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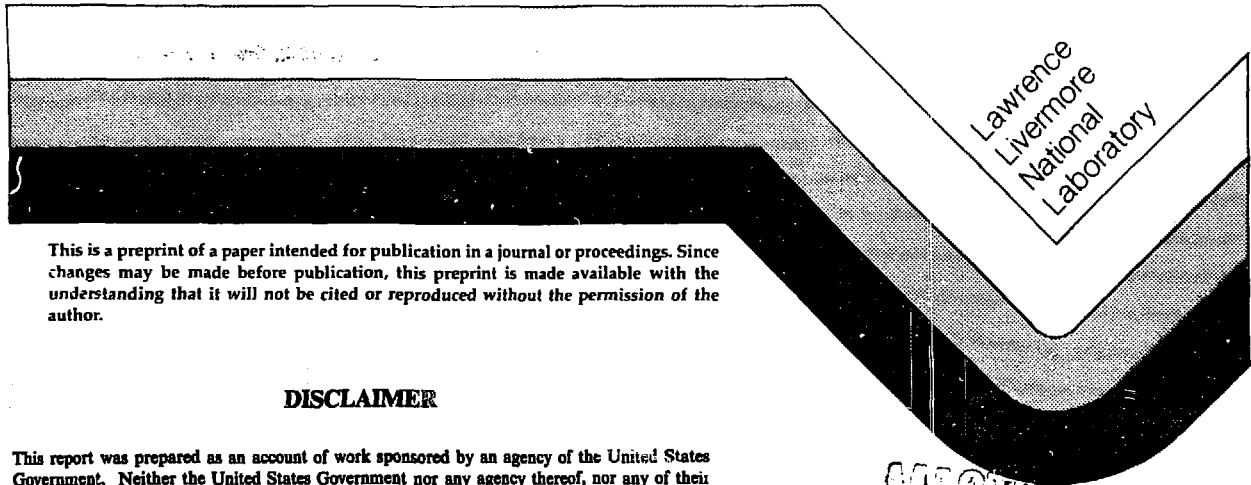
ULTRAVIOLET RADIATION-DAMAGE  
ABSORPTION PEAK IN SOLID DEUTERIUM-TRITIUM

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ABSTRACT

An ultraviolet absorption peak has been seen in solid deuterium-tritium and hydrogen-tritium at a sensor temperature of 5 K. The peak occurs at 3.6 eV and is about 1.5 eV wide. It bleaches out when the temperature is raised to about 10 K but reappears upon cooling and is, therefore, radiation induced. At 5 K, the peak forms on a time scale of minutes and appears to represent part-per-million levels of electron-mass defects. The suggested model is that of a trapped electron, where the peak is the ground state-to-the-conduction band transition. A marked isotope effect is seen between D-T and H-T.

INTRODUCTION

All irradiated solids show radiation defect absorption peaks and solid hydrogen is no exception. We previously found an infrared absorption peak in solid deuterium-tritium at a sensor temperature of 5 K.<sup>1</sup> The position of this peak relative to the collision-induced vibration-rotation band is shown in Fig. 1. Its peak is at about 0.7 eV and its half-width is about 0.4 eV.<sup>2</sup> If the sample is heated to 10 K, the peak is bleached out, but it reappears upon cooling. That this peak is caused by radiation damage was confirmed by proton bombardment by the Guelph/McMaster group.<sup>3,4</sup> The infrared absorption was quickly assigned to the  $1s \rightarrow 1p$  transition of a trapped

electron.<sup>1,2,5,\*</sup> This seemed an easy guess because the same type of peak is well known in liquid ammonia/metal solutions,<sup>6,8</sup> irradiated hydrocarbon glasses,<sup>9</sup> and F-centers in irradiated alkali halides.<sup>10</sup>

We here report the discovery of a second radiation-induced absorption peak in the near ultraviolet region. Just after our initial finding, the peak was confirmed in the proton irradiation experiment.<sup>11</sup>

EQUIPMENT AND PROCEDURE

The experimental system was the same as used previously, including the use of the 8 mm path absorption cell.<sup>12,13</sup> The temperatures reported here are those of the sensor mounted in the copper. We estimate that the internal temperatures might be 1 to 2 K higher.

The ultraviolet work was done by passing all of the source light through the 8 mm sample cell first; this light is provided by a 150 W xenon bulb operating at a temperature of 6000 K. The light is passed through a 99% neutral density filter and then into the sample cell. The light from the sample enters a 0.25 m monochromator with an 1180 grooves/mm grating, which is blazed for 300 nm and has a triangular band pass calculated to be 1.65 nm wide at half power.

