shift, which is created by the interaction between incident laser light and optical phonon. If the frequency of the scattered wave is increased, it is called anti-Stokes scattering. If it is decreased, it is called Stokes scattering. For example in Stokes scattering, the ground state phonon is excited to the virtual state by the incident laser wave, and then return to the first

excited state. So, it is inelastic scattering and Raman shift  $\Delta\nu$  includes the information about the lattice vibration.

In usual Raman spectroscopy, only the optical phonon is Raman active, while the acoustical phonon is inactive. This means that Raman spectroscopy is not appropriate for analyzing the lattice vibration of pure Pd, because a face centered cubic lattice with one atom per primitive cell only has acoustical lattice vibrations [1]. Fortunately, H-H (D-D) interactions in Pd induce optical vibrations [2], and we can use Raman spectroscopy for hydrogen storage Pd. In this case, Raman shift  $\Delta\nu$  directly includes the information about H-H (D-D) interactions. This was pointed out by R. Sherman *et al.* [3]. In this study, we observed the Raman shifts of PdH<sub>x</sub> and PdD<sub>x</sub>, and discussed the H-H (D-D) interactions.

## 2. Experimental

We used two types of samples. One is plate and the other is powder. The size of plate Pd is  $5 \times 5 \times 0.5$  mm, and the average radius of powder Pd is 0.5 mm. A sketch of the device for gas loading is shown in Fig. 1.



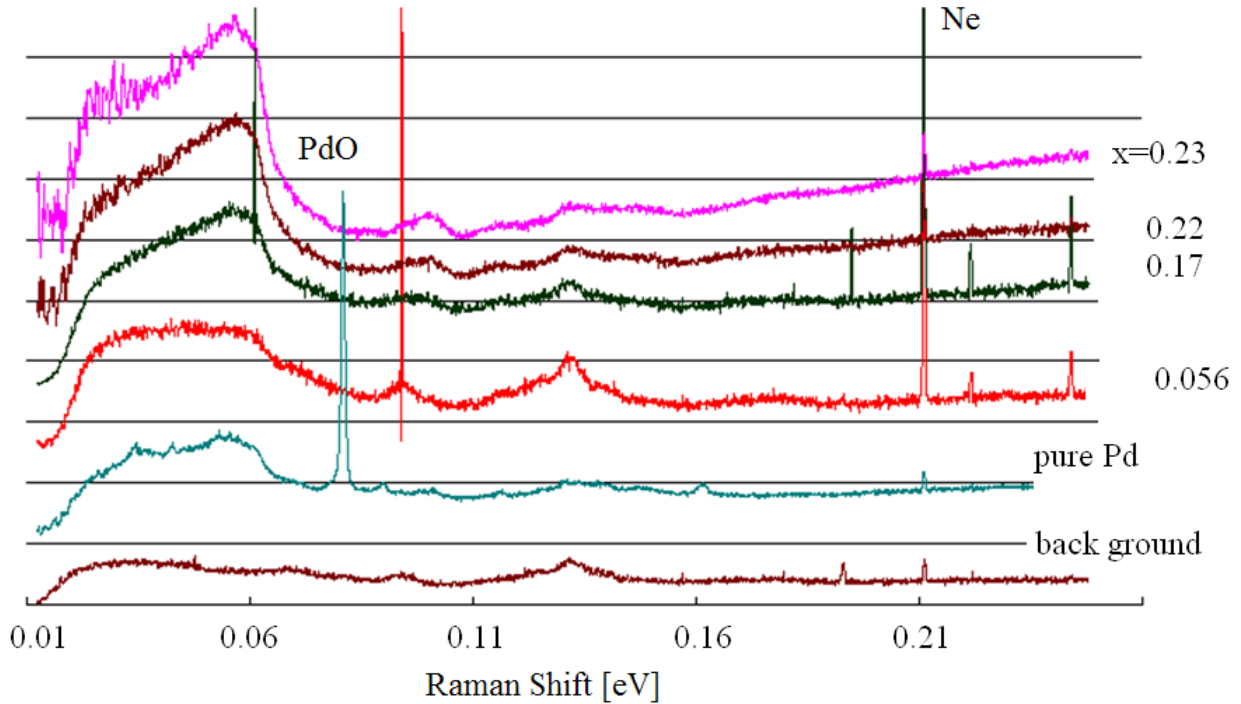
**Figure 1. Sketch of the hydrogen storage apparatus.**

We used 99.9% H<sub>2</sub>, 99.6% D<sub>2</sub> and 99.9% Pd. The atomic ratios of H/Pd and D/Pd were determined by constant volume method with the equation of states.

After loading, the tube C in Fig. 1 was removed by closing the cock, and put into the detection chamber of the Raman spectroscopy (NRS3100, JASCO). The excitation wavelength of the Raman spectroscopy is 532.25 nm.

