

Laser generation of transient photocurrents in liquids without the application of an electric field

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The first known observation of the Dember effect in liquids is reported using a pulsed nitrogen laser (337.1 nm) which generates photocarriers in a solution of anthracene in tetrahydrofuran. From the sign of the Dember signal (diffusion current), the majority photocarriers are determined to be positively charged anthracene ions. The decay of the Dember signal is exponential. This differs from the second-order decay kinetics reported previously in photoconductivity studies of aromatic molecules in solution. The exponential decay is interpreted as a bimolecular recombination process which includes trapping. The relaxation of the photocarriers is significantly altered when the solution is in contact with the electrodes. The Dember signal has a quadratic dependence on the excitation intensity. The photoionization mechanism is shown to result from at least two competing biphotonic absorption mechanisms, the consecutive absorption of two photons and triplet-triplet annihilation.

I. INTRODUCTION

In 1931, Dember¹ observed that the absorption of radiation by Cu_2O crystals creates a potential difference along the light path. Since then, the Dember effect has been observed in crystalline or powdered inorganic compounds,²⁻⁴ organic solids,⁵⁻⁹ and photographic emulsions.¹⁰ We present here the observation and measurement of the Dember effect in a tetrahydrofuran (THF) solution of anthracene using the 337.1 nm line of a pulsed nitrogen laser as the excitation source. We believe that this represents the first reported measurement of the Dember effect in liquids.

The theory of the Dember effect is quite complicated,^{11,12} but the underlying principles are rather simple. When one face of a sample is irradiated by a beam of light, the radiation is absorbed nonuniformly along the light path according to Beer's law. Hence, a concentration gradient of the photocarriers (dc/dl) is produced (see Fig. 1). Generally, the positive and negative photocarriers have different drift velocities v and diffusion lengths L in the medium. Consequently, a net current

$$\Delta J = |J_+ - J_-| \quad (1)$$

will result along the light path where

$$J = vL(dc/dl) \quad (2)$$

Often the diffusion length and drift velocity of one of the photocarriers is nearly zero because of trapping, scavenging, or solvation. In this case, the observed Dember current is due to the more mobile (majority) photocarrier and the sign of ΔJ indicates the sign of the majority carrier. The illuminated face (transparent electrode) of the sample cell acquires the opposite charge of the majority carrier which permits the diffusion current (of image charges) to be measured in an external circuit. Alternatively, the Dember effect in liquids may be likened to a special type of battery called a concentration cell, where the electrodes are identical but a potential difference results from the concentration gradient.

The Dember effect has been utilized primarily to determine the sign of the more mobile carriers in solids

where Hall effect measurements are extremely difficult.² However, the usefulness of the Dember effect has often been questioned because of the complications associated with possible contact potentials between the electrode and the irradiated sample. The observation of a "true" Dember effect in liquids seems to have been frustrated by this problem.¹³ Fortunately, this difficulty is overcome by placing thin, transparent sheets of insulation between the sample and the electrodes (Fig. 1). In this manner, we have measured photocurrents in the absence of an applied external field and without the necessity of electrode-sample contact. Many previous Dember effect measurements have utilized a continuous light source which also adds to the difficulty of interpreting the Dember signal because the system becomes electrically charged.² Since the light source used in these experiments is a pulse of several nanoseconds duration, this problem is removed allowing the direct observation of ion dynamics in a liquid.

The object of the present study is to demonstrate the Dember effect in liquids and to establish its use as a tool for the investigation of photoionization mechanisms in liquids. A solution of anthracene in tetrahydrofuran

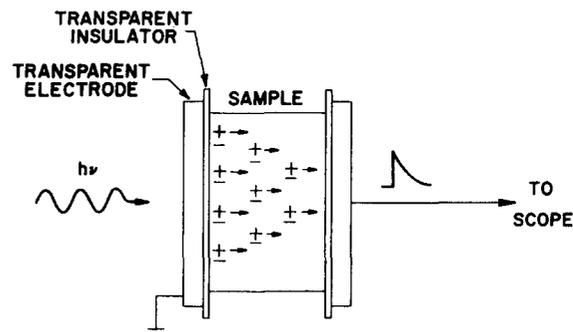


FIG. 1. Origin of the Dember signal. When light is absorbed nonuniformly by the sample according to the Beer-Lambert law, a concentration gradient of photocarriers is produced. If the diffusion lengths of the photocarriers are unequal, then a net diffusion current of one of the photocarriers results. The movement of image charges in an external circuit permits the observation of the Dember signal.

