

## Report on HD gas analysis by Raman spectroscopy technique. October 2010.

### - Initial Procedure

Five bottles of HD gas were sent to Rome from JLab during July 2010, in two different deliveries: first three identical samples of JMU-II gas arrived, to be used to study systematic errors; then two samples of *good* HD gas were received, respectively of JMU-III and USC HD gas.

The HD gas bottles have a volume of 75 cc and were pressurized at ~1900 mbar.

The Raman cell was connected to a new stainless steel pressure gauge from Wika, to measure the HD gas pressure after the filling procedure and to monitor the pressure as a function of time. A two-way stainless steel valve was connected to the pressure gauge, to isolate the cell. One cell output was connected to the pump, the other to the HD bottle.

At each filling the cell was pumped to vacuum up to the HD bottle valve. Then the pump valve was closed and the HD gas valve was opened for few seconds to allow gas into the cell. The HD gas bottle valve was then closed and the cell valve was closed to isolate the cell and disconnect it from the filling manifold.

The pressure gauge in the cell measured 1550 mbar, corresponding to a ratio of volumes  $\text{bottle}/(\text{bottle}+\text{cell})=0.816$ . From this ratio it is possible to estimate the cell volume, including the gauge:

$$\frac{\text{bottle}}{\text{bottle} + \text{cell}} = 0.816 \quad x = \frac{\text{cell}}{\text{bottle}} \quad \frac{1}{1+x} = 0.816 \quad x = \frac{1}{0.816} - 1 = 0.225$$

$$V_{\text{cell}} = 0.225 \times 75 \text{ cc} = 17 \text{ cc}.$$

The cell was filled on July 26<sup>th</sup> with the first JMU-II gas sample. The Raman optics was aligned during the following three days. The first

spectrum of maximized intensity was obtained in the evening of July 29<sup>th</sup>. All the other gas samples were analyzed on the next day July 30<sup>th</sup>, within approximately one hour from cell filling. JMU-III was measured twice, the second measurement being more reliable from the point of view of the Raman spectrum quality.

- Data analysis

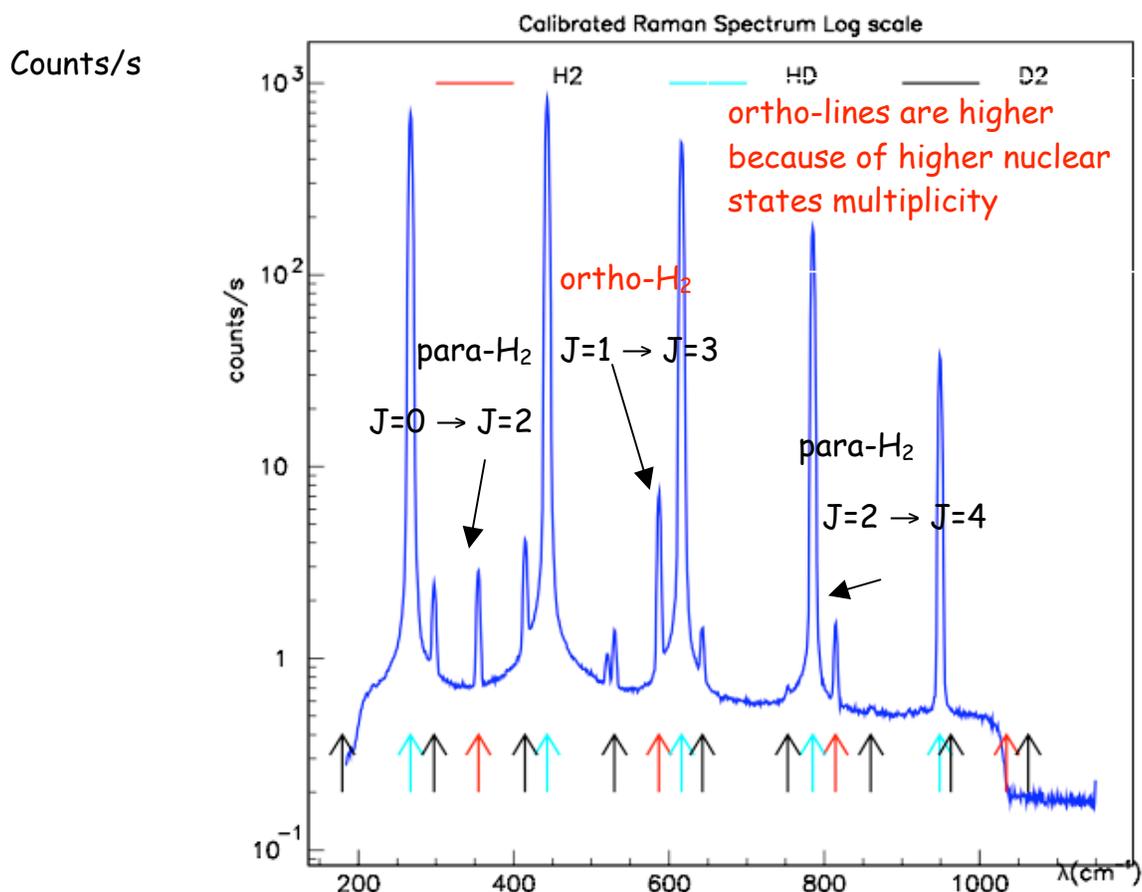


Figure 1 – Typical calibrated Raman spectrum of HD JMU-II sample. Light blue arrows point to HD lines. Red arrows point to H<sub>2</sub> lines. Black arrows point to D<sub>2</sub> lines. The first five HD lines corresponding to transitions among pure rotational states are visible. The first three H<sub>2</sub> lines corresponding to transition among para-(J=0 to J=2), ortho- (J=1 to J=3) and para-(J=2 to J=4) lines respectively, are visible. Five D<sub>2</sub> lines are visible, starting from the first transition among para- states (J=1 to J=3). The first D<sub>2</sub> line among ortho- states (J=0 to J=2) is not covered by the recorded spectrum.

The data analysis program to extract the H<sub>2</sub>/HD and D<sub>2</sub>/HD relative contents was substantially improved.

Figure 1 shows a typical Raman spectrum of HD gas with 10<sup>-3</sup> level contamination of H<sub>2</sub> and D<sub>2</sub>. By fitting each single peak of the spectrum it is possible to extract the experimental value of the peak intensity I(J), for all values of J covered by the spectrophotometer, for each gas species.

