### Journal Name

## ROYAL SOCIETY OF CHEMISTRY

#### ARTICLE TYPE

Cite this: DOI: 10.1039/xxxxxxxxx

# ESR study of atomic hydrogen and tritium in solid $T_2$ and $T_2$ :H<sub>2</sub> matrices below 1 K: supplementary information

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Received Date Accepted Date

DOI: 10.1039/xxxxxxxxx

www.rsc.org/journalname

#### 1 Tritium gas

The technique of condensing hydrogen onto a cold surface via a long and sufficiently cold capillary provides a rather efficient way of cleaning the condensed gas from any other contaminants except hydrogen and its isotopes. Therefore, for the experiments described in this work, we have not paid much attention to the chemical purity of T<sub>2</sub> gas, and utilized the most simple and cheap source available. The T<sub>2</sub> gas we used was extracted from commercially available tritium vials produced for use as luminescent fishing floats. Each such 5 mm diameter and 5 cm long vial contained about 5-10 $\mu$ moles of T<sub>2</sub>, which was sufficient for several experiments described in this work. The purity of the gas extracted from the vials was verified using a MKS-Granville-Phillips VQM 835 mass spectrometer with the main concern being the admixture of other hydrogen isotopes. It turned out that as the main impurity, the tritium gas in the vials typically contained about 15% of HT. It is known that the main impurity in the T<sub>2</sub> gas right after production should be  $DT(\sim 1\%)$ , while significant HT contamination appears during long term storage.<sup>1</sup> We found that  $T_2$  gas quickly degraded after extracting it from the glass vials. About 20% of it became converted to HT and H<sub>2</sub> after 3 months of storage. In order to minimize the HT content we used only fresh  $T_2$  gas for preparing our samples.

### 2 Accumulation of unpaired atoms in solid T<sub>2</sub> and T<sub>2</sub>:H<sub>2</sub> mixtures

The atoms were produced by the dissociation of molecules by the 5.7 keV electrons of the T<sub>2</sub>  $\beta$ -decay. We followed the kinetics of the growth of the atomic concentrations during the time inter-

val from several days up to two weeks, periodically recording the ESR spectra and following the QM frequency changes. The SC temperature was stabilized to several different values below 1K in order to study the sample properties as a function of temperature. It turned out that the presence of tritium introduces substantial heating in the SC and limits minimum attainable temperature to about 150 mK for the films with thickness about 300 nm. The sample cell temperature was also shortly raised by several tens of mK during the magnetic field sweeps due to eddy current heating. This was essential for triggering the explosive recombination in some of the samples. After finishing the measurements for each film, the sample cell and filling capillary were heated to a temperature above 20K and pumped for several hours in order to evacuate all hydrogen and clean all surfaces before creating a new sample. This cycle was repeated several times for samples of different H<sub>2</sub>:T<sub>2</sub> composition and thickness.

### 3 Accumulation of atomic hydrogen gas for calibration purposes

For calibration purposes we utilized the ability to accumulate the H gas in the upper volume of the SC. This is normally done by: 1) condensing a certain amount of molecular hydrogen into the H gas source; 2) condensing small amounts of helium inside the upper volume of the SC and the source, sufficient to form a several nm thick superfluid <sup>4</sup>He film; 3) running the rf discharge in the miniature rf coil inside the H gas source. The gas of atomic hydrogen is produced by dissociation by the electrons of the discharge. The helium film covering the surfaces prevents recombination of the atoms on the SC walls.

In the course of the experiments we found that atomic hydrogen gas can be accumulated (with a substantially smaller rate) also *without* running the discharge, once a helium film is present in the SC. This effect was only observed in the experiments with tritium-hydrogen mixtures. It indicates that a fraction of the

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atoms resulting from  $H_2$  dissociation in solid films by the electrons of the  $\beta$ -decay may be released out from the films into the bulk of the SC and get accumulated there. Unfortunately we were unable to observe the gas lines of spin-polarized tritium. This might be a result of substantially larger adsorption energy for T atoms on helium surfaces and also the possibility that atomic T may penetrate the helium film. The presence of a helium film in the SC leads to an extra heat load caused by the film re-condensing from the upper parts of the capillaries. In order to avoid this disturbance and reach the lowest temperatures most of the experiments described in this work were performed without helium film in the SC.

