

ESR investigation of hydrogen and deuterium atoms in impurity-helium solids

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Impurity–helium solids (Im–He solids) are porous solids created by injecting a beam of mixed helium and impurity gases into superfluid ^4He . In this work we use electron spin resonance (ESR) techniques to investigate Im–He solids containing atoms and molecules of hydrogen and/or deuterium. We have performed studies of low temperature ($T \sim 1.35$ K) tunnelling chemical reactions in which deuterium atoms replace the hydrogen atoms bound in H_2 or HD molecules to produce large (up to $7.5 \cdot 10^{17} \text{cm}^{-3}$) and relatively stable concentrations of free hydrogen atoms. The time dependence of H and D atom concentrations has been investigated for Im–He samples with different initial ratios of hydrogen and deuterium ranging from 1:20 to 1:1. The satellite ESR lines associated with the dipolar coupling of electron spins of H and D atoms to the nuclear moments of the hydrogen nuclei found in neighboring molecules have been observed in Im–He solids. The forbidden hyperfine transition of atomic hydrogen involving the mutual spin flips of electrons and protons has also been observed.

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1. Introduction

Investigations of hydrogen and deuterium atoms, stabilized in solid matrices at low temperatures, have attracted the attention of scientists for many years. Possible quantum effects associated with these systems are of special interest. Quantum behavior is expected when the thermal de Broglie wavelength of the atoms becomes comparable with their interparticle spacing. For the case of H atoms in the gas phase, this condition is satisfied for a concentration of $2.6 \cdot 10^{18} \text{cm}^{-3}$ at a temperature of 30 mK [1]. For the case of a solid phase, the temperature for the onset of any quantum effect may be lower because of the possibility of a larger effective mass. It is always desirable for investigations of quantum behavior to generate the highest possible concentrations of H or D atoms in solid matrices. Unfortunately, from the earliest investigations of H atoms in solid H_2 , it became clear that some tunnelling processes and molecular recombination could lead to a decrease in the concentration of stabilized H atoms [2]. The detailed investigations of the processes of quantum diffusion and tunnelling reactions of H atoms in solid H_2 at $T = 1.35\text{--}4.2$ K were

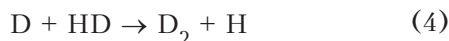
performed by Ivliev et al. [3] and later by Miyazaki et al. [4–6]. They established that the decay of H atoms could take place in solid H_2 by tunnelling migration, in which H atoms tunnel through a chain of H_2 molecules according to the reaction



thereby travelling through the solid H_2 to recombine with another H atom. The reaction rate constant k_1 , for reaction (1) was found to be $k_1 = 18 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ at $T = 4.2$ K [4]. This value remains the same even when the temperature is lowered to 1.9 K, confirming that tunnelling reactions are involved. The behavior of D atoms in solid D_2 is different. The rate constant for the reaction



is four orders of magnitude lower; $k_2 = 1.8 \cdot 10^{-3} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ [7] leading to a much lower recombination rate. Therefore it is possible to create a larger concentration of D atoms in solid D_2 as compared with concentrations of H atoms in solid H_2 [7–9]. The exchange tunnelling reactions



lead to the possibility of creating high concentrations of H atoms in solid mixtures of H_2 and D_2 at low temperatures [8,10,11]. When an H atom is surrounded by shell of D_2 molecules, it becomes very stable because it can neither migrate through the solid D_2 nor react further with D_2 by the reaction



