

## HD GAS DISTILLATION AND ANALYSIS FOR HD FROZEN SPIN TARGETS

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The production of HD targets relies on a longitudinal relaxation time switch mechanism. The longitudinal relaxation time of solid HD samples strongly depends on the concentration of ortho-hydrogen and para-deuterium in pure HD. At low temperatures these contaminants decay into  $H_2$  and  $D_2$  molecular ground states and the reduction of their concentration causes a dramatic increase of the longitudinal relaxation time of H and D in the HD solid. This is obtained by aging the target sample, keeping it at about 10mK temperature while a 15-17 Tesla magnetic field is applied. The ortho-hydrogen and para-deuterium concentrations in the HD gas to be polarized are therefore critical parameters for the whole polarization process. A careful procedure for distilling commercial HD gas and storing the purified gas has been developed. An accurate technique to analyze the HD gas before and after the polarization procedure, which is based on gas chromatography and Raman scattering, has also

been set-up to optimize the aging time as a function of the initial concentration of the contaminants.

*Keywords:* Solid polarized targets, Raman scattering, Gas Chromatography

## 1. Introduction

The use of polarized HD targets is becoming very attractive in nuclear and sub-nuclear physics experiments because of the several advantages provided by this new technology [1]. The fraction of free polarized protons exceeds any other type of polarized target and, considering the contribution from bound protons and neutrons in the polarized deuteron, very high dilution factors for both nucleons are obtained. H and D nuclei may be independently polarized and their polarization may be easily reversed. With present technologies the polarization degree may reach values as high as 95% and 66% for H and D respectively. When frozen-spin conditions are met targets may be *cold transported*, stored and used in experiments keeping them at values of temperatures (T) and magnetic fields (B) that are compatible with complex and large solid angle detectors ( $B = 1$  Tesla and  $T = 0.5K$ ) [2].

The price to pay is a long and complicated production cycle which may still need some research and development activity to be optimized. The whole procedure is based on symmetry properties of molecular hydrogen isotopes. Next section will point out how symmetry properties constrain the possibility of polarizing different molecular hydrogen isotopes. HD gas distillation and analysis will be covered in the following section and details about the Raman scattering technique set-up in Rome to analyze the relative content of isotopes in a mixture are finally explained.

## 2. Hydrogen isotopes properties and nuclear polarization

Homo-nuclear  $H_2$  and  $D_2$  molecules must obey to symmetry constraints. Since protons are spin 1/2 fermions, the molecular wave-function must be anti-symmetric under the exchange of identical nuclei. On the contrary the  $D_2$  molecular wave-function must be symmetric under the exchange of spin 1 deuterons.

In the Born-Oppenheimer approximation the molecular wave-function may be separated into the product of the nuclear, electronic, vibrational and rotational functions, each one dependent from the respective degrees of freedom only. Nuclear exchange corresponds to space inversions for electronic and space variables. Therefore the wave-function symmetry is directly related to its parity. Both vibrational and electronic ( $P = (-1)^L$  where L

is the orbital eigen-value) ground state wave-functions are symmetric with respect to space inversion. The rotational levels are symmetric for even values of the eigen-values  $J$ , and anti-symmetric for odd values ( $P = (-1)^J$ ). In the case of  $H_2$  molecules the nuclear wave-function is symmetric when the two nuclear spins couple to a total value  $I = 1$  (ortho-hydrogen) and anti-symmetric for  $I = 0$  (para-hydrogen). The result is that the wave-function symmetry limits the rotational and nuclear states combinations:  $J$  odd rotational eigen-values are coupled to ortho- $H_2$  while  $J$  even values are coupled to para- $H_2$ . For  $D_2$  molecules the nuclear wave-function is symmetric when the two  $I_d = 1$  nuclear spins couple to  $I = 0, 2$  (ortho-deuterium) and it is anti-symmetric for  $I = 1$  (para-deuterium). Again  $J$  odd rotational eigen-values may be coupled to  $I = 1$  nuclear state and the  $J$  even values to the  $I = 0, 2$  nuclear states, only.