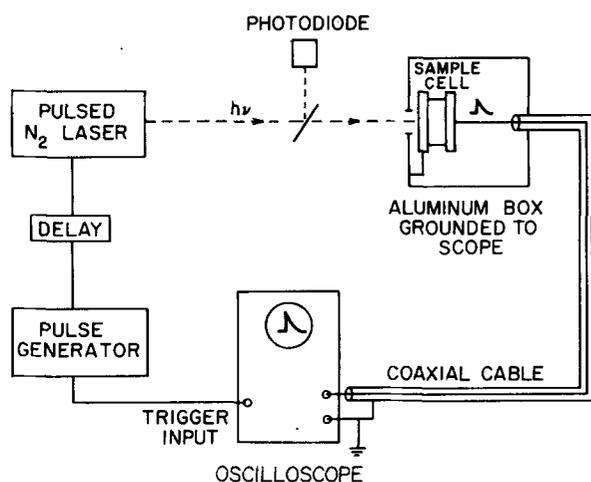


FIG. 2. Schematic diagram of the Dember effect apparatus.

was chosen for these experiments since it has been studied previously by xenon flash¹⁴ and pulsed laser¹⁵ irradiation. A study of the magnitude of the Dember signal as a function of light intensity and anthracene concentration provides information about the photoionization mechanism and the nature of the intermediate states. Also, the sign of the majority photocarriers is directly determined to be positive. Finally, we report here that the decay of the transient signal is exponential in time. We conclude that the ionic relaxation is described by a bimolecular mechanism which includes trapping. This differs from the findings of previous photoconductivity studies on aromatic molecules in solution. These results illustrate the simplicity of this new technique and the importance of measuring photocurrents in liquids without electrode-sample contact.

II. EXPERIMENTAL

The apparatus used to measure the Dember effect is shown in Fig. 2. It consists of a pulsed light source, a sample cell, an oscilloscope, and a trigger circuit. When the light pulse is absorbed by the sample, a transient photocurrent (the Dember signal) is observed on the oscilloscope.

A pulse generator (Data Dynamics Model 5109) triggers a nitrogen laser (Avco-Everett Model C950) which emits a 10 nsec pulse of light at 3371 Å (5×10^{-4} J/pulse). The light can be attenuated, if desired, by placing neutral density filters in front of the sample cell. In addition, the relative intensity of the laser beam is monitored using a fast photodiode (EG & G SGD-40).

The sample cell (Fig. 3) consists of two transparent electrodes of Nesa glass (glass coated with tin oxide on one surface and obtained from 3M Company, St. Paul, MN). Electrical contact to each electrode is made by means of an evaporated silver strip on the SnO surface. Thin sheets (≈ 1 mil thick) of mica are inserted between the electrodes and the solution to provide insulation. It is more convenient to sputter glass or quartz over the SnO coating to provide a permanent insulator coating, but this was not done for these preliminary experiments.

The electrodes are separated by Teflon spacers (0.8 mm thick). Holes in the Teflon spacers permit the filling of the cell with a hypodermic syringe. The magnitude of the Dember signal can be increased by decreasing the thickness of the spacers or by increasing the exposed area provided saturation is not taking place.¹⁰ The front electrode (closest to light source) is grounded to an aluminum box surrounding the sample cell. The aluminum box acts as a shield to eliminate electrical noise.

The Dember signal is displayed on a Tektronix RM 35A oscilloscope using a Tektronix 1A7A high-gain differential amplifier plug in. The bandwidth of the amplifier is ≈ 1 MHz, which permits the faithful reproduction of pulses having risetimes of 1–2 μ sec. The scope and aluminum shielding box must have a common ground. This is achieved through the shielding in the coaxial cable which connects the scope to the sample cell, eliminating spurious electrical noises. The oscilloscope is triggered before the laser is fired so the entire Dember signal can be observed. This is accomplished with the adjustable delay capabilities of the pulse generator.

It is important to stress that the Dember signal is not taken repetitively, but rather, one pulse is obtained by triggering the pulse generator manually. Several seconds are needed for the sample cell to become electrically relaxed (i.e., the dissipation of all built up charges). In these studies, we have taken care to avoid the above problem by allowing sufficient time for the sample cell to relax between measurements.

Zone-refined anthracene (99.99%) was used as received from Materials Limited, Fairfield, NJ. The tetrahydrofuran (obtained from Fisher Scientific Co.) was refluxed over LiAlH₄ to remove any water which may have been present. Dissolved oxygen was removed by bubbling nitrogen through the solvent prior to its use. Reasonable purification of the reagents is essential,