at low temperatures, since it is an endothermic reaction. Gordon et al. [8,12] suggested that high concentrations of H atoms could be stabilized at low temperatures by means of reactions (3) and (4). In their approach, a gas mixture of hydrogen, deuterium and helium gas was transported through a radio frequency discharge onto the surface of superfluid He contained in a small beaker, at a temperature 1.5 K. The jet of impurity and helium gases penetrates the surface of the superfluid He, and then forms a snow-like solid which settles to the bottom of the collection beaker. This solid became known as an Im-He solid [13,14]. In the case of heavy impurities, Im-He solids are built from a loosely connected aggregation of nanoclusters of impurities each surrounded by one or two layers of solid helium. These aggregates form extremely porous solids into which liquid helium easily and completely penetrates. This system, having the high thermal conductance and the high thermal capacitance of superfluid helium, allows preparation and storage of very high concentrations of stabilized atoms. To this date the structures of Im-He solids for light impurities such as hydrogen and deuterium atoms and molecules are not fully determined. Our preliminary x-ray investigations of D_2 -He samples showed the presence of nanoclusters of D_2 in these solids [15]. Therefore it is reasonable to assume that the structure of Im-He solids formed from light impurities is similar to that of Im-He solids formed from heavy impurities (Ne, N_2 , Kr) [16,17]. In this work we have studied impurity-helium solids formed by light impurities, namely hydrogen and deuterium atoms and molecules. The method of electron spin resonance (ESR) was used for detailed studies of H and D atoms stabilized in Im-He solids. We have performed studies of the exchange tunnelling chemical reactions (3) and (4) to produce large (up to $7.5 \cdot 10^{17} \text{ cm}^{-3}$) and relatively stable concentrations of H atoms. The kinetics of these reactions have been investigated for Im-He samples formed by introducing gas mixtures with different initial ratios of H_2 to D_2 , ranging from 1:20 to 1:1, into He II. We determined the exact positions of the H and D lines by using precise measurements of the magnetic field. Satellite ESR lines associated with the dipolar

coupling of the electron spins of H and D atoms to the nuclear moments of hydrogen nuclei in neighboring molecules have been observed. This observation allows us to determine the distances between stabilized H or D atoms and neighboring HD or H_2 molecules in Im-He solids [18]. From the analysis of line widths and the saturation behavior of H and D signals, we estimate the spin-spin relaxation time T_2 and the spin-lattice relaxation time T_1 of H and D atoms in Im-He solids.

2. Experimental method

The experiments were performed in a Janis cryostat with a variable temperature insert (VTI). The lower part of the cryostat was installed between the pole pieces of a Varian electromagnet for these ESR investigations. The home-made insert for the creation and investigation of Im-He solids with stabilized atoms shown in Fig. 1 was placed into the VTI. The details of the experimental procedure were described in our previous work [17,19]. For sample preparation, a gas mixture of H_2 , D_2 , and He was transported from a room temperature gas handling system to the cryogenic region. To provide H and D atoms, high power radio frequency was applied to the electrodes around the quartz capillary carrying the mixed gases. The jet ($dN/dt \sim 5 \cdot 10^{19} \text{ s}^{-1}$) of impurity atoms and molecules as well as helium gas emerged from a small (0.75 mm) orifice and then penetrated the surface of superfluid helium in the collection beaker. The temperature during sample preparation was 1.5 K. The liquid helium level in the beaker was maintained by a fountain pump connected to the main helium bath of the VTI. At the top of the beaker was a funnel that caught the sample as it emerged from the quartz capillary. A set of teflon blades was employed to scrape the sample from the funnel while the beaker was rotated so that the sample could fall to the bottom of the cylindrical part of the beaker. During a period of 10 minutes an impurity-helium solid sample with volume 0.35 cm^3 was formed in the beaker. Following this process, the beaker with the sample was lowered into the ESR cavity, which was situated near the bottom of the VTI in the homogeneous field region of the electromagnet. We used a cylindrical cavity operating in a TE_{011} mode. A ruby crystal was attached to the bottom of the cavity. The ruby was used as a secondary standard for the calibration of the measurements of the number of stabilized H and D atoms in Im-He solids. The calibration of the absolute value of number of atoms was made by using a DPPH sample with a known number ($2.4 \cdot 10^{17}$) of spins with measurements being carried out at $T = 1.35 \text{ K}$. Special measurements were made to determine the dependence of the signal of the small calibration sample of DPPH on the position along the axis of the cavity. This