$I = 1$  molecular nuclear states are the only ones that are easily polarizable, but, being coupled to  $J$  odd values of rotational states, they are meta-stable. Decays from  $I = 1$  and  $J = 1$  ortho- to  $I = 0$  and  $J = 0$  para- states are inhibited (“forbidden”) because two transitions must happen simultaneously within the same molecule: an E1 molecular transition to change the rotational state and an M1 nuclear spin-flip to preserve the symmetry of the wave-function. The consequence is that homo-nuclear  $H_2$  and  $D_2$  ground states may not be used to produce polarized targets. For ethero-nuclear HD molecules these constraints do not apply and H and D nuclei may be independently oriented in the molecular ground state. This property makes HD molecules ideal for polarized targets. High magnetic fields ( $B = 15 - 17$  T) at very low temperatures ( $T = 10mK$ ) may align their nuclear spins in the direction of the magnetic field. The maximum degree of polarization that can be obtained at thermal equilibrium is ruled by the Brillouin function:

$$P = B_I(x) = \left(\frac{2I+1}{2I}\right)\coth[(2I+1)x] - \frac{1}{2I}\coth(x) \quad (1)$$

where  $x = \mu B/K_B T$  depends on the ratio  $B/T$ , the nuclear magnetic moment  $\mu$  and the Boltzmann constant  $K_B$ . The highest obtainable degree of polarization is  $P = 0.91$  for hydrogen and  $P = 0.30$  for deuterium for  $B/T = 15T/10mK$ .

These extreme environmental conditions, that allow for high nuclear polarization at thermal equilibrium, are not compatible with any particle detector typical of nuclear and sub nuclear experiments. Moreover it has been found [3] that for pure HD solid direct spin-lattice relaxation mechanisms are suppressed and both longitudinal relaxation time for hydrogen

( $T_1^H$ ) and deuterium ( $T_1^D$ ) in HD solid are extremely long.

If *impurities* of ortho-hydrogen molecules are present in HD solid, an important relaxation mechanism is due to cross-relaxation of polarized nuclei in  $H_2$  with neighbor protons in HD, which have the same Larmor frequency [4]. Longitudinal relaxation time  $T_1^H$  is strongly dependent upon the concentration of ortho- $H_2$  *contaminants*:  $T_1^H$  is as low as few minutes for ortho- $H_2$  concentrations of the order of  $10^{-3}$  and increases to the order of months for concentrations of  $10^{-6}$ .

Since the energy difference between ortho- and para- $H_2$  molecular states corresponds to  $\Delta T = 172K$ , if the HD sample is kept at low temperatures the ortho- $H_2$  contaminants decay into the para- $H_2$  state with a decay time  $\tau_H = 6.3$  days. By preparing the initial concentration of ortho- $H_2$  contaminants in the HD gas to be of the order of  $10^{-4}$ , the relaxation time  $T_1^H$  may be kept short enough to reach the equilibrium polarization value in a few days [2]. Leaving the HD at low temperatures and high magnetic field for a period of time longer than four times the ortho- $H_2$  decay time (one or two months) the concentration of contaminants decreases by two orders of magnitude and the relaxation time  $T_1^H$  increases to values of the order of few months. This spin-lattice relaxation *switch* is the key feature of the whole polarization procedure: by aging the solid HD sample at  $T = 10mK$  and  $B = 15 - 17 Tesla$  for some months a frozen-spin polarized H target is obtained.

The same procedure could be applied to polarize deuterium nuclei by introducing para- $D_2$  contaminants in the HD gas. However the para- $D_2$  decay time  $\tau_D = 18.6$  days requires very long and impractical aging time and the final thermal equilibrium degree of polarization is quite low. An *adiabatic fast passage* [2] has been developed to transfer the polarization from  $H$  to  $D$  in the HD solid. Details of the polarization instrumentation, technologies and applications may be found in [5].

### 3. HD gas distillation and analysis

The polarization procedures critically depends on the initial concentration of ortho- $H_2$  in the HD gas. Commercial HD gas is 98% pure and contains concentrations of  $H_2$  and  $D_2$  contaminants at the level of 1.5% and  $< 0.5\%$ , respectively. Concentrations useful for a frozen-spin target are two order of magnitudes smaller. A distillation procedure as been developed at the James Madison University to purify the HD gas and optimize the ortho- $H_2$  concentration. The principle of operation is based on the fact that at low temperatures the vapor pressures of  $H_2$ ,  $D_2$  and  $HD$  differ. The distiller

operates at  $T = 20$  K. It is cooled by a Gifford-McMahon refrigerator and a temperature gradient is set along the distiller tube between the lower still pot, connected to a boil-up heater, and the upper cold finger. A Stedman packing, made of 30 double layers stainless steel screen mesh and located along the distillation tube, amplifies the vapor pressure difference among the different isotopes and enables the purification of contaminants by one order of magnitude for each distillation cycle. The gas is distilled in batches of 12 moles. Once the system reaches a steady state the gas stratifies in the distiller column and may be extracted at a rate of 1 mole/day. First 3 extracted moles consist of  $H_2$  enriched HD gas, 6 moles of purified HD gas follow while the 3 moles remaining in the still pot consist of  $D_2$  enriched HD gas. The extracted gas is stored in tanks each containing 2 moles of gas. A double-distillation process allows to reduce contaminants to the required level of few hundred parts per million.