### - Peaks Intensities – experimental determination

Data analysis is based on the experimental determination of the Raman peaks intensities, as a function of the rotational value J of each gas species. Raman spectra are in general the very clean and peaks are well described by a Gaussian fit on a constant background. However at very intense powers of the Laser beam (which are necessary to evidence the presence of small H<sub>2</sub> and D<sub>2</sub> peaks in the dominating HD spectrum) the peak shape of the dominant HD gas shows a tail due to charge drift from the highly populated CCD channels. These tails are visible only plotting the spectra in logarithmic scale, but they are a non-negligible fraction of the superimposed H<sub>2</sub> and D<sub>2</sub> peaks.

Two methods have been developed to extract the peaks intensities: Gaussian plus constant background fit and spectrum integration with background subtraction.

### - First method: Gaussian fit on a constant background (G+back)

Each of the Raman peaks was fitted using the function:

$$f(x) = A e^{\frac{-(x-x_0)^2}{s^2}} + B$$

where the peak position is given by the parameter x<sub>0</sub>, the width is given by the parameter s and the amplitude over the background B is given by A.

The peak intensity is obtained by the relation:

$$I(J) = \sqrt{\pi} A s$$

Figure 2 shows typical fits of the five HD Raman lines. While most of the peak intensity is contained in the fitted Gaussian, the result is very

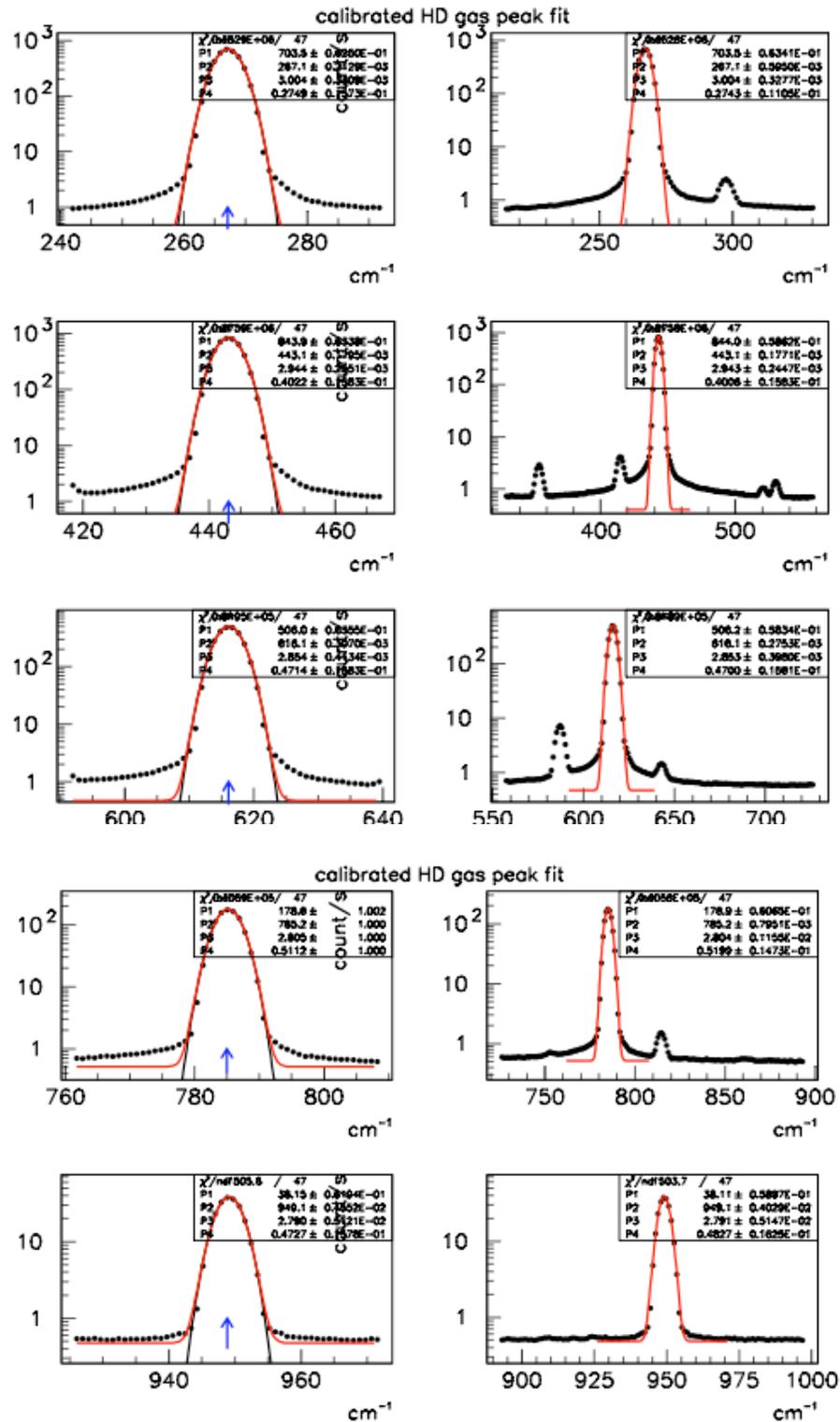


Figure 2. Gaussian plus constant background fit of each of the five HD Raman peaks, shown in logarithmic vertical scale (left panels). The same fits are shown in a wider energy range in the right panels.

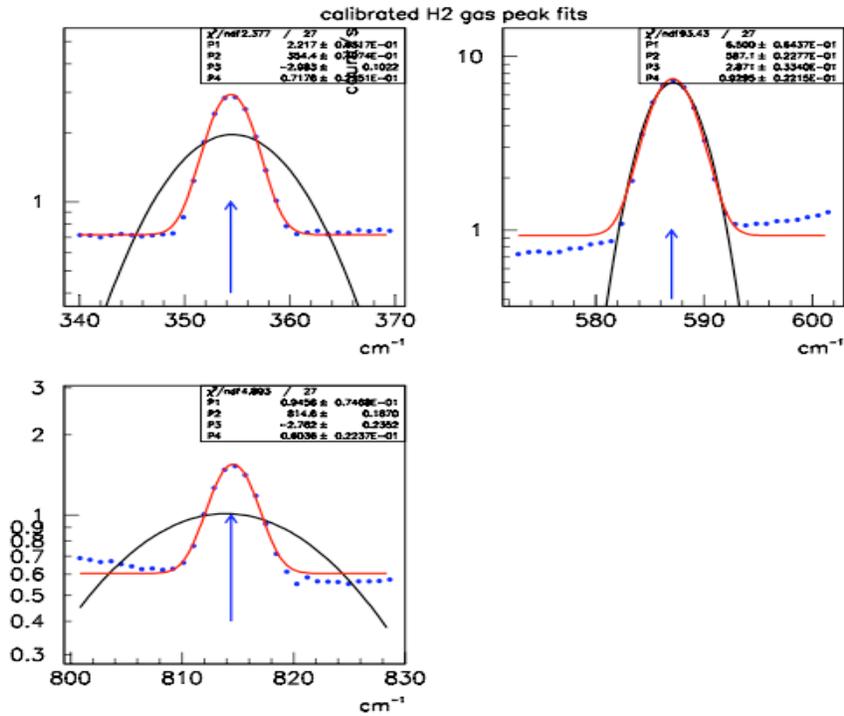


Figure 3. Gaussian plus constant background fit of three H<sub>2</sub> Raman peaks, shown in logarithmic vertical scale.