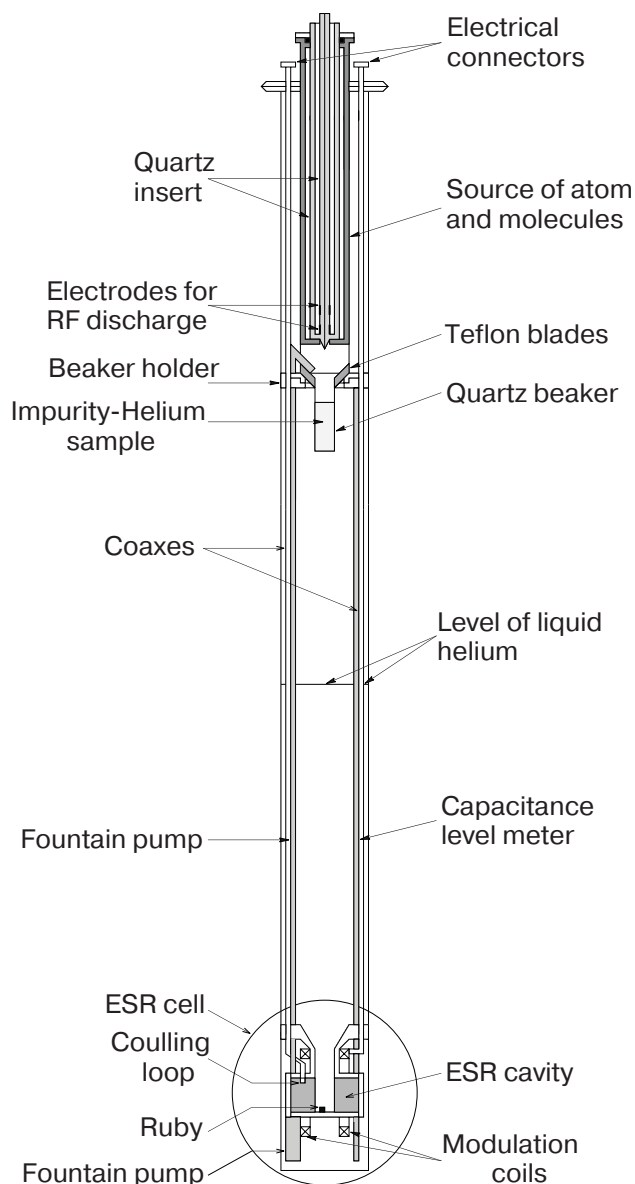


Fig. 1. Low temperature insert for Im-He sample preparation and ESR investigations. The quartz beaker is lowered into the ESR 9.12 GHz TE_{011} resonant cavity for measurements after sample preparation.

dependence is consistent with the calculated distribution of the microwave magnetic field in the cavity. ESR signals were measured using a CW reflection homodyne spectrometer ($f_r = 9.12$ GHz, $f_{\text{mod}} = 100$ kHz). All measurements have been done for Im-He samples at temperatures of 1.35 K and 1.8 K. A calibrated Ge thermometer was used for temperature measurements. Continuously pumping the VTI while supplying liquid helium from the main bath allows us to conduct long term investigations of the Im-He samples. In this paper we present reaction kinetics studies of H and D atoms which continued for ~ 8 hours at $T = 1.35$ K.

3. Results

Figure 2 shows the ESR derivative spectra of H and D atoms in Im-He solids prepared from an initial gas mixture in the ratio of $\text{H}_2:\text{D}_2:\text{He} = 1:4:100$. The positions of observed lines are shown in Table.

Table

Observed positions of ESR lines for H and D atoms in Im-He solids at $T = 1.8$ K and a frequency 9.12 GHz

Line	Transition (F, m_F)	Field, G
H_1	$(1,1) \leftrightarrow (0,0)$	2976.3
H_2	$(1,0) \leftrightarrow (1,-1)$	3484.7
H_f	$(1,0) \leftrightarrow (0,0)$	3205.7
D_1	$(3/2, 3/2) \leftrightarrow (1/2, 1/2)$	3171.7
D_2	$(3/2, 1/2) \leftrightarrow (1/2, -1/2)$	3247.4
D_3	$(3/2, -1/2) \leftrightarrow (3/2, -3/2)$	3326.9

The allowed H and D lines are each accompanied by two satellite lines. The intensity of the small forbidden hydrogen line H_f is about 200 times smaller than that of the allowed hydrogen lines. Figure 3 shows the microwave power saturation behavior of H and D atoms in Im-He solids. Unlike the behavior of H atoms produced by radiolysis in solid H_2 [11], H atoms in Im-He solids saturate at a larger microwave power ~ 16 μW . ESR signals were normally measured at a microwave power ~ 5 μW , significantly below the saturation limit.

