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G. W. Collins, F. Magnotta,
E. R. Mapoles, and H. E. Lorenzana

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Trapped Electrons in Solid Hydrogen

G. W. Collins, F. Magnotta, E. R. Mapoles, H. E. Lorenzana

Lawrence Livermore National Laboratory

Livermore, Ca 94550

The discovery of trapped ions in tritiated solid hydrogen was made by P. C. Souers et. al. through the observation of stark shifted lines in the collision induced infrared absorption spectra of solid hydrogen¹. One line was found 100 cm^{-1} below the $Q_1(1,0)$ line, and was assigned to a Stark shifted $Q_1(1,0)$ transition for molecules near a positive ion. Another line was found $\sim 25\text{ cm}^{-1}$ below $Q_1(1,0)$ and was assigned to a Stark shifted $Q_1(1,0)$ transition for molecules near a negative ion. Thus the positive ion which tends to contract the neighboring molecules gives rise to a larger stark shift than negative ions which push away neighboring molecules due to the fermi interaction. There have also been weak absorptions found between these two stark shifted transitions that have been assigned to next nearest neighbors of the positive ion². From timing experiments Brooks et. al. determined that there were two types of positive charges and negative charges. The most mobile was the negatively charged polaron, then a D_3^+ "small polaron hole", while a D_9^+ and an electron bubble were determined to be immobile over the period of hours³. After the discovery of these stark shifted lines, two broad absorptions, not related to the collision induced hydrogen spectra, were observed in tritiated solid hydrogen and in proton irradiated solid hydrogen^{4,5,6,7}. In analogy with F-centers in Alkali Halides and from the time resolved data, it was postulated that these two absorptions were due to transitions of an electron bubble. From a simple spherical square well model, the electron bubble radius was determined to be 5.38 \AA , with a well depth of 3.81 eV , and it was estimated by Poll et. al. that an electron in the first excited state would

dilate the lattice an additional 15%. The IR absorption band was assigned to the 1S to 1P transition and the UV absorption was assigned to the 1S to continuum transition. There appeared to be an isotope shift in both the IR and UV transitions, and the UV band was broader in H₂ than in D₂ both doped with tritium, implying a broader conduction band in irradiated H₂. This result is similar to the work of Gedanken et al.⁸ who studied trapped excitations in solid H₂ and D₂.

We then discovered an emission at 800 nm⁹ in solid D-T that appeared to have the same temperature dependence as the hydrogen atoms in D-T as measured by electron spin resonance (ESR). This emission was confirmed by a group at the University of Guelph and the Riso Laboratory¹⁰. No assignment has been given to this emission, and correlation with previous absorption features seemed dubious since the timing data for this emission was very different than the timing data for the stark shifted collision induced lines and the UV line. Finally, unlike the UV and IR "bubble" absorptions, there appears to be no isotope shift in the 800 nm emission.

We report here a relatively large increase in emission of the integrated 800 nm line when pumping the UV absorption and a much smaller increase (by a factor of ~15) upon pumping the IR absorption band in solid D-T at 4.6 K. These data show the 800 nm emission is most likely the result of an electron bubble transition. We also present ESR data for electrons in D₂ and H₂ doped with 2% T₂ and pure T₂. We find there are two components to this absorption, a narrow line component which we attribute to trapped electrons and a broad line component which we attribute to delocalized electrons. The narrow ESR linewidth in the H₂ and D₂ samples are commensurate with the idea of electrons localized in vacancy seeded traps. In solid T₂ the broad line dominates, implying that most electrons are delocalized due to the large concentration of electrons and other impurities. We find that the temperature

and time dependence of the electron concentration from the 800 nm line is similar to the unpaired atoms as measured previously with ESR¹¹.

Figure 1 shows the integrated emission intensity from 740 to 860 nm as a function of the wavelength of light incident onto solid D-T at 6K. Also plotted in Fig. 1a is the UV absorption data of solid D-T at 5 K of Fearon et. al.⁶ and in Fig. 1b is the 8 K T₂ IR absorption data of Richardson et. al.⁴ The relative absorbance strength of the UV line to the IR line in solid DT is not known and the absolute frequency and shape of the IR line is also unknown. The shape of the UV enhancement follows closely the published UV absorption spectrum for solid D-T presumed to be due to the 1S to continuum transition of the electron bubble. The enhancement with IR pumping suggests that the response is related to the IR absorption band, presumed to be due to the 1S to 1P transition of the electron bubble, but due to the lack of data in the region around the emission itself (i.e. from 0.8 μm to 1.2 μm), the case is not as convincing as that for the UV response. Fig. 1a and 1b show that the 800 nm emission, the UV absorption and the IR absorption are related. Using a simple square well model with the previously published parameters (radius = 5.38A, depth = 3.81eV) it can be shown that there are 4 bound states, the 1S, 1P, 1D, and 2S states 3.0 eV, 2.2 eV, 1.2 eV, and .8 eV below the conduction band edge respectively. Obviously any excited state will severely increase the size of the well, but this simple example shows there are other bound states to the proposed bubble and one candidate for the emission is due to the 2S to 1P decay during bubble formation. Fig. 1a also shows an additional feature at about 425 nm not observed in the UV absorption spectra. This is close to the 1p->cont transition. Finally, we note that between 440 nm and the onset of the 800 nm emission there are no additional features.