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\* In a square potential well, the ground-to-first excited state is  $1s \rightarrow 1p$ . In an electrostatic well, i.e., inversely proportional to the distance, this transition is  $1s \rightarrow 2p$ . The actual well of a trapped electron lies between these models, but it is surprisingly close to the square well.

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<sup>a</sup> Consultants to Lawrence Livermore National Laboratory

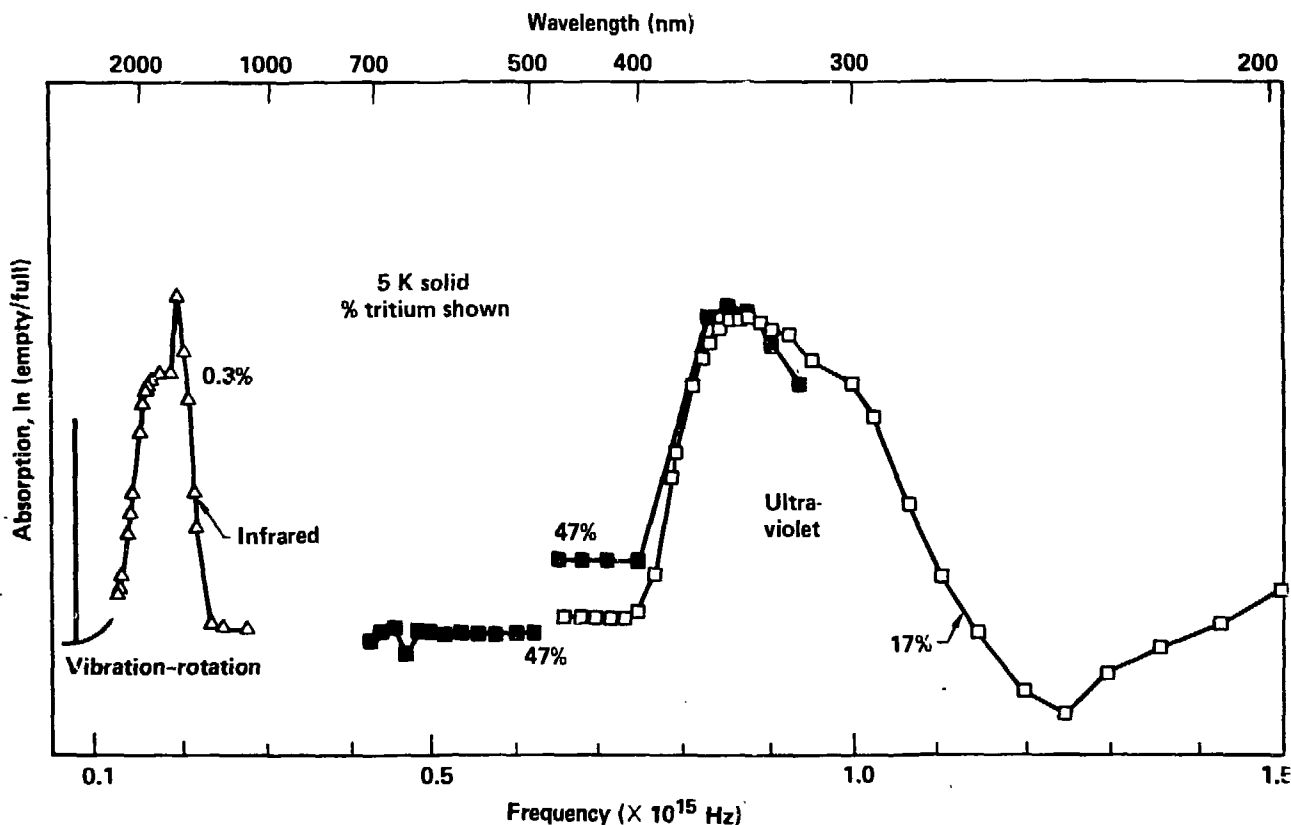
The photomultiplier tube was an EMI 9558 QB, Type S-20, operated at 295 K with an 810 V bias. The dark current of 0.06 to 0.1 nA is subtracted from the total reading. The photomultiplier is operated always at a current of 1  $\mu$ A or less to keep it linear, and this corresponds by rough calibration to about  $10^7$  photon/s entering the photomultiplier. We estimate that  $10^{12}$  to  $10^{13}$  photon/s of all frequencies pass through the sample. The ultraviolet band is roughly 1/3 the lamp's energy spectrum; the spectrum extends to the infrared line, which covers about 5%. The maximum absorbed light energy is about 5  $\mu$ W as compared with 3 mW from the radioactive decay.