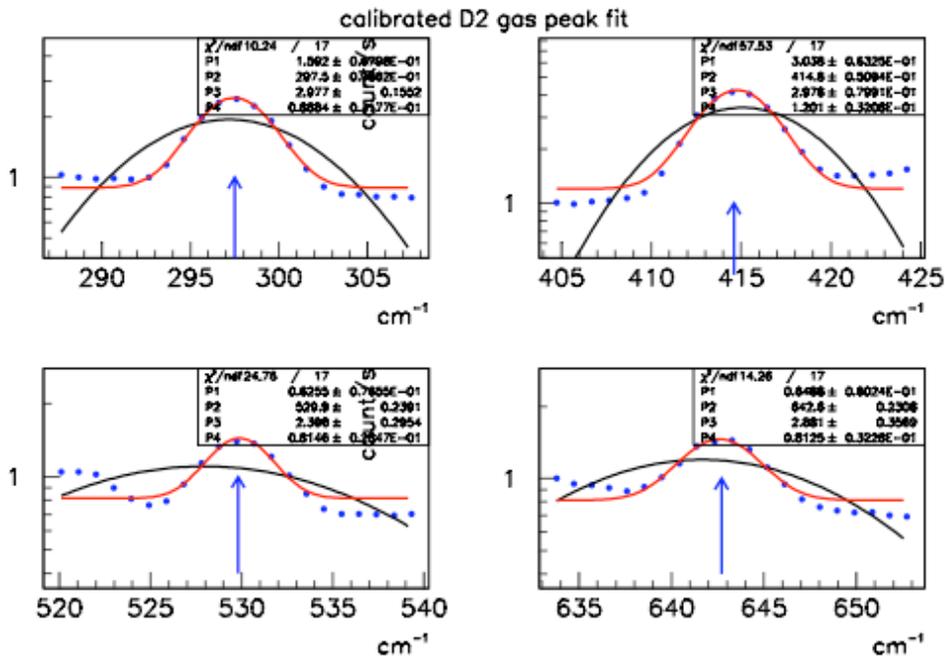


Figure 4. Gaussian plus constant background fit of four (to six) D<sub>2</sub> Raman peaks, shown in logarithmic vertical scale.

sensitive to the background value. Most Gaussian fits converge to parameters values that do not take into account the tails.

Figures 3 and 4 show results of Gaussian plus constant fit of  $H_2$  and  $D_2$  contaminants respectively. Values obtained for the background parameter tend to be higher than those obtained for HD peaks, due to the contribution of the HD peaks tails.

- **Second method: spectrum integration and background subtraction (Int+back)**

An alternative way of obtaining the HD peak contents is to integrate the experimental spectrum over a large window under each HD peak, that would completely include the tails. An average constant background area is then subtracted.

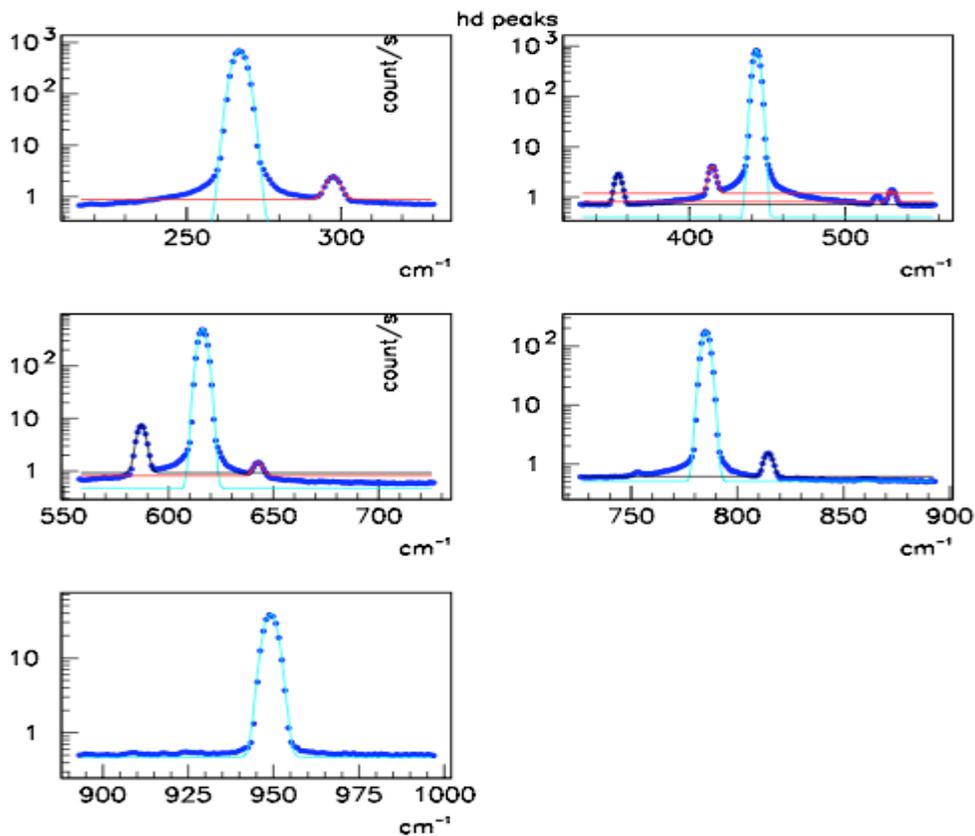


Figure 5. The five energy regions in which the spectrum has been integrated to take into account the HD peaks tails. Red curves show the fit of the subtracted  $H_2$  and  $D_2$  peaks. The overall background was estimated as the average of the valley values among dominant peaks.