The absorption shown in Fig 1b is that for solid T₂.⁴ Based on the line shifts for H₂ and D₂ doped with small amounts of T₂, it is estimated that the IR absorption

of DT should be close to that of T₂. It should be noted that the "steady state" time response of the enhancement is also somewhat different for UV vs IR enhanced emission. For both UV and IR pumping, the emission increases rapidly on a time scale of ~ 20 μs, however, the UV enhanced signal overshoots a steady state value by perhaps 5-10% whereas the IR enhanced signal overshoots by 50 to 75 % both having a settling time of ~25 seconds. We currently do not understand the nature of the overshoot but it is probably related to secondary heating of the sample. In figure 1b, we plot both the instantaneous and steady state enhanced signal for IR pumping while in figure 1a, we only plot the final steady state enhanced signal for UV pumping.

Figure 2 shows that the temperature dependence of the 800 nm emission in solid D-T is very similar to the atom density in solid D-T and T₂. This implies that whatever process limits the recombination of atoms, also limits the recombination of centers responsible for the 800 nm line; possibly electron bubbles. It has been shown that at temperatures above half the triple point, the activation energy calculated from the hydrogen atom recombination data in solid H₂¹² and D₂¹³, follows the vacancy diffusion model of Ebner and Sung¹⁴ developed to describe the diffusion of molecules¹⁵. Recently in solid para H₂, the diffusion coefficient of electrons in solid parahydrogen has been measured and appears to follow the same temperature dependence as the atoms and molecules¹⁶. Moreover, the diffusion of the electrons appears to follow the temperature dependence of Ebner and Sung's model to temperatures well below half of the triple point, where NMR measurements of molecular motion are difficult. Therefore, the agreement for the temperature dependence of the atoms and the 800 nm emission agrees with the inference that the 800 nm line is due to trapped electrons and the speculation that atoms and electrons have the same vacancy diffusion mechanism.

The ESR spectrum of the middle line of the D atom hyperfine triplet in solid $D_2+2\%T_2$ at 1.4 K is shown in Fig. 3 at several different times during the experiment. This lineshape is near $g=2$ and shows a doublet structure not seen in the other hyperfine lines. The left absorption of this double peak is due to the middle D atom and the right absorption is assigned to trapped electrons. From top to bottom, Fig. 3a shows the electron and middle D atom lineshape after 4 min, 30 min, 54min, and a few minutes after a heat spike. The lineshape in Fig. 3b shows the same spectrum after 500 minutes at 1.4 K when no heat spikes are observed. During a "heat spike" when the atoms recombine en masse as described previously¹⁷, the electron concentration also decreases. Moreover, when the sample is sitting in liquid helium, the effective heat capacity and thermal conductivity of the sample is increased and the time between heat spikes is increased. When no heat spikes occur during the timescale of hours the narrow electron line is completely lost under the middle D atom line. We find that the electron linewidth in H_2 or D_2 is roughly 30% smaller than the linewidth of hydrogen atoms in the same matrix. That is for $D_2+2\%T_2$ sitting at 1.4K for 1 hour there are about 110 ppm of D atoms, 32% J=1 concentration, and 25 ppm electrons, the linewidth for atoms is about $2.2 \pm .2$ Gauss and the linewidth of the electron is about $1.7 \pm .3$ Gauss. $H_2+2\%T_2$ sitting at 1.7 K for 32 hours has about 15 % J=1 concentration, and 135 ppm atom concentration the linewidth for the H atom is $0.9 \pm .2$ Gauss and the linewidth of the electron is slightly less, but our signals were too noisy to make an accurate measurement. The J=1 concentration was calculated from the J=1 to J=0 conversion time constants reported previously of 30 hours in $D_2 +2\%T_2$ and 22 hours for $H_2+2\%T_2$ both at about 1.4 K. From these linewidths and a theoretical model for the linewidth we can estimate a nearest neighbor distance. Two models are typically used for analyzing the linewidth. For interacting dipoles with no wave function overlap we use the formalism described by Kittel and Abrahms¹⁸, while when there

is significant overlap of the electron wave function with neighboring molecules we use the formalism developed by Kip, Kittel, Levy and Portis¹⁹ for analyzing F-centers. Hydrogen atoms are presumed to sit at vacancy like sites, producing a lattice dilation for the first shell of neighbors of about 6% in H₂ as calculated by Danilowitz and Eters. For D atoms in D₂ the lattice expansion will be reduced to roughly 4% due to the smaller zero point motion. From the ESR linewidths we can estimate the electron in D₂, located at a vacancy seeded site, has a lattice dilation of 8% larger than the atom, or about 12 %. This would give a bubble radius of about 0.4 nm.