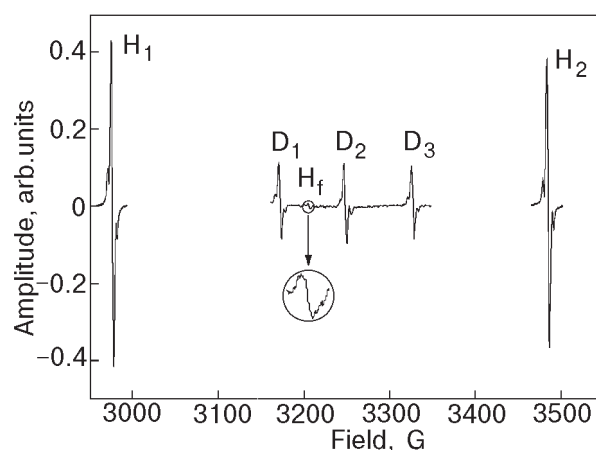


Fig. 2. ESR spectra of H and D atoms for an Im-He solid prepared from the gaseous mixture $\text{H}_2:\text{D}_2:\text{He} = 1:4:100$. Spectra observed at $T = 1.8$ K, 182 min after sample collection. The width of each of the main hydrogen and deuterium lines is 3 G. Seven fold magnification of the forbidden line is shown in the inset.

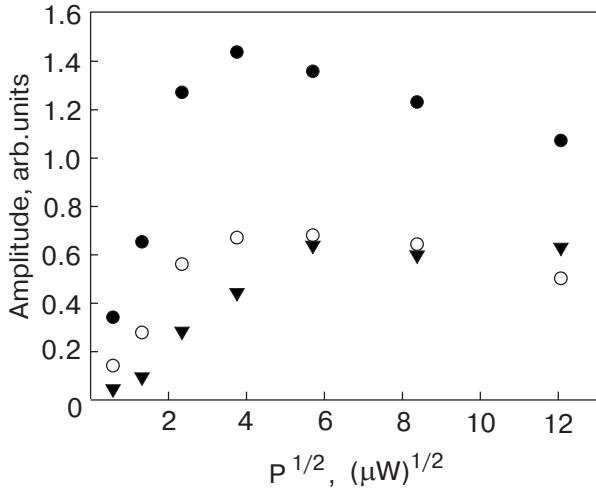


Fig. 3. Microwave power saturation behavior for different ESR lines of H and D atoms in Im-He solid at $T = 1.35$ K (see Fig. 2): H_1 (●), D_1 (○), H_f (▼). Im-He solid was formed by initial gas mixture $H_2:D_2:He = 1:4:100$.

The spin-spin relaxation time T_2 is calculated from the line-width below saturation by means of the expression [20]:

$$T_2 = \frac{2}{3^{1/2}\gamma\Delta H_{pp}} \quad (6)$$

where γ is the gyromagnetic ratio, and ΔH_{pp} is the line width obtained from the peak to peak separation for the derivative of the ESR signal. The line width of ESR lines for H and D atoms was found to be 3 G (see Fig. 2), leading to a value of $T_2 = 2.2 \cdot 10^{-8}$ s for H and D atoms in our Im-He solids. The observed line width is far larger than the inhomogeneous broadening expected from our magnet (~ 0.1 G). We used a saturation method for determination of the spin-lattice relaxation time T_1 for H and D atoms in Im-He solids. For estimating T_1 , we determined the dependence of the signal amplitude on the square root of microwave power as plotted in Fig. 3 for hydrogen and deuterium atoms. Values of T_1 were determined by means of an expression for the maximum values of the peak amplitude of the derivative signal [20]:

$$T_1 = \frac{1.98 \cdot 10^{-7} \Delta H_{pp}}{gH_1^2} \quad (7)$$

where g is the spectroscopic splitting factor. For H and D atoms $g \simeq 2$. We performed calculations of the microwave magnetic field according to the equation [20]:

$$H_1^2 = 2 \cdot 10^{-3} P Q \eta \frac{V_c}{V_s} \quad (8)$$

where P is the microwave power; Q is the quality factor; η is the filling factor; V_c is the cavity volume, and

V_s is the sample volume. When we substitute the geometric parameters for our cavity, expression (8) becomes $H_1^2 = 8P$. From the plot in Fig. 3 we obtained the value of the power $P_{\max} = 16 \mu\text{W}$ for which the amplitude of the derivative of the ESR signal of the H atoms has a maximum value. From the expression (7) we then find a value of $T_1 = (2.3 \pm 0.5) \cdot 10^{-3}$ s for H atoms in Im-He solids. For D atoms ($P_{\max} = 25 \mu\text{W}$, see also Fig. 3) we find a value $T_1 = (1.5 \pm 0.5) \cdot 10^{-3}$ s. The relatively small values of T_1 for D and H atoms in Im-He solids show that the atoms are stabilized in solid clusters of mixtures HD and D_2 molecules, rather than being isolated in liquid and solid helium. In latter case, the T_1 values should be much larger [21].