#### 4 ESR line broadening and sample magnetization

For high densities of atoms studied in this work, the effects of dipole-dipole interactions between atoms start to play an important role by influencing the shape and position of the ESR lines. It has been shown in our previous work<sup>2</sup> that the dipole-dipole interaction leads to a homogeneously broadened Lorentzian lineshape with the width linearly increasing as a function of density. This dependence can be used for the absolute determination of atomic density. A second important high density effect is an emergence of a large magnetization of the sample, which leads to shifts of the ESR lines. This effect depends on the geometry of the sample, and for thin films perpendicular to the main polarizing field the net dipolar field is opposite to the main polarizing field. This leads to the linear density-dependent shift of the ESR lines towards the larger magnetic fields, i.e. to the right in the spectra as they are recorded by our technique. Having the possibility of using the H gas lines as absolute field markers, these shifts can be accurately measured and provide an additional measure of the absolute density of atoms in the solid films.

For the high density samples and thick (> 350 nm) films, another ESR line broadening effect caused by the radiation damping brings extra complications to the analysis of the ESR spectra. The effect of radiation damping is related to spontaneous and coherent emissions of energy stored in the spin system into the resonant cavity at the electron Larmor frequency.<sup>3</sup> It typically occurs in spin systems strongly coupled to the microwave field of the cavity, when the relaxation time due to the interaction of the spin system with the cavity field becomes comparable to the spin-spin relaxation time  $T_2$ , i.e.

$$T_2 \sim T_{rad} = (2\pi M_0 Q\eta)^{-1}$$

Here  $M_0$  is the sample magnetization, Q is the resonator quality factor and  $\eta$  is the resonator filling factor. In this case the effective relaxation time of the system  $1/T'_2 = 1/T_2 + 1/T_{rad}$ . This leads to an additional line broadening proportional to the number of spins in the sample. The radiation damping effect depends on the detuning of the spectrometer frequency from the center of the cavity resonance, and it is possible to reduce it to a negligible level by increasing the detuning to several cavity resonance widths. This was verified for the thickest films of the Sample 1, where the effect was strongest. We observed a factor of 2 decrease in the ESR linewidth after such detuning. For all other samples the



**Fig. 1** The ESR line width and shift from the H gas-phase line as a function of the atomic concentration. Inset: a typical spectrum of the H and T low field lines fitted by 3 Lorentzian curves. The concentration-dependent (dipolar) shift from the H-gas line  $(H\downarrow)$  is labeled as  $\Delta B(n)$  in the inset.

radiation damping effects were substantially weaker and added not more than 20% to the actual linewidth.

A typical dependence of the tritium ESR line shift and width on the total atomic density measured for the Sample 2 is presented in Fig.1. In the inset we show a real spectrum of the low field line with all three components: T and H lines from the atoms in the solid film, and the H gas line from the atoms in the bulk of the SC. Even though the difference in the hyperfine constants is relatively large, for the very high densities studied in this work the density dependent broadening was so large that it was not always easy to resolve the H and T ESR lines from each other. The H gas line is very narrow and easily distinguishable in the spectrum. We fitted such lineshapes with three Lorentzian functions, also presented in the inset.