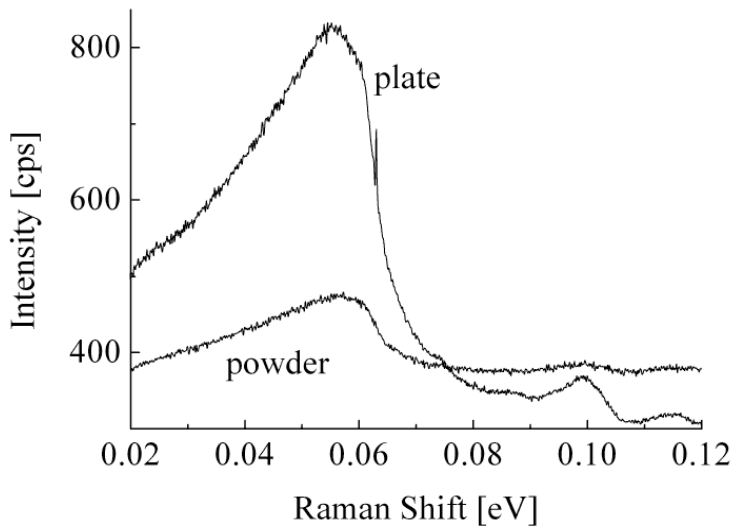
### 3. Results and Discussion

The Raman spectra of plate  $\text{PdH}_x$  are shown in Fig. 2. In all cases, the peak position is 56 meV, which is consistent with the Sherman's results [3]. The peak at 210 meV corresponds to Ne, which was used as a reference signal. The peak at 80 meV corresponds to PdO. The surface of the pure Pd plates we used was slightly oxidized and PdO peak was detected. In order to compare the results for each hydrogen concentration, the arbitrary unit is adopted for vertical axis.



**Figure 2. Raman spectra of plate  $\text{PdH}_x$ .**

Raman spectra of  $\text{PdD}_x$  for powder and plate samples are shown in Fig. 3. The equivalent D/Pd ratios for powder and plate samples are 0.90 and 0.14, respectively. A broad peak exists at 59 meV for powder sample, and a sharp peak exists at 57 meV for plate sample. The differences between two spectra in Fig. 3 depend on the shape of the samples and D/Pd ratio. In the Sherman's result for  $\text{PdD}_x$ , a peak exists at 40 meV [3], which is smaller than our results. These differences depend on the temperature. Our experiments were done at room temperature, while Sherman's were done at 84 K.



**Figure 3. Raman shift for powder PdD<sub>0.90</sub> and plate PdD<sub>0.14</sub>.**

Twenty-four hours after the first measurement, we tried to measure the Raman spectra of the same samples. In all cases, results were nearly the same as first spectra (Figs. 2 and 3). If nuclear reactions had occurred in the sample during the 24-hour period, large changes between the spectra should have been observed. However, we did not find them. In near future, we will try to stimulate the hydrogen (deuterium) storage Pd by laser light with a wavelength different from the incident wave in Raman spectroscopy. If reactions are induced by this stimulation, large changes in spectra should be seen.

#### 4. Conclusions

- (1) In this study, we have demonstrated a method of getting information about optical phonon in palladium hydrides (and deuterides) using Raman spectroscopy. The elementary results for the Raman spectra of hydrogen storage Pd were obtained.
- (2) In Raman spectra of PdH<sub>x</sub>, a peak exists at about 56 meV for all concentrations. It is consistent with Sherman's results [3].
- (3) In Raman spectra of plate PdD<sub>x</sub>, a peak exists at 57 meV. With powder PdD<sub>x</sub>, a peak exists at 59 meV. They are not consistent with Sherman's results at 40 meV [3]. These differences depend on the temperature. Our experiments were done at room temperature, while Sherman's were done at 84 K.
- (4) The optical phonon in palladium hydrides (and deuterides) is induced by H-H (D-D) interactions. So, large changes of the spectra should indicate the effects of nuclear reactions. However, such large changes were not observed.
- (5) In near future, we will try stimulation by laser light with palladium hydrides (and deuterides), and we will measure the Raman spectra. If the large changes in Raman spectra are found, this may help explain nuclear reaction effects in condensed states of hydrogen in Pd.

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## References

1. C. Kittel, *Introduction to Solid State Physics*, John Wiley and Sons, Section 5.
2. J. M. Rowe, J. J. Rush, H. G. Smith, M. Mostoller and H. E. Flotow, "Lattice Dynamics of a Single Crystal of PdD<sub>0.63</sub>", *Phys. Rev. Letts.*, **33**,1297(1974)
3. R. Sherman, H. K. Birnbaum, J. A. Holy and M. V. Klein, "Raman studies of hydrogen vibrational modes in palladium", *Phys. Lett.*, **62A**(1977)353