We also investigated the evolution of Im-He solids containing H and D atoms as well as H_2 , HD, and D_2 molecules in an attempt to maximize the H atom concentration. The investigations were performed for a variety of initial gas mixtures of H_2 , D_2 , and He. The initial $H_2:D_2$ ratio was varied from 1:20 to 1:1. The ratio of the concentration of the impurity gases to the He gas in the mixtures was always equal to 1:20. The yields of H and D atoms leaving the radio frequency discharge were proportional to the concentrations of H_2 and D_2 in the initial gas mixture [12]. Figure 4 shows the time evolution of the H and D concentrations in Im-He solids formed by two different initial mixtures. Immediately after preparation of all the Im-He samples, a large enhancement of the concentration of H atoms relative to D atoms was observed compared with the ratio of H_2 to D_2 in the initial gas mixture. This fact indicates that at the earliest stages of sample preparation at $T = 1.5$ K, a fast exchange tunnelling reaction leads to a large reduction in the number of D atoms and a corresponding increase in the number of H atoms. According to the calculation by Takayanagi et al. [22] the rate constant for reaction (3) is found to be $5.4 \cdot 10^{-2} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$, so that the enhancements of the H atom concentrations are attributed to this reaction with a time constant on the order of a few minutes for our samples. Later on, a steady increase of the ratio H:D takes place over a period of hours, during the storage of our Im-He sample at $T = 1.35$ K. The kinetics of the changing concentrations of H and D atoms for the sample prepared from the initial gas mixture $H_2:D_2:He = 1:20:420$ is similar to that observed by Lukashevich et al. [10] and Miyazaki et al. [11] for atoms trapped in solid H_2 - D_2 mixtures. The concentration of H atoms grows, but the concentration of D atoms is decaying, just as in our Im-He studies. At this stage we believe that the behavior of atoms in our solid is governed by reaction (4) with rate constant $1.9 \cdot 10^{-3} \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$ [22] which further reduces the number of D atoms and in-

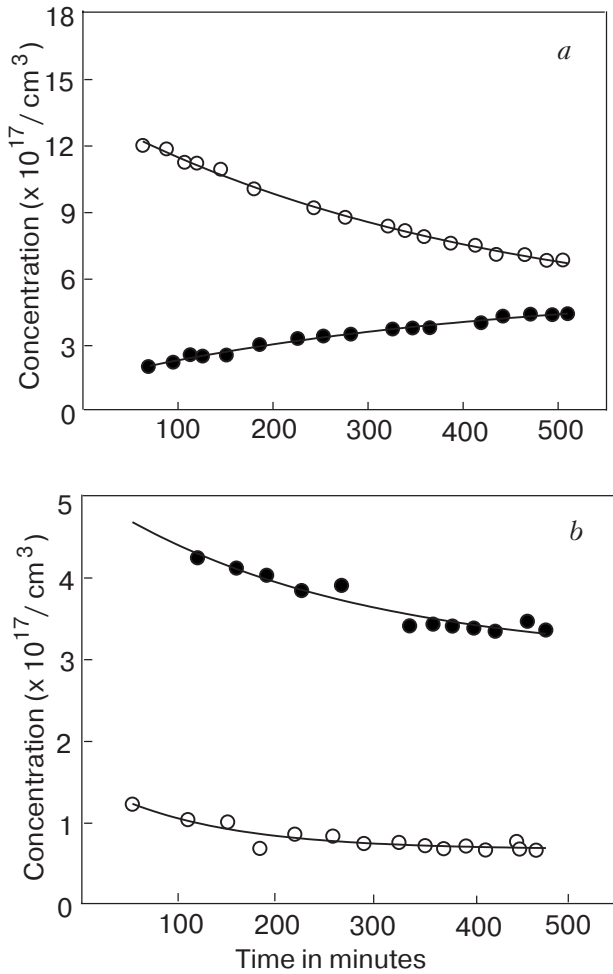
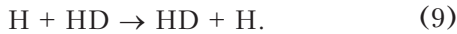