Figures 4a and 4b show the ESR absorption's corresponding to electrons and the high field line of the T atoms in solid T₂ sitting at 6.3 K for 4 hours. The concentration of electrons here is roughly 50 ppm while the concentration of atoms is about 120 ppm. There is only a small signature of the narrow ESR "electron" line seen in H₂ and D₂, because of the large, broad absorption feature. This broad feature at $g \sim 2$ is much broader than the corresponding T atom lineshape. One possible explanation (mentioned above) for this broad line is that most of the electrons in solid T₂ are delocalized as compared to the localized electrons seen in H₂ and D₂ samples doped with only 2% T₂. There was also a broad underlying absorption component in the H₂+2%T₂ and D₂+2%T₂ samples but the signal to noise for this feature was very low. These data show that there are at least two different types of electrons in solid tritiated hydrogen, those localized in "bubbles" and those that are possibly delocalized.

We conclude with the following somewhat speculative picture. Solid Hydrogen containing tritium contains many neutral atoms, positive ions, and electrons. The concentration of electrons is typically about an order of magnitude lower than the concentration of atoms. The electrons, after being slowed well below the ionization threshold, form electron bubbles until the concentration of trapped electrons gets to several parts per million molecules. Afterwards, many of the

electrons cannot form a bubble defect due to the large degree of radiation damage, and these electrons remain in the conduction band of the solid until inialation with a positively charged impurity. The electron bubbles have many bound states for the electrons which give rise to an IR absorption, a UV absorption, and an emission at 800 nm. Finally, these electron bubbles move through the lattice with the same vacancy diffusion mechanism as the atoms and molecules.

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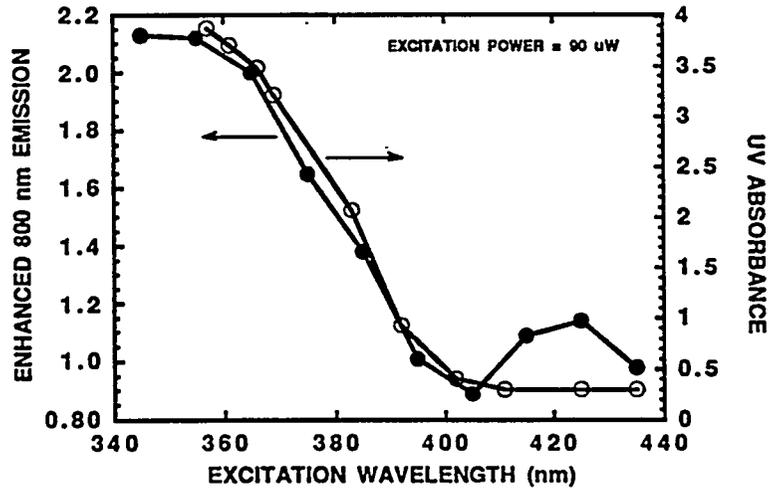


