Spontaneous optical flashes in proton-irradiated solid deuterium

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Samples of solid deuterium, cooled below 4.2 K, and irradiated by 15 MeV protons, will spontaneously flash. The flash-spectrum occurs in the near infrared with a maximum close to 920 nm. The flash intensity is two to three orders of magnitude greater than a steady-state emission observed in the same spectral region. The flash frequency is 1 every 1 to 3 min after several hours of irradiation of 10 nA/cm^2. Heat pulses have been detected accompanying many of the flashes and both can be stimulated by the application of external heat triggers. Following the optical flash, the steady-state emission intensity decreases by an amount that is wavelength dependent. While it is thought that these flashes are caused by atomic association in the solid, the species responsible for the optical emission is uncertain as is the transition itself.

I. INTRODUCTION

Irradiated solid hydrogens at temperatures near 4 K have shown many effects not present in unirradiated samples.[1,2] The existence of immobile charged species has been used to explain many new spectral features in both infrared and ultraviolet[2,3] absorption studies, and is reasonably well understood.[3–5] The method of irradiation for these absorption studies was either proton beam irradiation or doping with tritium.[6] Irradiated hydrogens have also been studied by ESR. These experiments, involving tritium doping,[7,8] γ irradiation,[9] or condensation of RF discharge products,[10] reveal the presence of large concentrations of stored atoms.

The recombination of atoms in solid hydrogens has been studied with different methods of atom production. Iskovskikh *et al.*[10] have studied the recombination of H and D atoms in their respective molecular solids at temperatures near 4 K. These experiments involved the condensation of microwave discharge products with a large initial concentration of atoms. By monitoring the decay of the ESR signals the authors are able to determine the rate constant. The only studies at temperatures lower than 4.2 K are those in tritiated solid hydrogens by Collins *et al.*[8] These studies examine the turn-on behavior of the atom concentration in tritiated samples as studied by ESR. By fitting the data to second-order kinetics they obtain values for the production rate of atoms as well as recombination constants. The recombination coefficient in D-T mixtures was measured to be larger than those measured by the Russian group in pure D_2 by about an order of magnitude where the temperatures of the studies overlap. The rates at temperatures lower than 5 K were 3–5 orders of magnitude larger than extrapolation of the Russian data. The production rate in the D-T samples also showed an unexplained temperature dependence.

Solid-hydrogen matrices have also been studied as a medium for storing large concentrations of unpaired atoms. Webeler[11] found the first evidence of large atom concentrations in low-temperature solid H_2 doped with 0.03% T_2. He found that at temperatures between 0.2 and 0.8 K after sufficient storage time the samples exhibited spontaneous recombination in which some fraction of the atoms recombined. It was later reported by Rosen[12] that the maximum decrease in the atom concentration in these samples was 3×10^{17} cm^{-3}, but there was no direct observation of the atoms. A theoretical model by Rosen[12] and Zeleznik[13] using two species of atoms (trapped and mobile) was able to satisfactorily explain the observations. More recently, Collins *et al.*[14] observed spontaneous recombination (in the form of thermal pulses) in solid T_2 and D-T at temperatures below 2.2 K. These experiments used ESR to measure the atom concentration simultaneously with the temperature. The authors state that during one of these heat pulses the atom concentrations became immeasurably small. They show data in D_2 with 2% T_2 that shows 4 recombination spikes in 10 000 min. In addition to thermal recombination spikes the tritiated samples also exhibited "triggered" optical flashes.[15] D-T samples cooled between 2.4 and 4 K exhibited triggered flashes where the application of an external heat source made the sample flash in the near-infrared region of the spectrum. These optical flashes were accompanied by smaller temperature changes than those observed in thermal recombination spikes. The authors measure the reduction in sample heating after a triggered flash, and calculate 5×10^{18} atoms cm^{-3} recombine during the flash ($\sim$10% of the total). These experiments did not measure the atom concentration directly. The triggered flashes were later shown to have a spectrum, limited to about 800–950 nm by the detector response, similar to a steady-state red emission in the irradiated solid.[16] Proton-irradiated samples also show triggered optical flashes at temperatures near 4.2 K. We have recently observed spontaneous optical flashes at cell temperatures lower than 4.2 K in proton-irradiated solid deuterium in which the optical intensity in the near infrared momentarily rises 2 orders of magnitude above its steady-state value. These flashes are related to the spontaneous heat pulses of Ref. 14 and, as such, are a signature of spontaneous atom recombination in the solid. It is these flashes that are the subject of this work.