Fig. 4. Time dependence of the concentration of H atoms (●) and D atoms (○) in Im-He solids at temperature $T = 1.35$ K prepared from different initial mixtures: $H_2:D_2:He = 1:20:420$ (a); $H_2:D_2:He = 1:2:60$ (b).

creates the number of H atoms. Figure 4,a shows that the increase in the number of H atoms is smaller than the decrease in the number of D atoms. This observation could be explained by recombination of H atoms. In this process, the hydrogen atoms migrate through the solid via reaction (1) or the reaction



A succession of these reactions allows the transport of H atoms to neighboring positions in the Im-He solid where they recombine to form H_2 or HD molecules via the reactions:



This mechanism is supported by the results of investigations of Im-He samples prepared from the gas mixture $H_2:D_2:He = 1:2:60$ (see Fig. 4,b). In this sample the concentration of H_2 and HD molecules is about

one order of magnitude larger compared with the former sample, so therefore reactions (1) and (9) should accelerate the recombination processes (10) and (11). It can be seen that the decay of D atoms is more rapid and the H atom population also decays steadily throughout the experiment. The exchange tunnelling reactions can be used to produce very large concentrations of atomic hydrogen in our samples. As discussed earlier, these large concentrations could allow us to enter the regime where the thermal de Broglie wavelength becomes comparable to the spacing between H atoms, provided that the temperature is low enough. In our experiments we have investigated samples obtained from a variety of initial gas mixtures to determine the one which yields the highest hydrogen atom concentration. The experimental plots shown in Fig. 5 correspond to the H and D atom average concentrations after a storage time ~ 500 minutes following initial sample preparation. For the optimal gas mixture $H_2:D_2:He = 1:4:100$, the largest H atom concentration $(7.5 \pm 3.0) \cdot 10^{17} \text{ cm}^{-3}$ was obtained. We are planning investigations with even longer storage times of this optimal sample to obtain the largest possible concentration of H atoms due to exchange tunnelling reactions.

4. Conclusion

The observation of satellite lines and the relatively short longitudinal relaxation times T_1 for H and D atoms in impurity-helium solids show that the H and D atoms are stabilized in clusters of solid mixtures of H_2 , D_2 , and HD. We did not observe any signatures of

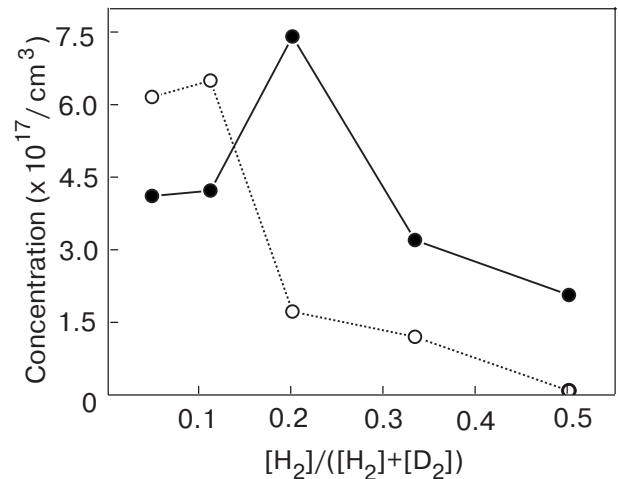


Fig. 5. The dependence of the average concentrations of H atoms (●) and D atoms (○) in Im-He solids on the fraction of hydrogen gas in the make up gas mixture, $[H_2]/([H_2]+[D_2])$. For each point the concentrations were determined after a waiting period of 500 minutes following sample collection.

single atoms perfectly isolated by helium. Observation of these isolated atoms requires the application of much lower microwave power levels to avoid saturation. Our spectrometer was not capable of providing such low powers.

The time dependence of the populations of H and D atoms in the Im-He solids at $T = 1.35$ K proves the occurrence of the exchange tunnelling reaction $D + HD \rightarrow H + D_2$. The exchange tunnelling reactions are capable of producing very high concentrations of hydrogen atoms. Our estimations from ESR line intensity measurements indicate that the largest concentration we have obtained is $(7.5 \pm 3.0) \cdot 10^{17} \text{ cm}^{-3}$. For this concentration the onset of quantum overlap phenomena may be found at $T \sim 13$ mK which can be reached by means of a dilution refrigerator.

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