A residual gas analyzer (RGA) is part of the system. It uses an electric quadrupole field to momentum analyze ionized particles flowing at a fixed velocity, to determine their mass. Since for hydrogen isotopes the molecular dissociation energy is lower than ionization energy, introducing pure HD gas in the RGA results in some recombination of dissociated H and D atoms into  $H_2$  and  $D_2$ , and a small fraction of  $H_2$  and  $D_2$  is always observed. The sensitivity of this device is limited to some percents and it is used only to monitor the extraction of the first  $H_2$  enriched moles of HD gas.

To quantify the content of hydrogen isotopes in a mixture at sensitivities higher than few percents gas chromatography and Raman spectroscopy may be used. A commercial instrument for gas chromatography has been used at JMU to analyze the distilled gas. The technique consists in the measurement of the thermal conductivity difference of the gas to be analyzed with respect to a Neon gas carrier, as a function of the retention time in a capillary column. A sensitivity of the order of  $10^{-3}$  has been obtained for the hydrogen isotopes separation. This encouraging result is however not enough to measure the ortho- $H_2$  concentration at the level of  $10^{-4}$ , useful for HD polarized targets.

#### 4. Raman spectroscopy of hydrogen isotopes mixtures

Raman spectroscopy offers a very interesting alternative to analyze the relative content of hydrogen isotopes in a mixture. The Laser light is scattered by the molecules, which may change their rotational state by  $\Delta J = \pm 2$ . Raman scattering therefore correspond to transitions among ortho- $H_2$  states (or among para- $H_2$ ) and enables for a direct measurement of ortho- $H_2$  con-

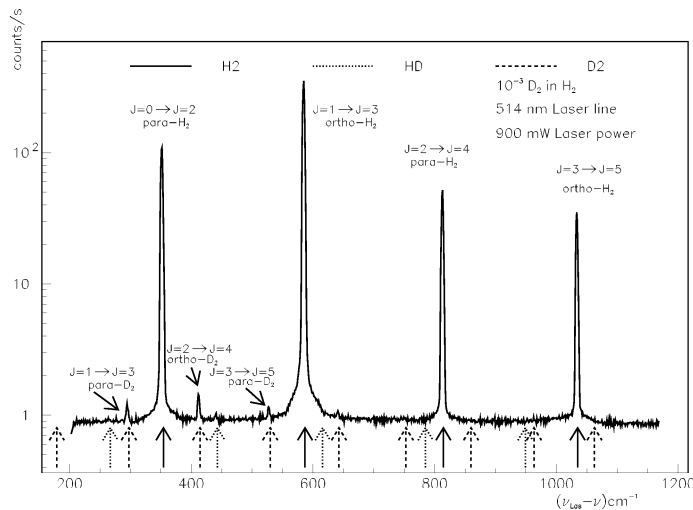


Fig. 1. Raman spectrum of a mixture of  $10^{-3}$  concentration of  $D_2$  in  $H_2$  gas at 2 atm pressure on a logarithmic scale. The incoming light is the 514 nm green line of an Ion-Argon Laser. Laser power was 900 mW. The arrows point to the position of the Raman peaks of the different hydrogen isotopes.

tent. In the Rome set-up the light spectrum is measured by means of a triple monochromator and a charged coupled device (CCD). Figure 1 shows the Raman spectrum of a mixture of  $10^{-3}$  concentration of  $D_2$  in  $H_2$  gas at 2 atm pressure on a logarithmic scale, obtained using the 514 nm green line of an Ion Argon Laser, having 900 mW output power. The horizontal axis shows the energy difference between the the incident Laser light and the scattered light, expressed in  $cm^{-1}$  units. The molecular rotational energy levels are given by the relation  $E_R = (\hbar^2/2I)J(J+1) = hcb_0J(J+1)$ , where  $I$  is the molecular moment of inertia and  $b_0$  is the corresponding Raman constant. The Raman peaks positions correspond to the energy differences:

$$\Delta E = hcb_0[(J+3)(J+2) - J(J+1)] = hcb_0(4J+6) \quad (2)$$

which, for each molecular species, are equally separated by  $4hcb_0$ . The intensity of the Raman peaks is a function of the gas mixture temperature and it is given by the following relation [6]:

$$I(J, T) = I_0 A(\nu) \nu^3 f(J) \gamma^2 \frac{45\pi^4}{7} \frac{N}{Q(T)} g_s(J) \frac{3(J+1)(J+2)}{2(2J+3)} e^{-\frac{hcb_0J(J+1)}{K_B T}} \quad (3)$$