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II. EXPERIMENT

In our experiments the sample is irradiated by a beam of 15 MeV protons. Beam currents range from 1 to 20 nA, but most studies were done with a current density of 10 nA/cm^2. The sample is contained in a copper cell with interior volume of 0.8 cm^3 which is mounted on the end of a liquid-helium transfer-line cryostat, to which is attached a calibrated silicon diode thermometer. The exhaust of the transfer line is pumped by a large rotary pump. The lowest stable temperature attainable with this system is 2.6 K. The system temperature has been calibrated below 4.2 K by measuring the equilibrium vapor pressure of helium in the sample cell. This calibrated value will be quoted throughout. The temperature inside the sample while the proton beam is on may be about 0.5 K higher than our quoted values.[3]

The light emitted by the sample is focused onto the entrance slit of a McPherson model 218 scanning monochromator equipped with a 600 l/mm grating blazed for 1 μm. The dispersed light is then focused onto the photocathode of a cooled Hamamatsu R-3310 photomultiplier tube. A 515 nm long-pass filter is included for order sorting. The signal from the photomultiplier was preamplified and then input to a Stanford Instruments SR-400 photon counter. For time scales of less than 100 ms the photon counter was used essentially as a rateme-ter, the output from the D/A port being fed to the input of a Hewlett-Packard HP8450 digitizing oscilloscope. The data were then transferred to a microcomputer. For longer times the data from the photon counter was simply read into the microcomputer.

III. RESULTS

After proton irradiation is started, one generally has to wait 10–15 min before the first flash occurs. The flash rate slowly increases with additional irradiation, and generally takes a number of hours before the average rate of flashes approaches a steady-state value. This behavior is difficult to quantify, as it seems to be sample dependent. What does seem to be independent of the sample, however, is the final average time between flashes. Once the sample has been irradiated for a sufficient time, termination of irradiation seems to have no effect on the rate of spontaneous flashes when irradiation is resumed. This is consistent with the very low recombination coefficients of D atoms in solid D_2 at these temperatures.[8,10]

For most flashes a temperature change accompanies the flash, and is believed to be the spontaneous heat spikes of Ref. 14. The flashes are then accompanied by decreases in the stored atom concentration. These thermal pulses range from a few tenths of a K to about 5 K. The differences in time scales between the time it takes for the flash frequency to build up, and that between flashes at the steady state, also suggest that in each flash only a small fraction of the stored atoms recombine. Figure 1 shows the statistics of the time between flashes for a sample that had reached a steady-state value. The sample had been irradiated at 10 nA/cm^2 for 12 h before these data were taken. The data in Fig. 1 are taken from a scan lasting between 2 and 3 h, producing nearly 100 spontaneous flashes. Some of the data involving long times between flashes correspond to fluctuations in the proton beam current, and the charge delivered in those time periods is comparable to those in shorter time intervals. The rapid decrease in frequency of flashes that are separated by more than the most probable time suggests that there is a critical condition beyond which any additional irradiation makes the system unstable.

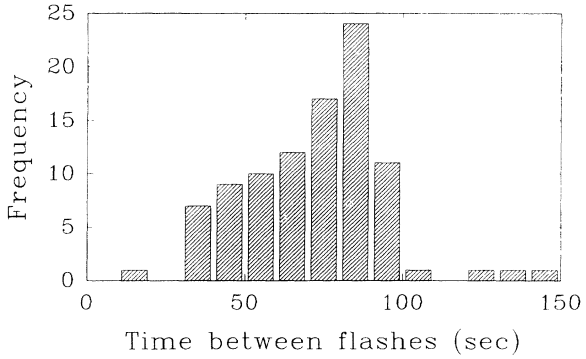

FIG. 1. Time separation between spontaneous optical flashes in proton-irradiated solid deuterium. Temperature 2.6 K and proton beam current 9 nA/cm^2.

The rate of flash occurrence is also a function of temperature, being greatest at the lowest temperature; most of the data presented here were taken at 2.6 K. When looking for the highest temperature at which spontaneous flashes occur, we observed one flash in 40 min at 3.6 K, and observed no flashes at 4.0 K in 70 min. In a later experiment, involving extended periods of irradiation at 4.2 K, we observed one spontaneous flash at that temperature after 5 h of irradiation.