Fig. 1a

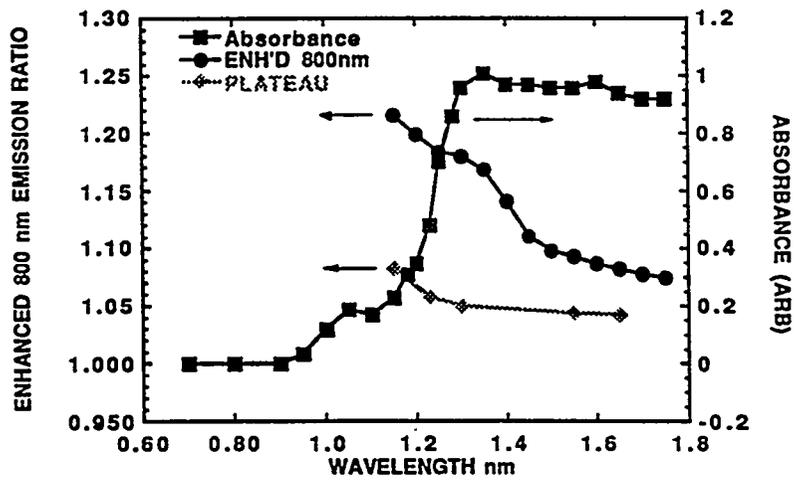


Fig 1b

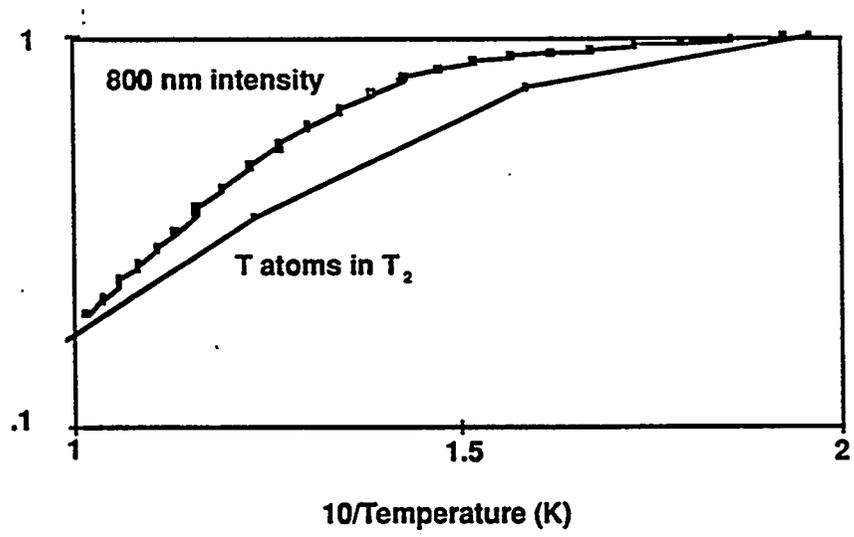


Fig. 2

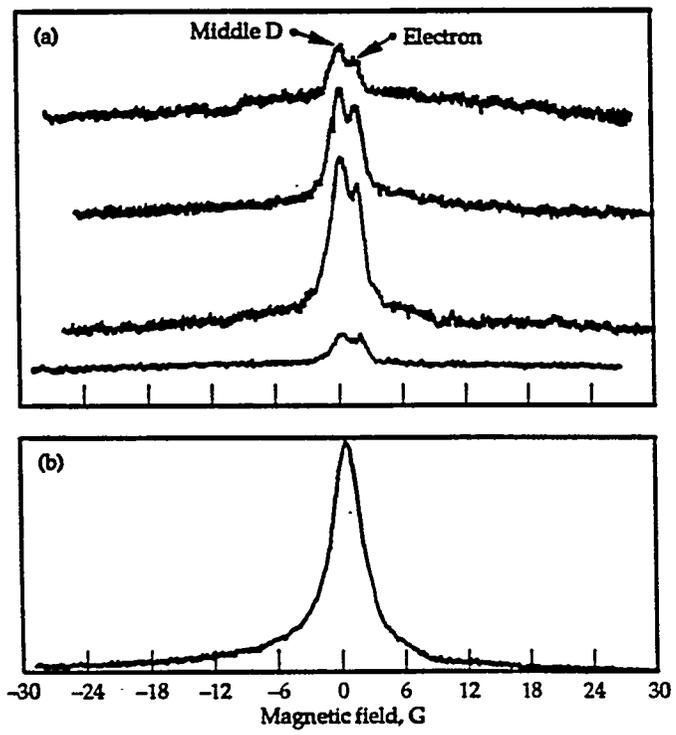


Fig. 3

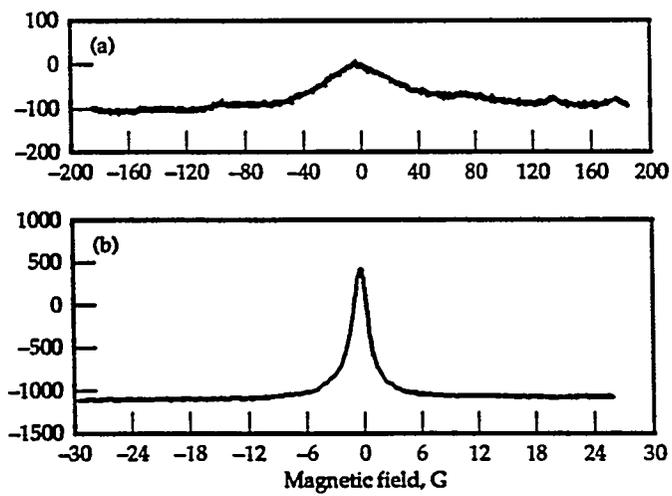


Fig. 4

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