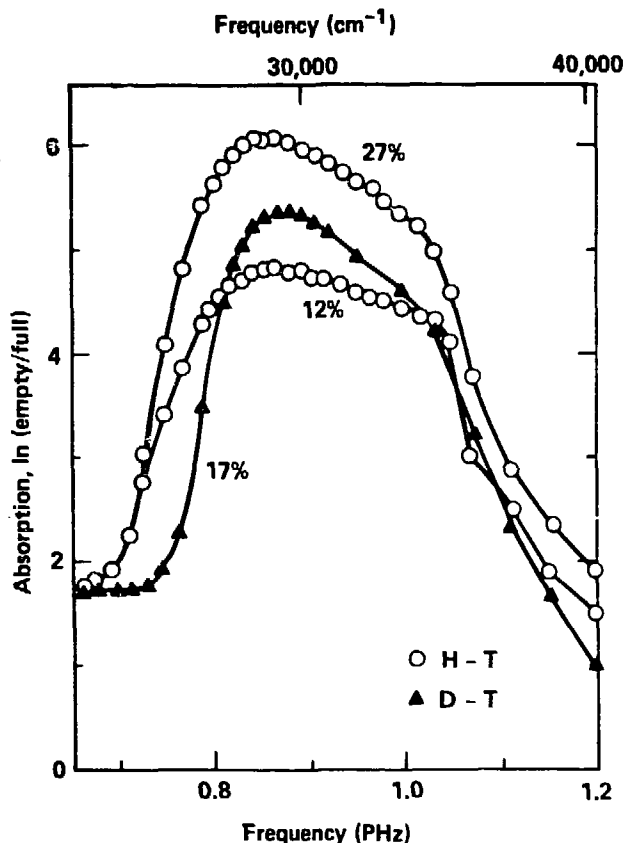
In order to extend our work into the visible range, we used a monochromator with an 1180 grooves/mm grating, blazed at 500 nm. The sweep speed for all runs is 19.8 nm/min.

We assume all samples to be equilibrated to the room temperature mix of hydrogens, i.e., with exchange equilibrium constants of 3.82 for D<sub>2</sub>-DT-T<sub>2</sub> and 2.58 for H<sub>2</sub>-HT-T<sub>2</sub>.<sup>14,15</sup> A 50-50 atomic mix is presumed, therefore, to be roughly 25-50-25 for the three components. Because we do not actually know this, we report atomic compositions.

## EXPERIMENTAL RESULTS

Figure 1 shows the ultraviolet absorption peak in relation to the vibration-rotation and infrared peaks. The new peak has its maximum at about 3.6 eV and its half-width is 1.5 eV. The dip at 1.25 PHz ( $10^{15}$  Hz) is almost certainly from an emission from the beta particle-bombarded sapphire window. No such effect was seen in the proton experiment, so that it is not an effect of the hydrogen. No absorption is seen in the visible region, although an unmeasured gap of 0.14 PHz remains. This region has been investigated in the proton-beam experiment and no absorption was seen.<sup>11</sup>





The ultraviolet absorption peak bleaches away when the sensor temperature is raised to 11 K, nor is it present in the liquid. Cooling the sample to 5 K causes the absorption peak to form again. The troublesome emission occurs at all temperatures.

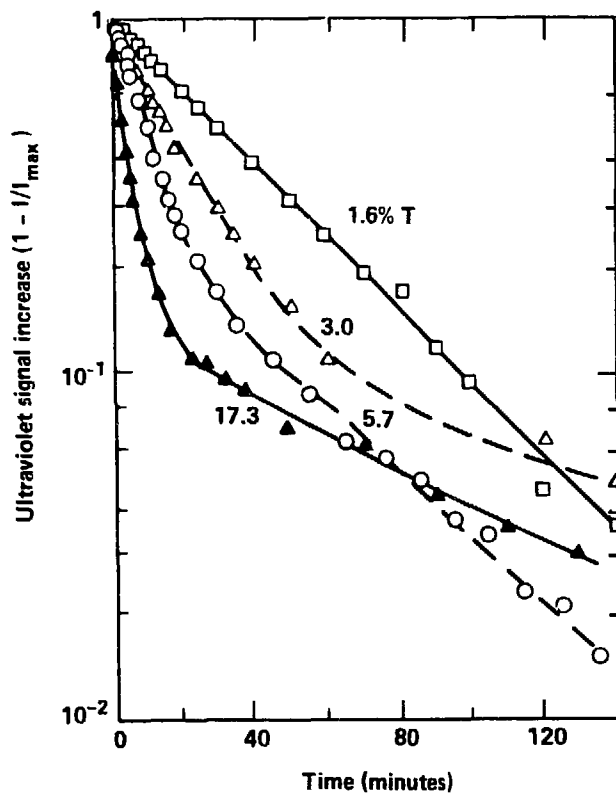
The same absorption is seen in both solid D-T and H-T, as shown in Fig. 2. The width of the H-T peak is slightly broader.