In order to find the pulse shape of the flash, a digitizing oscilloscope was used with a photon counter dwell time of 1 ms; the flash shape obtained at 2.6 K is shown in Fig. 2. The decay portion of the spontaneous flash curve has been discretized at approximately 1-ms intervals and has been fit by a single exponential with a lifetime of 25±3 ms

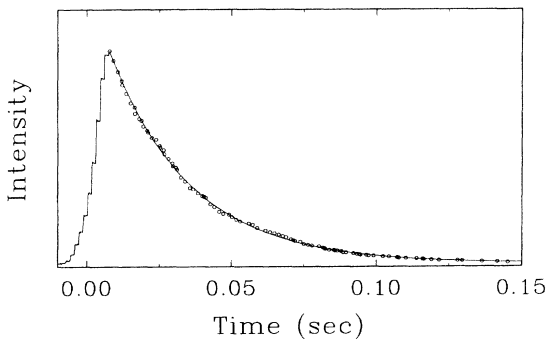

FIG. 2. Temporal distribution of optical intensity during a spontaneous flash. The solid line in the decay portion of the curve is a fit to a single exponential.

for most (10 of 12) of the flashes we have tried fitting. The remaining ones are distorted, but decay in the same time period. Our timing measurements do not seem to be wavelength dependent. The flashes that were fit by single exponentials cover the full range of wavelengths studied. The rise to the maximum of a flash also shows no noticeable variations always being 9–10 ms regardless of the actual intensity. This turn-on behavior of the spontaneous flashes is qualitatively different from the triggered flashes we have observed which exhibit a much longer rise time.

We have also examined the spectral shape of a spontaneous flash by collecting a number of flashes with the oscilloscope and averaging them at each wavelength. The spectrum of the flashes is redshifted by about 100 nm compared to the steady-state emission as shown in Fig. 3. These intensities have been corrected for photomultiplier tube (PMT) response. The intensity values shown in Fig. 3 for the steady-state emission were acquired from the same sample as that used for the flashes, hence the ratios of these intensities should be quite reliable. Intensities here are peak intensities (counts/s) which for the flash were determined for a 1-ms dwell time. More recent studies in proton-irradiated samples have shown that the steady-state emission itself becomes substantially redshifted at temperatures greater than 10 K.[17]

Immediately after a spontaneous optical flash the steady-state emission becomes temporarily reduced in intensity, which we call bleaching. This bleaching effect was observed for triggered pulses as well, and strongly suggests a common origin for the flashes and at least some fraction of the steady-state emission. In Ref. 15 it was reported that flashes could be reliably triggered providing 10 min had elapsed since the previous flash. Obviously, for the flashes reported here, such long times are not necessary, but we have never seen a spontaneous flash before the steady-state emission had recovered to its preflash value.

The growing-in of the emission after bleaching is not simply a thermal recovery of the sample. This is shown by the wavelength dependence of the bleaching; both the fraction of the steady state that is bleached, as well as the time constant of the recovery are functions of the wavelength. This effect is shown in Fig. 4. At the lowest wavelengths (720 nm) the fraction of the emission that is bleached is close to 0.5, and the lifetime of the recovery is 10 s. As the wavelength is increased this fraction decreases until, at wavelengths near 920 nm (close to the wavelength of the flash maximum) no bleaching is observed. Since not all flashes are followed by the same bleaching, the data in Fig. 4 are taken from an average of 3–5 flashes depending on the wavelength. That the bleaching fraction has a wavelength dependence almost certainly means that the steady-state emission is not a simple transition. The lifetime of the recovery of the emission after bleaching decreases almost linearly with increasing beam current.

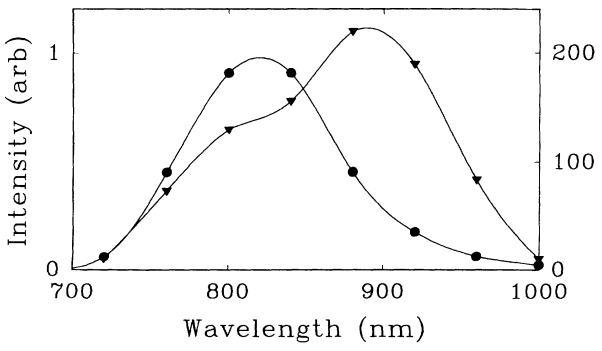

FIG. 3. Spectral shape of the steady-state emission (circles, left axis), and the flash (triangles, right axis). The intensity scale is normalized to the steady-state emission.