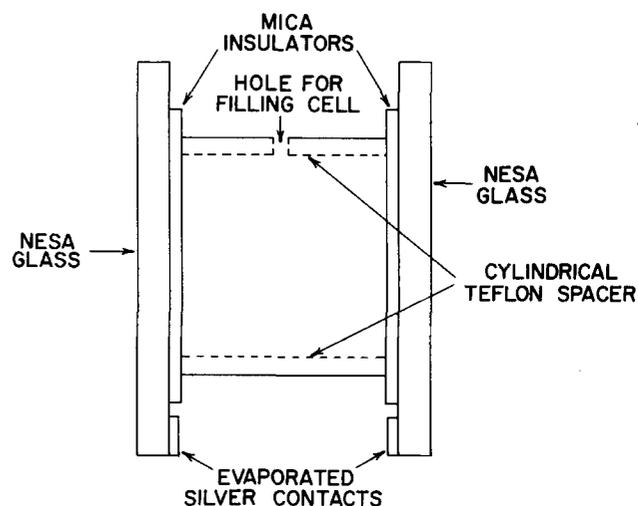


FIG. 3. Details of the sample cell. Two pieces of conducting Nesa glass with evaporated silver contacts are sandwiched together with a 0.8 mm thick Teflon spacer. The cell is filled through a hole in the spacer. Thin sheets of mica insulate the solution from the electrodes.

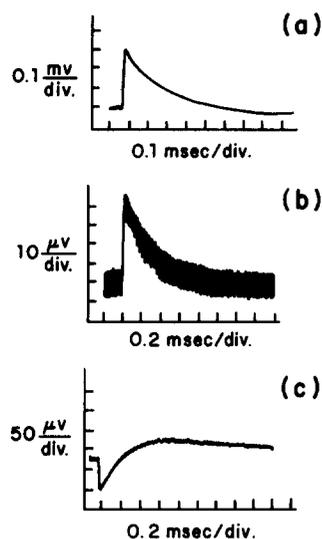


FIG. 4. Oscilloscope traces of (a) the Dember signal of anthracene powder; (b) the Dember signal of a $10^{-1}M$ solution of anthracene in THF; (c) the same as (b), but the solution is in contact with the electrodes.

since a slight Dember signal was observed in impure THF. Neither the sample cell nor the purified solvents used for these experiments generated a Dember signal in the absence of anthracene.

III. RESULTS AND DISCUSSION

A. Nature of the Dember signal

A typical oscilloscope trace demonstrating the Dember effect for a $10^{-1}M$ solution of anthracene in THF is shown in Fig. 4(b). The pulse is positive implying that either the majority photocarriers are positive ions moving away from the front electrode or negative ions moving toward the front electrode. We dismiss the second possibility because the flow direction is against the concentration gradient produced by the absorption of the incident radiation. Because the sample cell containing only pure solvent gives no signal, we also reject the possible explanation that the signal we observe arises from electron or hole injection from the electrode structure. When a powdered sample of anthracene (no THF present) is placed in the sample cell, a similar positive pulse but with a much greater magnitude¹⁶ (≈ 10 times) is obtained [Fig. 4(a)]. This is evidence that the Dember signal is due to the photoionization of anthracene (A) and involves the immediate "trapping" or solvation of the electron on a time scale much faster than 10 nsec (the pulsewidth of the laser). While this result is not surprising,^{6-8,17} we wish to emphasize the simplicity by which the Dember effect unambiguously determines the majority photocarriers as positively charged species moving away from the front electrode. It is reasonable to believe that the signal in solution is caused by the migration of the anthracene radical cation A^+ , while in the solid it is probably bulk migration of holes. Another possibility for the signal obtained for the solution is that charge exchange takes place between A^+ and A , leading to a holelike motion in the solution which would be faster than purely ionic motion.¹⁸

If the insulating sheets are removed, then an oscilloscope trace of the resulting photoconductivity pulse is shown in Fig. 4(c). In contrast to the Dember signal,

both a positive and negative component to the pulse exists. The negative component can be interpreted as the movement of A^+ toward the front electrode, or electron injection from the Nesa glass into the solution. As will be shown in the next section, the positive component cannot be interpreted simply as the diffusion of A^+ away from the front electrode, but also involves the interaction of the sample and electrode.

B. Time decay of the Dember signal

Figure 5 plots the logarithm of the Dember signal as a function of time for both the anthracene crystal and the solution. From the linearity of this plot we conclude that the decay of the Dember signal is exponential. This result differs from the second-order decay kinetics observed by others who studied the photocurrent of aromatic molecules in solution in the presence of an applied field.^{14,19-23} Consequently, we believe that the interpretation of traditional photoconductivity studies may involve electrode-solution interface mechanisms as well as the inherent relaxation processes of the solution.

The exponential decay found in the Dember effect can be explained by including trapping in the recombination mechanism. If the recombination rate constant is k_1 and the trapping rate constant is k_2 , then the time dependence of $[A^+]$ (after the excitation is removed) is

$$d[A^+]/dt = -k_1[A^+]^2 - k_2[N][A^+] \quad (3)$$

where $[N]$ is the number of traps per unit volume.