A zero-concentration or matrix width of  $\approx 5$  G for H and T lines in pure normal T<sub>2</sub> can be found as an offset on the vertical axis of the width vs. density plot (see Fig.1). This value is relatively large compared to the width of ESR lines in other hydrogen matrices. The line broadening due to ortho-T<sub>2</sub> molecules should rapidly vanish due to the fast ortho-para conversion which is catalysed by high concentrations of atoms. The conversion should proceed for the molecules in the closest neighbourhood of T and H atoms with a time constant of about 10s and to be of order of  $\simeq 10^3$ s for the whole sample.<sup>4</sup> We suggest that the main contribution to the matrix width of H and T in our T<sub>2</sub> samples comes from a large HT impurity. A HT molecule is composed of distinguishable atoms and the magnetic moments of the proton and triton contribute to the line broadening. The matrix width for unpaired atoms in HD, 2.8G is larger than that in  $n-H_2$  (1.1G) and  $o-D_2$ (1.3G). Taking into account that the deuteron magnetic moment is about 3.5 times smaller than that of T, one may expect a nearly 2 times larger matrix width in pure HT than in HD and some fraction of that in our samples.

For the measurement of the absolute density of atoms in thin solid films we used the known dependence of the ESR line width and shift on density. This dependence was verified during several experimental runs with respect to the calorimetric method of measurement of the absolute number of hydrogen atoms.<sup>2</sup> The



**Fig. 2** Fitting of experimental data by rate equation 6. The constant accumulation rate, k, was varied for better fitting. See the table for fitting parameters.

Curve	$k (\text{cm}^{-3}\text{s}^{-1})$	$k^{ex}/[H_2](cm^3s^{-1})$	$k^r$ (cm <sup>3</sup> s <sup>-1</sup> )
blue	$3 \times 10^{14}$	$3.4 \times 10^{-26}$	$1.1 \times 10^{-24}$
red	$5 \times 10^{14}$	$2.2 \times 10^{-26}$	$8.8 \times 10^{-25}$
magenta	$7 \times 10^{14}$	$1.0 \times 10^{-26}$	$6.4 \times 10^{-25}$

Table 1 Parameters used to fit the experimental data presented in Fig.2

calorimetric method is based on the measurement of the energy released in ESR induced recombination of the atoms of the H gas along with the reduction of their ESR signal. This method agreed to within 20% accuracy with calibrations based on the linewidth and shift measurements, and we consider 20% as an upper limit estimate of the error in absolute density determination in this work.

### 5 Estimate of the rate of reaction $T+H_2 \rightarrow TH+H$

In this appendix we provide supplementary information on calculating the rate constant of reaction  $T+H_2 \rightarrow HT+H$  (1). The experimental data of the [H] concentration growth presented in Fig.8 of the main article was plotted in coordinates d[H]/d[t]([H]) and the experimental points were averaged and fitted by the parabolic functions,  $f(x) = k + k^{ex}x - k^{r}x^{2}$ , which follow eq.6 of the main article (Fig.2). Here  $x \equiv [H], [T], k$  is the time independent rate of molecular dissociation by  $\beta$ -particles,  $k^{ex}$  is the pseudo-first order rate of exchange reaction (1),  $k^{r}$  is the temperature dependent recombination rate which includes different recombination channels,  $H+H\rightarrow H_2$  and  $H+T\rightarrow HT$ .

The experimental points were fitted by 3 different parabolic functions where *k* was adjusted as a parameter. We constrained *k* between  $3 \times 10^{14}$  cm<sup>-3</sup>s<sup>-1</sup> and  $7 \times 10^{14}$  cm<sup>-3</sup>s<sup>-1</sup>. These limits were estimated from the comparison with the constant accumulation rate measured in sample 3 and assuming a possible difference in the HT content. The lower limit comes from the assumption that sample 4 contains about 4% of H<sub>2</sub> and 14% of HT (see Table 1 in the main article). The parameters used in fitting presented in figure are also collected in Table 1.

#### References

- 1 P. Souers, *Hydrogen Properties for Fusion Energy*, University of California Press, 1986, p. 112.
- 2 J. Ahokas, O. Vainio, S. Novotny, J. Järvinen, V. V. Khmelenko, D. M. Lee and S. Vasiliev, *Phys. Rev. B*, 2010, **81**, 104516.
- 3 N. Bloembergen and R. V. Pound, Phys. Rev., 1954, 95, 8.
- 4 J. R. Gaines, R. T. Tsugawa and P. C. Souers, *Phys. Rev. Lett.*, 1979, **42**, 1717.