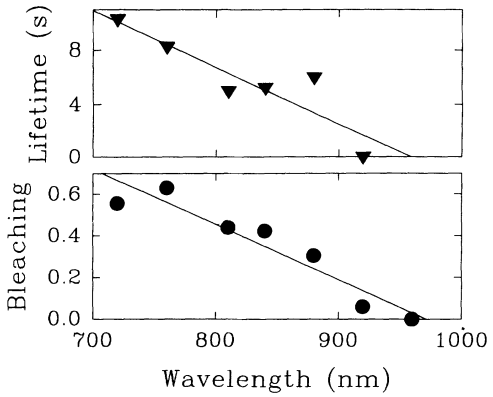

FIG. 4. Wavelength dependence of the amount of bleaching after a flash (circles, lower), and the time constant of the recovery (triangles, upper).

IV. DISCUSSION AND CONCLUSION

Even though we have never observed a direct signature of atoms in proton-irradiated solid deuterium it is expected that the properties of our irradiated samples should closely resemble those of D-T samples. In all other observations of radiation-induced features this has indeed been the case. For this reason it may be useful to try to estimate the number of atoms recombining during a flash. The largest temperature pulse we have observed corresponds to the recombination energy of 2×10^{17} atoms/cm^3. We can also estimate the number of atoms produced in the time interval between flashes. If one uses a beam current of 10 nA/cm^2, a constant atom production rate of 10^5 atoms/proton, and an average time between flashes of 70 s (from Fig. 1), then one obtains 4×10^{17} atoms/cm^3 produced in the time interval between flashes. Both of these estimates are a small fraction of the total atom population expected to exist in the sample. By comparison with D-T results, we expect the maximum atom concentration in our samples at 3 K to be about 2×10^{19} cm^{-3}. This value is also much smaller than the difference between the steady-state atom concentrations at the two different temperatures (during our largest temperature spike) which is greater than 8×10^{18} cm^{-3}. This observation suggests that the temperature pulse through

the sample is not long enough to allow the atom concentration to reach steady state at the higher temperature, but instead the sample maintains an excess of atoms.

The occurrence of optical flashes is most likely a result of the transient heat pulses created by the atomic association. These heat pulses will increase the mobility of all species in the sample and allow reactions, some of which may be radiative. An example of this process involves electrons radiatively recombining with a D atom. The resulting D^- has a large cross section for association with any D atom and may therefore catalyze atomic association. This conjecture is supported by the fact that the red emission spectrum closely resembles that of the inverse (photodetachment) process.

It is also possible that the electrons recombine radiatively with any of the positively charged species known to exist in the sample. The time scale of the decay indicates that at least one of the species involved has a high mobility, which is an indication of a high sample temperature during the flash. The fact that a small fraction of the total atoms recombines, as well as the fact that the atom concentrations cannot track the temperature changes in the sample, indicates that the recombination is being quenched. Further experiments which will monitor the signature of charged species during a flash, as well as stimulate detrapping of electrons, are in progress.

As remarked previously,[16] the species (and its transitions) responsible for the optical emission of the flash is not identified. Besides this uncertainty these studies have identified a phenomenon qualitatively different from those previously studied. This is the fact that spontaneous flashes occur with such frequency that the atom concentrations between flashes cannot be significantly depleted. Yet previous studies, that directly monitored the atom concentration using ESR, demonstrated that following a thermal pulse atoms are mostly depleted and a significant time ($\simeq 10$ min) is needed between stimulation of optical flashes in D-T. Clearly atom-atom association must be mediated by a number of different processes and identification of the ones responsible in low-temperature irradiated solids has yet to be satisfactorily performed.

ACKNOWLEDGMENT

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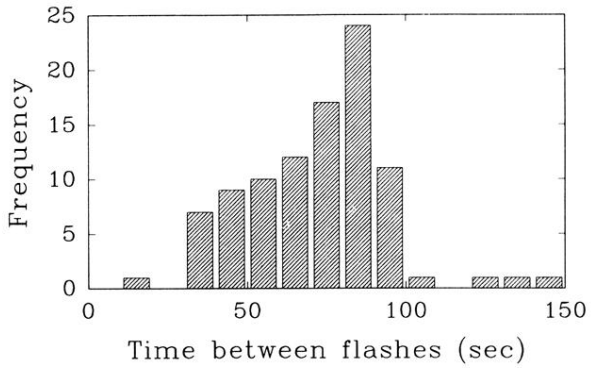

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