We also observed the ultraviolet peaks grow with time at the fixed frequency of 0.87 PHz (345 nm or 29 000  $\text{cm}^{-1}$ ). Some results for D-T at 5 K are shown in Fig. 3. The Y-axis is  $1 - I/I_{\text{max}}$ , where  $I$  is the signal intensity at time  $t$  and  $I_{\text{max}}$  is the final equilibrium value. The  $1/e$ -times are on the order of minutes and they are inversely proportional to the tritium concentration. Three of the curves are not single exponentials but appear to contain 20 to 30% of a one-hour-long component. Table 1 compares the measured  $1/e$ -times with those

for the infrared absorptions at 2593 nm, which are true exponentials. The time scales are comparable, and the infrared time constants are proportional to the  $-0.85$  power of the tritium concentration. These similarities suggest that the infrared and ultraviolet peaks may be related.

Spectral Region	% Tritium	$1/e$ -time (minutes)
Ultraviolet 345 nm	1.6	45
	3.0	20-25
	5.7	10
	17.3	4
Infrared 1593 nm	0.3	40
	2	9
	5	4
	10	2

Table 1. Time constants for the growth of the ultraviolet and infrared absorption peaks in solid D-T at a 5 K sensor temperature.



We next want to integrate the intensity  $(1/L)\ln(I_0/I)dv$  under the absorption peaks, where  $L$  is the path length and  $v$  the frequency. We first correct the ultraviolet peaks for the sapphire window emission, which creates a small tail to the high frequency side. We next put a baseline through the 0.7 PHz point. We may remove the effects of crystallite scattering by subtracting the base line in units of  $\ln(I_0/I)$ .

The integrated intensity data at equilibrium (2 hours and older) at a sensor temperature of 5 K is shown in Fig. 4. We may approximate the actual density of defects using the relation