If any of the H<sub>2</sub> or the D<sub>2</sub> peaks were included in the wide integration region, their area (calculated using the previous method) was subtracted as well.

### - Peaks Intensities - theory

The intensity of the Raman peaks for each species follows the following relation:

$$I(J,T) = I_0 A(\nu) \nu^3 f(J) \gamma^2 \frac{45\pi^4}{7} \frac{N}{Q(T)} g_s(J)(2J+1) \frac{3(J+1)(J+2)}{2(2J+1)(2J+3)} \exp\left(-\frac{hcb_0 J(J+1)}{KT}\right)$$

where I<sub>0</sub> is the Laser intensity, A(ν) is the spectral response of the spectrometer as a function of the light frequency ν, f(J) is the an-harmonic correction of the rotational energy level J, γ<sup>2</sup> is the anisotropic matrix element. The product

$$C = I_0 A(\nu) \nu^3 f(J) \gamma^2 45 \pi^2 / 7$$

is approximately constant for all lines and species, for a specific spectrum. This approximation may be corrected using data from literature. N is the number of molecules of the species we want to determine, Q(T) is the partition function at temperature T and it is given by the following relation:

$$Q(T) = \sum_J g_s(J)(2J+1) \exp\left(-\frac{hcb_0 J(J+1)}{KT}\right)$$

g<sub>s</sub>(J) is the nuclear spin multiplicity; it depends on the rotational level and on the molecular species as following:

|                          |   |                      |
|--------------------------|---|----------------------|
| HD gas                   | (2I <sub>H</sub> +1)x (2I <sub>D</sub> +1) with I <sub>H</sub> =1/2 I <sub>D</sub> =1 | g <sub>s</sub> (J)=6 |
| Ortho-H <sub>2</sub> gas | J odd I <sub>H2</sub> =1  | g <sub>s</sub> (J)=3 |
| Para-H <sub>2</sub> gas  | J even I <sub>H2</sub> =0   | g <sub>s</sub> (J)=1 |
| Para-D <sub>2</sub> gas  | J odd I <sub>H2</sub> =1  | g <sub>s</sub> (J)=3 |
| Ortho-D <sub>2</sub> gas | J even I <sub>D2</sub> =0,2.  | g <sub>s</sub> (J)=6 |

The quantity  $E_R(J)=hcb_0J(J+1)$  is the rotational energy level, where  $b_0=K/8\pi^2I$  is the Raman constant ( $I$  being the molecular moment of inertia);  $K$  is the Boltzman constant and  $T$  is the gas temperature.

### - Data analysis: first method

From literature [1] an isotopic equilibrated mixture of  $H_2$ -HD- $D_2$  gas shows the following ratio at room temperature of the most intense Raman lines 100:58:47, where 100 correspond to the  $H_2(584\text{ cm}^{-1})J=1\rightarrow J=3$  transition, 58 corresponds to the  $HD(443\text{ cm}^{-1})J=1\rightarrow J=3$  transition and 47 to the  $D_2(415\text{ cm}^{-1})J=2\rightarrow J=4$  transition.

This provides a simple relation for equilibrium temperature relative content of  $H_2/HD$  and  $D_2/HD$  from measured peak intensities:

a. if  $N(H_2)/N(HD)=1$  corresponds to  $I_{H_2}(J=1)/I_{HD}(J=1)=100/58=1.7241$  then measured  $I_{H_2}(J=1)/I_{HD}(J=1)$  ratio provides the measured  $N(H_2)/N(HD)$  ratio through the relation:

$$1:1.7241 = N(H_2)/N(HD): I_{H_2}(J=1)/I_{HD}(J=1)$$

or equivalently:

$$\begin{aligned} N(H_2)/N(HD) &= I_{H_2}(J=1)/I_{HD}(J=1) / 1.7241 \\ &= I_{H_2}(J=1)/I_{HD}(J=1) \times 0.58 \end{aligned}$$

b. if  $N(D_2)/N(HD)=1$  corresponds to  $I_{D_2}(J=2)/I_{HD}(J=1)=47/58=0.810344$  then measured  $I_{D_2}(J=2)/I_{HD}(J=1)$  ratio provides the measured  $N(D_2)/N(HD)$  ratio through the relation:

$$1:0.810344 = N(D_2)/N(HD): I_{D_2}(J=2)/I_{HD}(J=1)$$

or equivalently:

$$\begin{aligned} N(D_2)/N(HD) &= I_{D_2}(J=2)/I_{HD}(J=1) / 0.81033 \\ &= I_{D_2}(J=2)/I_{HD}(J=1) \times 1.2340. \end{aligned}$$

This method only applies to equilibrium temperature mixtures and only considers three of the several measured Raman peaks. However it may provide lower absolute error in determining the  $H_2$  and  $D_2$  concentrations in HD since only the errors on single peak intensity are involved in the calculation.

Moreover this method does not use any hypothesis on the values of the constant C and provides an independent check on systematic errors.

**- Data analysis: second method**

The intensity formula may be rewritten as:

$$I(J) = CN/Q(T) h(J) \exp[-hcb_0J(J+1)/KT]$$

where:

$$h(J) = g_s(J)(2J + 1) \frac{3(J + 1)(J + 2)}{2(2J + 1)(2J + 3)}$$

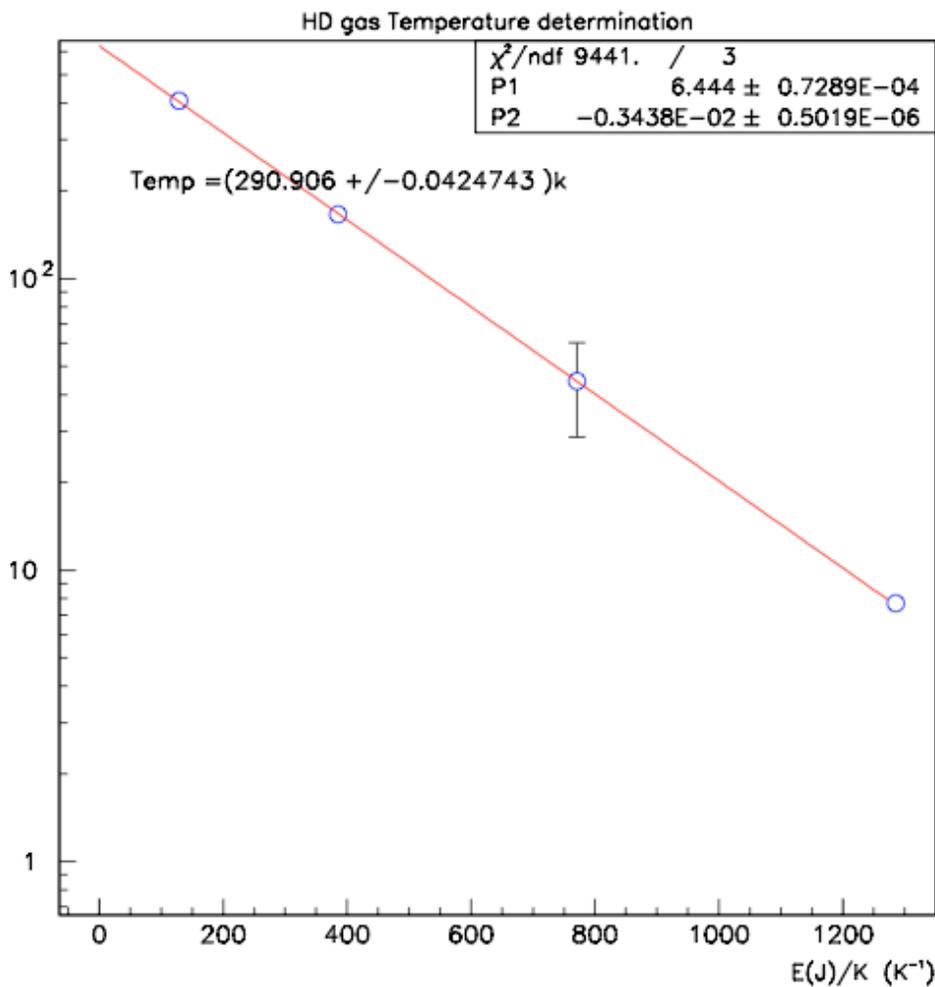


Figure 6 – Linear fit of the ratio I(J)/h(J) in logarithmic scale as a function of E(J)/K for five HD peaks corresponding to J=0,1,2,3,4. The slope provides 1/T and the intercept provides A=ln(CN/Q).

For each line the corresponding values of  $h(J)$  and  $E_R(J)$  may be calculated. For each gas species one may fit the linear dependence of the ratio  $I(J)/h(J)$  with respect to  $E_r(J)/K$  in log scale: the slope will provide  $1/T$  and the intercept provides  $A=\ln(CN/Q(T))$ , as shown in figure 6.

Once the temperature is extracted, one may calculate the partition function  $Q(T)$  from its definition and determine for each peak the quantity:

$$CN = \frac{I(J)Q(T)}{h(J)\exp[-E_R(J)/KT]}$$

which should be independent from  $J$ .

A fit (weighted average) of the results, provides the factor  $CN$  for the single gas species.

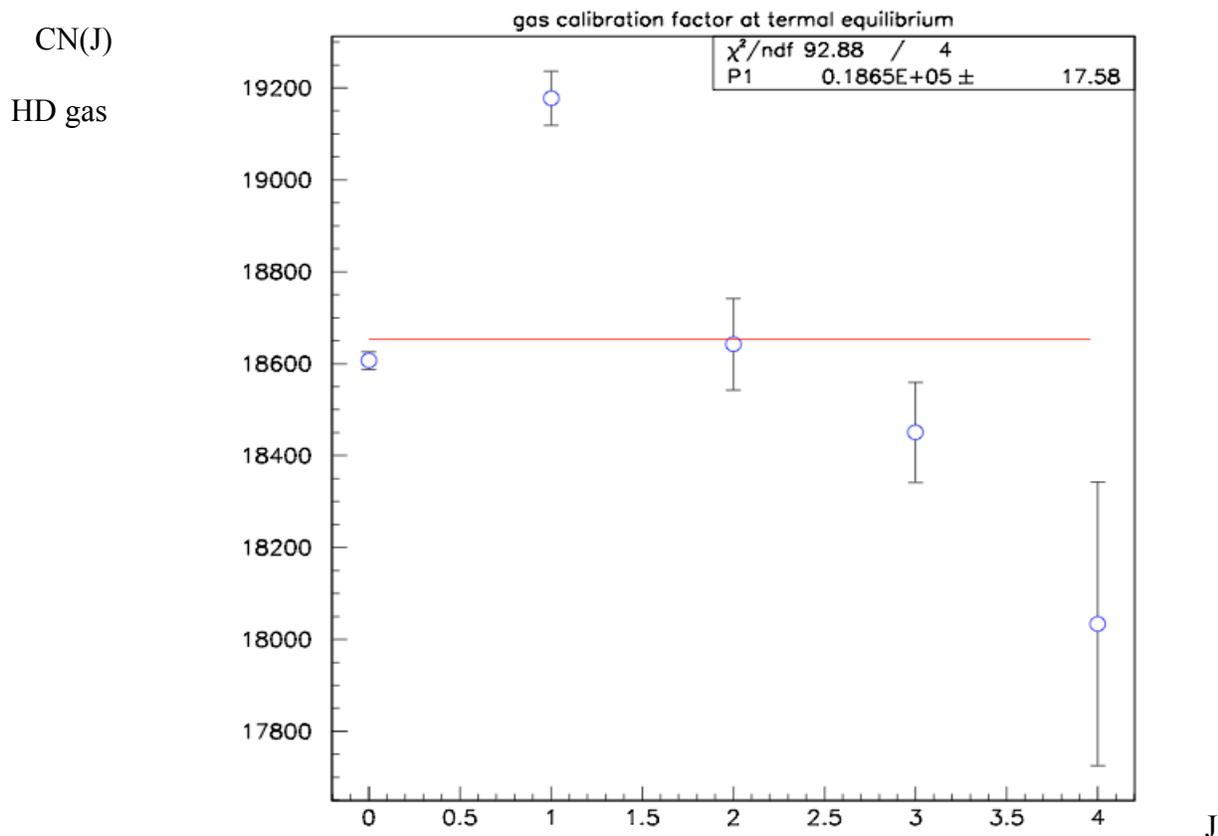


Figure 7 – Weighted average of the five values of the product  $CN$  extracted from each of the five HD Raman peaks.