where  $I_0$  is the Laser intensity,  $A(\nu)$  is the spectral response function of the experimental set-up,  $f(J)$  is the an-harmonicity correction,  $\gamma$  is the anisotropic matrix element,  $N$  is the total number of molecules of the species,  $Q(T)$  is the partition function given by:

$$Q(T) = \sum_J g_s(J)(2J+1)e^{-\frac{hcb_0J(J+1)}{K_B T}} \quad (4)$$

and  $g_s(J)$  is the nuclear spin multiplicity. For a single hydrogen isotope, neglecting the an-harmonicity dependence upon the rotational state and the frequency dependence of the spectral response function, the product  $C = I_0 A(\nu) \nu^3 \gamma^2 (45\pi^4/7)$  is constant. The intensity of each Raman peak may be expressed by an exponential dependence upon the gas temperature:

$$I(J, T) = \frac{CN}{Q(T)} h(J) e^{-\frac{hcb_0J(J+1)}{K_B T}} \quad (5)$$

where:

$$h(J) = g_s(J) \frac{3(J+1)(J+2)}{2(2J+3)} \quad (6)$$

is a function of the rotational index  $J$ , only. The Raman spectrum has been fitted using Gaussian functions for the peaks and a constant value for the background. Measured intensities for each peak  $I_{meas}(J)$  may be obtained by integrating the fitted Gaussian functions. The gas mixture temperature  $T$  and the constant product  $CN/Q(T)$  may be extracted fitting the ratio  $I_{meas}/h(J)$  by a linear dependence upon  $hcb_0J(J+1)/K_B$  in a semi-logarithmic scale. Once the temperature  $T$  is known, the partition function  $Q(T)$  may be explicitly evaluated and it is possible to extract, for each value of  $J$ , the product:

$$CN(J) = \frac{I_{meas}(J)}{h(j)} Q(T) e^{-\frac{hcb_0J(J+1)}{K_B T}} \quad (7)$$

which, at thermal equilibrium, should be constant for all peaks of the same hydrogen isotope. An average value of the product of the total number of molecules times the constant factor  $C$  may be obtained. Moreover, for  $H_2$  and  $D_2$  gasses, peaks corresponding to transitions among ortho- and para- states may be analyzed as if belonging to different nuclear species, by evaluating the partition function for odd or even values of  $J$  separately. Repeating the same analysis procedure for peaks separately connecting even and odd values of  $J$ , one may obtain the average values of the products  $CN_{para}$  and  $CN_{ortho}$ , in addition to  $CN_{tot}$ , where  $N_{para}$ ,  $N_{ortho}$  and  $N_{tot}$  are the number of molecules of ortho- para- and total molecules of each hydrogen isotope and the constant  $C$  assumes the

same value for different nuclear species of the same isotope. The relative ortho- or para- content of an isotope may be directly obtained by the ratio of the previous products:  $c_{ortho} = CN_{ortho}/CN_{tot} = N_{ortho}/N_{tot}$  and  $c_{para} = CN_{para}/CN_{tot} = N_{para}/N_{tot}$ .

The determination of the relative content of different isotopes requires the normalization of the C constants corresponding to different isotopes. This may be inferred by the published values of relative Raman intensities [7]. Using the ratio of the  $D_2(J = 2 \rightarrow J = 4)$  and the  $H_2(J = 1 \rightarrow J = 3)$  peak intensities ( $I(2)_{D_2}/I(1)_{H_2} = 0.47$ ), it is found that  $C_{D_2}/C_{H_2} = 0.95$ . The result for the measured relative content of the gas mixture of  $D_2$  in  $H_2$  at 2 atm, shown in figure 1, is  $N_{D_2}/N_{D_2} = (3.2 \pm 0.3)10^{-3}$ , where the error of the measurement is in the  $10^{-4}$  range.

Improvements of the present set-up are foreseen to increase the signal to noise ratio by a factor ten. A more powerful Coherent Sabre Laser will be shortly available which should allow to increase sensitivity of the analysis based on Raman scattering to the required hundreds parts per million.

## 5. Conclusions

A systematic study of the dependence of the longitudinal relaxation time  $T_1^H$  upon the ortho- $H_2$  concentration in HD gas to be polarized may be performed to optimize the solid HD target aging time, if precise measures of relative content of hydrogen isotopes mixtures would be possible. After double distillation of commercial HD gas the gas content may be analyzed by Raman scattering before and after polarization to monitor the quality of the sample.

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