$$\frac{1}{L} \int \ln(I_0/I) dv = \frac{e^2}{4\epsilon_0 mc} Nf \quad (1)$$

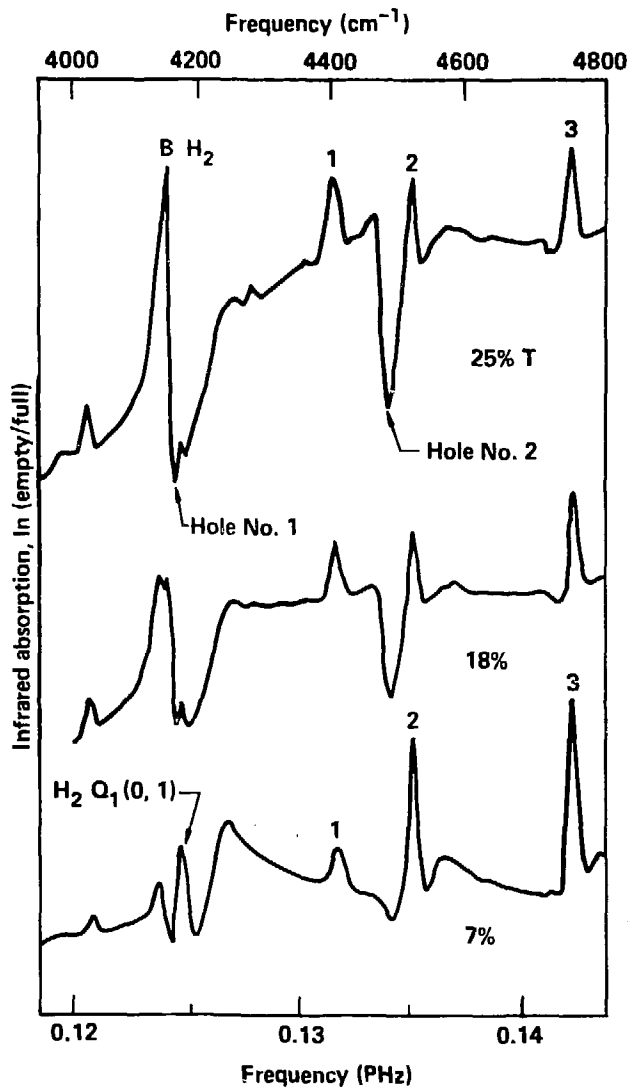
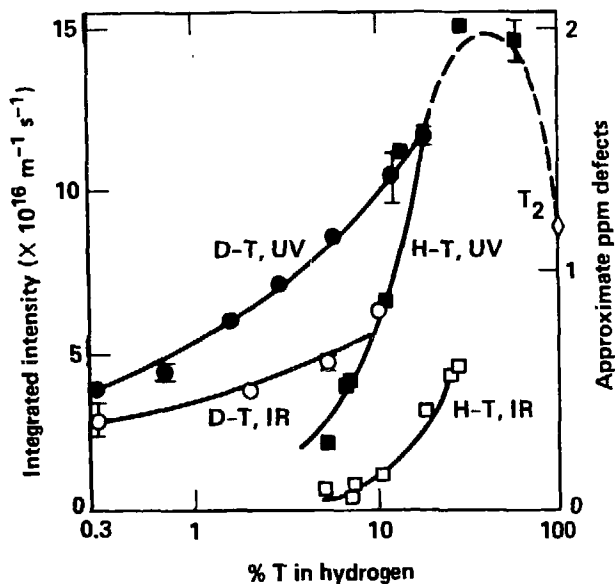
where  $e$  is the electronic charge ( $1.602 \times 10^{-19}$  C),  $\epsilon_0$  is an SI Metric constant ( $8.854 \times 10^{-12}$  C/V.m),  $m$  is the mass of the electron,  $c$  is the speed of light,  $N$  is the defect density (per  $m^3$ ) and  $f$  is the oscillator strength. If we use the actual electron mass and set  $f=1$  (which assumes no relation between the two absorption peaks), we find that defect densities are in the part-per-million range for both the ultraviolet and infrared species. We see, too, that the ultraviolet and infrared concentration curves appear similar for solid D-T and also for H-T, although the two hydrogens show a surprisingly different concentration

behavior. We believe that this is further evidence that the two kinds of absorption peaks may belong to the same defect.

The D-T curves in Fig. 4 show integrated intensities increasing as the 0.2 to 0.3 power of the tritium concentration. The H-T curves, however, appear to "turn on" at some critical concentration and then increase as the 1.1 to 1.6 power. The drop at high concentrations is likely caused by self-heating, which produces partial bleaching.

## DISCUSSION

We have been working toward the hypothesis that both the infrared and



ultraviolet absorption peaks belong to the trapped electron defect. Our assignment of the infrared line rests mainly on a comparison with other materials. But there is one other bit of evidence shown in Fig. 5. We here see a narrow portion of the infrared peak for solid H-T of various compositions. For H-T (but not D-T), the collision-induced vibration-rotation spectrum of one specie ( $H_2$ ) overlaps the infrared peak. Consider first the 7% T-sample, where the infrared peak is small. We see the usual collision-induced peaks, led off first by the  $Q_1(0,1)H_2$ . Peaks 1, 2 and 3 are the  $Q_1(0,1)H_2 + S_0(0)HT$ ,  $Q_1(0,1)H_2 + S_0(0)H_2$ , and the  $Q_1(0,1)H_2 + S_0(1)H_2$  peaks, respectively. The higher %-tritium spectra in Fig. 6 possess strong infrared peaks, and we see two "holes" at  $4151-4155\text{ cm}^{-1}$  and at  $4472-4476\text{ cm}^{-1}$ . These "holes" indicate an interaction between certain vibration-rotation peaks and the infrared spectrum. These holes were first found by the Guelph/McMaster group,<sup>16</sup> but we here show our measured result. The two holes come at the positions where the B and D lines are expected. These lines are satellites of the collision-induced vibration-rotation spectrum, and they appear only in the irradiated solid below 10 K. The B-line was considered to be the  $Q_1(0,1)$  line for

perturbed molecules adjacent to trapped electrons.<sup>13</sup> The D-line was assigned to the corresponding perturbed  $Q_1(0,1) + S_0(0)$  transition.<sup>16</sup> Thus, we link certain vibration-rotation lines and the infrared absorption with the trapped electron.