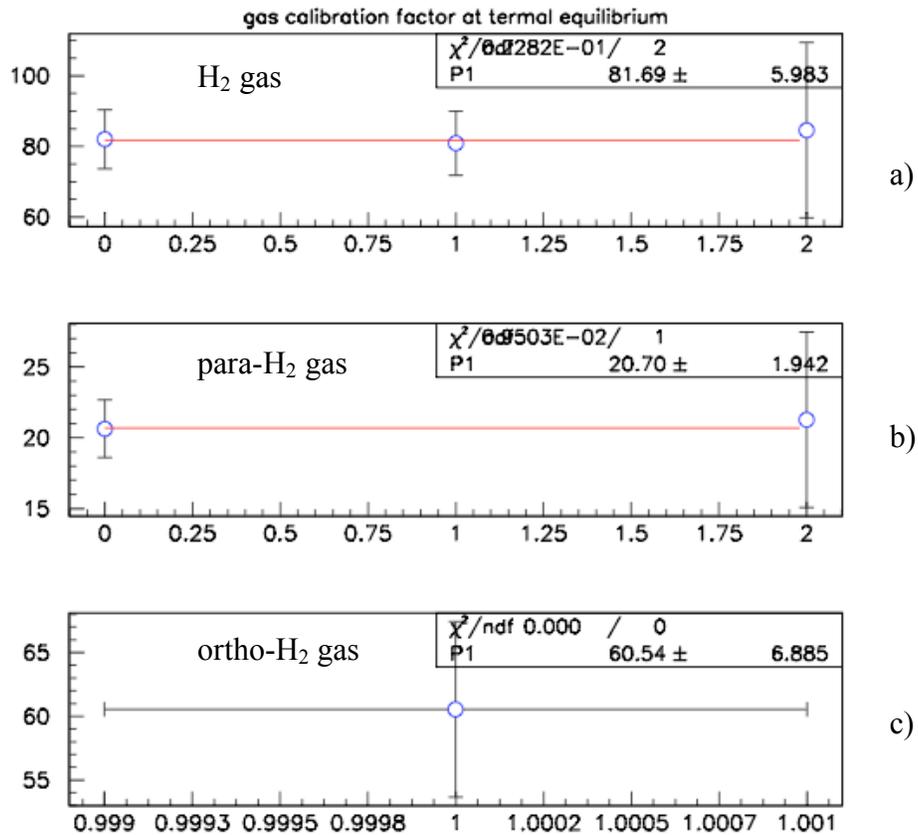


Figure 8 – a) Weighted average of the three values of the product CN extracted from all the H<sub>2</sub> Raman peaks. b) Weighted average of the two CN product values from the para-H<sub>2</sub> Raman peaks corresponding to J even→J even transitions. b) Value of the CN product from the ortho-H<sub>2</sub> Raman peak corresponding to the J=1 (odd) →J=3 (odd) transition.

The same procedure may be applied for each gas: for the three H<sub>2</sub> peaks and for the visible (four to six) D<sub>2</sub> peaks, as shown in Figures 8 and 9. In the case of these two gases, it is also possible to separately analyze the content of the ortho- and para- species separately; they correspond to the J-odd→J-odd and J-even→J-even Raman lines, respectively for H<sub>2</sub> and J-even→J-even and J-odd→J-odd Raman lines, respectively for D<sub>2</sub>. The procedure is very similar, only the value of the partition function Q(T)

must be appropriately calculated to include only the energy levels corresponding to J-odd (or J-even) rotational levels.

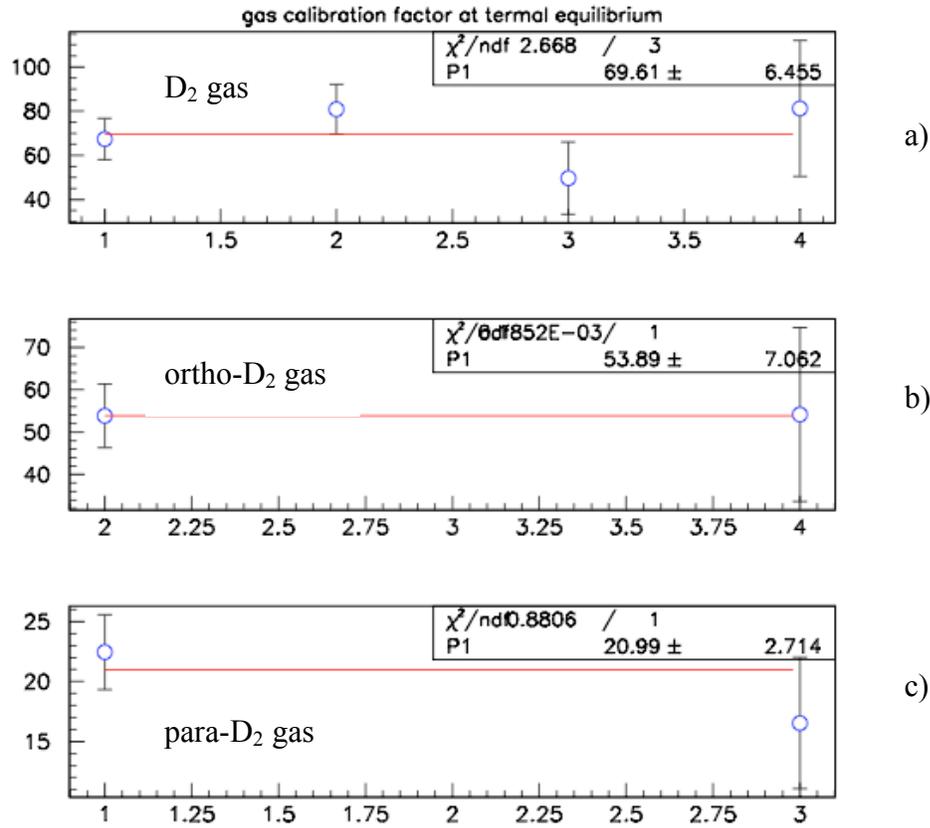


Figure 9 – a) Weighted average of the four values of the product CN extracted from all the D<sub>2</sub> Raman peaks. b) Weighted average of the two CN product values from the ortho-D<sub>2</sub> Raman peaks corresponding to J even → J even transitions. b) Weighted average of the two CN product values from the para-D<sub>2</sub> Raman peaks corresponding to the J odd → J odd transitions.

In case of thermal equilibrium the following relations must be satisfied:

$$\text{CN}_{\text{para-}} + \text{CN}_{\text{ortho-}} = \text{CN}$$

H<sub>2</sub>:       $\text{CN}_{\text{para-}} / \text{CN} = 1/4 = 0.25$        $\text{CN}_{\text{ortho-}} / \text{CN} = 3/4 = 0.75$   
D<sub>2</sub>:       $\text{CN}_{\text{ortho-}} / \text{CN} = 6/9 = 0.666$        $\text{CN}_{\text{para-}} / \text{CN} = 3/9 = 0.3333$ .

The information from [1] on relative peak intensities of an isotopic equilibrated mixture of H<sub>2</sub>-HD-D<sub>2</sub> may be used to extract the ratio of the constants C for different gasses, at room temperature. The intensity formula for each peak reduces to:

$$I(J,T) = CN f(J,T)$$

where  $f(J,T) = h(J) / Q(T) \exp[-E_R(J)/KT]$  may be calculated for each peak at a fixed temperature, for each gas type.

Imposing  $N_{HD} = N_{H_2}$  one obtains

$$\begin{aligned} I_{HD}(J=1) / I_{H_2}(J=1) &= 0.58 = \\ &= C_{HD} N_{HD} f_{HD}(J=1, T) / C_{H_2} N_{H_2} f_{H_2}(J=1, T) = \\ &= C_{HD} f_{HD}(J=1, T) / C_{H_2} f_{H_2}(J=1, T) \end{aligned}$$

from this relation one may extract the correction factor, among the different gases:

$$\begin{aligned} C_{HD} / C_{H_2} &= I_{HD}(J=1) / I_{H_2}(J=1) \times f_{H_2}(J=1, T) / f_{HD}(J=1, T) = \\ &= 0.58 * f_{HD}(J=1, T) / f_{H_2}(J=1, T) = 0.98756. \end{aligned}$$

Similarly

$$\begin{aligned} I_{D_2}(J=1) / I_{HD}(J=1) &= I_{D_2}(J=1) / I_{H_2}(J=1) \times I_{H_2}(J=1) / I_{HD}(J=1) = \\ &= 0.47 / 0.58 = 0.8103 = \\ &= C_{D_2} N_{D_2} f_{D_2}(J=2, T) / C_{H_2} N_{H_2} f_{H_2}(J=1, T) \times \\ &C_{H_2} N_{H_2} f_{H_2}(J=1, T) / C_{HD} N_{HD} f_{HD}(J=1, T) = \\ &= C_{D_2} f_{D_2}(J=2, T) / C_{HD} f_{HD}(J=1, T) \end{aligned}$$

from this relation one may extract the correction factor for D<sub>2</sub>/HD

$$\begin{aligned} C_{D_2} / C_{HD} &= I_{D_2}(J=1) / I_{H_2}(J=1) \times I_{H_2}(J=1) / I_{HD}(J=1) \times f_{HD}(J=1, T) / f_{D_2}(J=2, T) = \\ &= 0.8103 * f_{HD}(J=1, T) / f_{D_2}(J=2, T) = 1.0343 \end{aligned}$$

Finally it is possible to determine the  $N(H_2)/N(HD)$  and  $N(D_2)/N(HD)$  ratios:

$$\begin{aligned} N(H_2) / N(HD) &= CN_{H_2}(\text{fit}) / CN_{HD}(\text{fit}) \times C_{HD} / C_{H_2} = \\ &= 0.98756 \times CN_{H_2}(\text{fit}) / CN_{HD}(\text{fit}) \end{aligned}$$

$$\begin{aligned} N(D_2)/N(HD) &= CN_{D_2}(\text{fit})/ CN_{HD}(\text{fit}) \times C_{HD}/ C_{D_2} \\ &= 1.0343 \times CN_{D_2}(\text{fit})/ CN_{HD}(\text{fit}). \end{aligned}$$

## -Results

The analysis program was used twice for each spectrum, using the two different methods to extract the peak intensities from the Raman spectrum. The analysis program provides two different estimates of the H<sub>2</sub> and D<sub>2</sub> concentrations in HD, so we have four different results for each Raman spectrum. The first set of measurements are summarized in table I.

Table I. Results from measurements taken on July 29<sup>th</sup> and July 30<sup>th</sup>.

| H2/HD                          | JMU-II 1        | JMU-II 2        | JMU-II 3        | USC             | JMU-III         |
|--------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| G+back<br>Peaks Ratio          | 0.03407±0.00007 | -               | 0.00438±0.00006 | 0.00455±0.00006 | 0.00365±0.00006 |
| G+back<br>Global Fit           | 0.03373±0.00006 | 0.00475±0.00006 | 0.00432±0.00006 | 0.00441±0.00006 | 0.00359±0.00006 |
| Int+back<br>sub<br>Peaks Ratio | 0.0341±0.0003   | 0.0047±0.0006   | 0.00439±0.00007 | -               | 0.00365±0.00007 |
| Int+back<br>sub<br>Global Fit  | 0.0332±0.0001   | 0.00463±0.00006 | 0.00426±0.00005 | -               | 0.00354±0.00006 |
| Weighted<br>mean               | 0.03376±0.00004 | 0.00466±0.00004 | 0.00433±0.00003 | 0.00449±0.00004 | 0.00360±0.00003 |

| D2/HD                          | JMU-II 1       | JMU-II 2      | JMU-II 3        | USC             | JMU-III         |
|--------------------------------|----------------|---------------|-----------------|-----------------|-----------------|
| G+back<br>Peaks Ratio          | 0.0342±0.0007  | -             | 0.0046±0.0001   | 0.0046±0.0001   | 0.0038±0.0001   |
| G+back<br>Global Fit           | 0.0343±0.0001  | 0.0046±0.0001 | 0.0048±0.0001   | 0.0051±0.0001   | 0.0038±0.0001   |
| Int+back<br>sub<br>Peaks Ratio | 0.0340±0.0009  | -             | 0.0046±0.0001   | -               | 0.0038±0.0001   |
| Int+back<br>sub<br>Global Fit  | 0.0338±0.0002  | 0.0046±0.0001 | 0.0047±0.0001   | -               | 0.0038±0.0001   |
| Weighted<br>mean               | 0.03417±0.0001 | 0.0046±0.0001 | 0.00467±0.00006 | 0.00484±0.00008 | 0.00380±0.00007 |

Sometimes fits did not converge and the corresponding results are not reported in the tables.

The first striking result is that the first sample of JMU-II gas shows H<sub>2</sub> and D<sub>2</sub> contaminations at the level of 3 %, one order of magnitude higher than the other two samples of the same gas.