We have related the infrared and ultraviolet peaks by the similarities in their formation times and tritium concentration behavior. The model that we propose is shown in Fig. 6. The ultraviolet peak is here the  $1s$ -to-conduction band transition, i.e., it empties the electron trap. The half-width of 1.5 eV is caused, in this model, by the width of the electron conduction band. This width is in agreement with band calculations.<sup>17,18</sup>

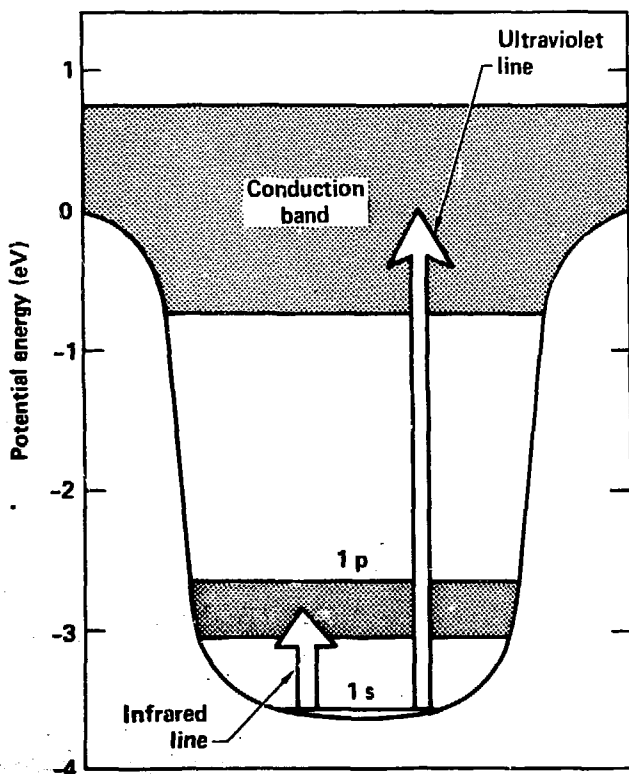
It is important to note that this model requires a potential energy well close to being a square one. Only in this way can we obtain a  $1s \rightarrow 1p$  energy that is much smaller than the energy to empty the trap.

We now return to Eq. 1. By the Thomas-Reiche-Kuhn rule, the two transitions must add to  $f=1$ . Because we do not know the effective electron masses, we can only compare integrated intensities. For D-T with 0.3% tritium,  $f$  for the ultraviolet line is 0.6 and for the infrared 0.4.

We have noted the remarkable difference in the production of absorption peaks in tritiated solid  $H_2$  and  $D_2$ , as shown in Fig. 4. We note that the crystal lattice zero-point energy of the solid  $H_2$  is larger than that of  $D_2$ . This causes the larger molar volume of the  $H_2$ . We presume, then, that electrons and/or ions can diffuse more quickly, and therefore recombine more quickly in solid  $H_2$  than in  $D_2$ . This may be the reason why no spectra are obtained in solid H-T containing only a little tritium. This effect has been seen in the proton-irradiated samples.<sup>16</sup> An isotope effect has also been seen for atoms in irradiated solid  $H_2$ - $D_2$  mixtures,<sup>19</sup> but we cannot as yet relate this to our results.

#### NUCLEAR SPIN POLARIZATION

The presence of a trapped electron defect in solid DT would appear to be only a curiosity. Yet, there is a possible application in nuclear spin polarization, a technique that offers laser fusion at a lower pulse energy.<sup>20,21</sup> We are presently conducting the first experiments at LLNL intended to align the nuclear moments in solid DT using the conventional dynamic



method of microwave pumping of the atoms created by the radiation damage. A second method might be to pump the trapped electrons themselves by way of either the infrared and ultraviolet peaks. We do not know, of course, whether such optical pumping would indeed polarize the nuclei.

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**Figure Captions to glue below figs.**

**Fig. 1.** The infrared, visible and near ultraviolet regions in solid deuterium-tritium.

**Fig. 2.** Ultraviolet absorption in solid D-T and H-T at a 5 K sensor temperature.

**Fig. 3.** Growth of the ultraviolet peak in solid D-T.

**Fig. 4.** Equilibrium integrated intensities in 5 K solid D-T and H-T.

**Fig. 5.** Holes in the infrared peak of 5 K H-T.

**Fig. 6.** Proposed model for the trapped electron.