All measurements were taken within one hour from the filling of the Raman cell with the gas to be analyzed, except the one on the first JMU-II gas sample, which was filled 4 days in advance.

We wanted to check the hypothesis that the new installed pressure gauge, despite is made of Stainless Steel, has been causing HD dissociation and recombination into H<sub>2</sub> and D<sub>2</sub> at a high rate. So a new measurement was taken on the last measured cell (JMU-III) six days after, on August 5<sup>th</sup>.

Table II. Results from measurements taken on July 30<sup>th</sup> and August 5<sup>th</sup> on the same gas sample in the cell connected to the pressure gauge

| H2/HD                          | JMU-III         | JMU-III days    | D2/HD                          | JMU-III         | JMU-III days  |
|--------------------------------|-----------------|-----------------|--------------------------------|-----------------|---------------|
| G+back<br>Peaks Ratio          | 0.00365±0.00006 | 0.1347±0.0002   | G+back<br>Peaks Ratio          | 0.0038±0.0001   | 0.1441±0.0008 |
| G+back<br>Global Fit           | 0.00359±0.00006 | 0.13288±0.00009 | G+back<br>Global Fit           | 0.0038±0.0001   | 0.1427±0.0002 |
| Int+back<br>sub<br>Peaks Ratio | 0.00365±0.00007 | 0.1364±0.0008   | Int+back<br>sub<br>Peaks Ratio | 0.0038±0.0001   | 0.144±0.001   |
| Int+back<br>sub<br>Global Fit  | 0.00354±0.00006 | 0.13097±0.00009 | Int+back<br>sub<br>Global Fit  | 0.0038±0.0001   | 0.1407±0.0005 |
| Weighted<br>mean               | 0.00360±0.00003 | 0.13223±0.00006 | Weighted<br>mean               | 0.00380±0.00007 | 0.1426±0.0002 |

The result is shown in Table II and confirms that a rapid recombination process occurs in the cell in the presence of the pressure gauge, so that the H<sub>2</sub> and D<sub>2</sub> concentrations increased by almost two orders of magnitude in less than one week.

The pressure gauge was removed from the cell. Since the pressure in the gas samples had dropped to 1550 bar after the first filling, the estimated pressure in the cell at a second refill may be calculated to be:

$$P_{\text{IIfill}} \geq 0.816 \times 1550 \text{ mbar} = 1264 \text{ mbar},$$

Which is enough for a second set of Raman measurements.

All gas samples were measured again on the same day and results are shown in Table III.

Table III. Results from measurements taken on August 5<sup>th</sup>, after removing the pressure gauge on the Raman cell.

| H2/HD                    | JMU-II 1        | JMU-II 2        | JMU-III         | USC             |
|--------------------------|-----------------|-----------------|-----------------|-----------------|
| G+back Peaks Ratio       | 0.00479±0.00007 | 0.00447±0.00007 | 0.00227±0.00007 | 0.00395±0.00007 |
| G+back Global Fit        | 0.00471±0.00007 | 0.00441±0.00007 | 0.00220±0.00007 | 0.00381±0.00007 |
| Int+back sub Peaks Ratio | 0.005±0.001     | 0.00448±0.00009 | 0.0022±0.0007   | 0.00397±0.00009 |
| Int+back sub Global Fit  | 0.00465±0.00007 | 0.00434±0.00008 | 0.00217±0.00007 | 0.00376±0.00008 |
| Weighted mean            | 0.00472±0.00004 | 0.00442±0.00004 | 0.00220±0.00004 | 0.00387±0.00004 |

| D2/HD                    | JMU-II 1        | JMU-II 2        | JMU-III       | USC             |
|--------------------------|-----------------|-----------------|---------------|-----------------|
| G+back Peaks Ratio       | 0.0040±0.0001   | 0.0042±0.0001   | 0.0025±0.0001 | 0.0042±0.0001   |
| G+back Global Fit        | 0.0043±0.0001   | 0.0045±0.0001   | 0.0025±0.0002 | 0.0046±0.0002   |
| Int+back sub Peaks Ratio | 0.004±0.002     | 0.0042±0.0001   | -             | 0.0043±0.0002   |
| Int+back sub Global Fit  | 0.0042±0.0002   | 0.0044±0.0001   | 0.0025±0.0002 | 0.0046±0.0002   |
| Weighted mean            | 0.00416±0.00008 | 0.00433±0.00007 | 0.0025±0.0001 | 0.00442±0.00008 |

Comparing the results from the two JMU-II samples one may conclude that the systematic error is slightly higher than the error given by the weighted mean of the four different results for each spectrum.

The H<sub>2</sub> and D<sub>2</sub> contamination is lowest for the JMU-III gas sample, followed by the USC. The JMU-II sample is however comparable to the USC gas.

Table IV. Results from measurements taken on August 5<sup>th</sup> and September 1<sup>st</sup> on the same cell, without the pressure gauge

| H2/HD                       | USC                 | USC-27days      | D2/HD                       | USC                 | USC-27days          |
|-----------------------------|---------------------|-----------------|-----------------------------|---------------------|---------------------|
| G+back<br>Peaks Ratio       | 0.00395±0.0000<br>7 | 0.01225±0.00008 | G+back<br>Peaks Ratio       | 0.0042±0.0001       | 0.0119±0.0001       |
| G+back<br>Global Fit        | 0.00381±0.0000<br>7 | 0.01213±0.00007 | G+back<br>Global Fit        | 0.0046±0.0002       | 0.0121±0.0002       |
| Int+back sub<br>Peaks Ratio | 0.00397±0.0000<br>9 | 0.0122±0.0001   | Int+back sub<br>Peaks Ratio | 0.0043±0.0002       | 0.0118±0.0002       |
| Int+back sub<br>Global Fit  | 0.00376±0.0000<br>8 | 0.01193±0.00009 | Int+back sub<br>Global Fit  | 0.0046±0.0002       | 0.01193±0.0002      |
| Weighted<br>mean            | 0.00387±0.0000<br>4 | 0.01233±0.00004 | Weighted<br>mean            | 0.00442±0.000<br>08 | 0.01196±0.0000<br>8 |

A final check on the recombination rate in the cell was done by re-measuring the Raman spectrum of the last used cell, after a period of time of 27 days. The contaminations increased by about a factor 3 in 1 month, at a much lower rate than previously observed when the pressure gauge was mounted on the cell.

## Bibliography

[1] K. Okuno, T. Uda, S. O'Hira, Y. Naruse Journal of Nuclear Science and Technology 28 pp509-516 (1991)