Equation (3) has the solution

$$\frac{[A^+]}{[A_0^+]} = \frac{\exp(-k_2[N]t)}{1 + ([A_0^+]/[N]k_2)[1 - \exp(-k_2[N]t)]} \quad (4)$$

where $[A_0^+]$ is the initial concentration of A^+ (after the excitation is removed). For the condition that $k_2[N] \gg k_1[A^+]$, the solution of Eq. (3) is

$$[A^+]/[A_0^+] = \exp[-k_2[N]t] \quad (5)$$

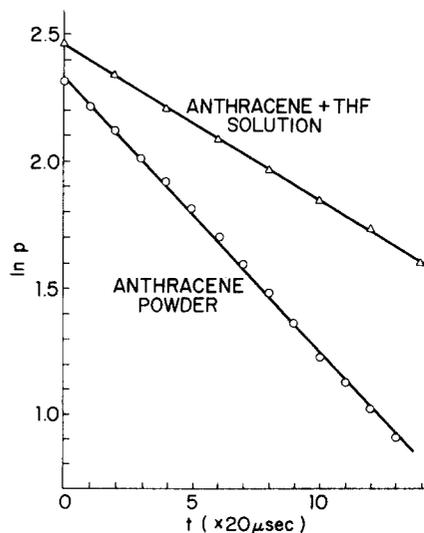


FIG. 5. A plot of the logarithm of the peak Dember signal as a function of time for (1) a solution of anthracene in THF, and (2) anthracene powder. The linearity of the plots demonstrates the exponential decay of the Dember signal.

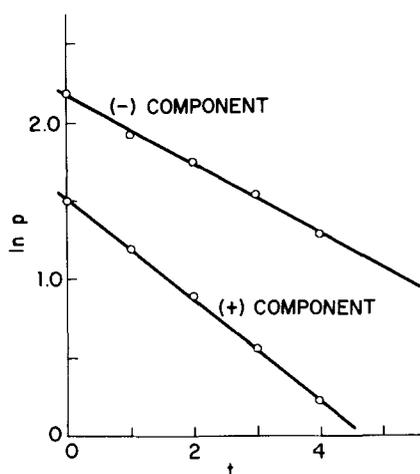


FIG. 6. A plot of the logarithm of the peak photocurrent as a function of time for the positive and negative component of the signal displayed in Fig. 4(b). The time scale for the (+) component is 20 msec/div, while that for the (-) component is 40 μ sec/div. The entire signal is the sum of these two exponential decays.

which describes the decay we observe in Fig. 5. Thus, it appears that a bimolecular recombination mechanism which includes trapping is a more realistic model for ionic relaxation in solution. This model implies that one A^* does not simply recombine with a trapped e^- as the rate determining step in the relaxation process, but the A^* becomes scavenged, solvated, or trapped before recombination. This type of kinetics is well known in the decay of photocurrents in solids,^{24,25} but this appears to be the first time an exponential decay of the photocurrent has been seen in liquids.

Traditionally, most photoconductivity studies apply an external electric field having the solution in contact with the electrodes. Otherwise, most of the potential drop is across the insulators instead of the solution. Consequently, charge can be rapidly furnished to neutralize the ions in solution. Thus, the replenishing of charges at the electrode interface occurs in a simple bimolecular fashion since the trapping effect is overwhelmed. The kinetic decay scheme then is represented by

$$d[A^*]/dt = -k[A^*]^2, \quad (6)$$

which has the solution

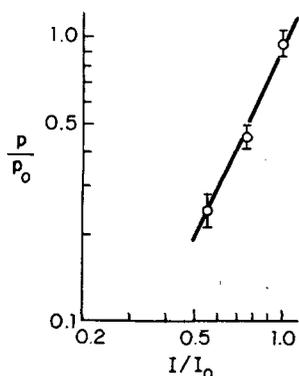


FIG. 7. A log-log plot of the relative peak Dember signal as a function of relative excitation intensity. The slope of the straight line is 2.2 ± 0.5 , indicating that a biphotonic process is occurring.

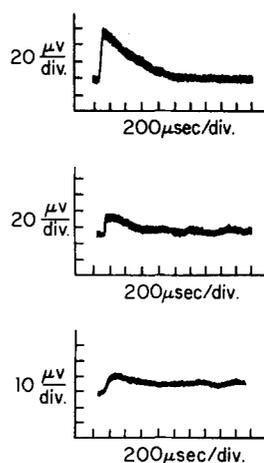


FIG. 8. Variation of the Dember signal with excitation intensity for a $10^{-1}M$ solution of anthracene in THF. From top to bottom, the relative intensity is 100%, 75%, and 55%, respectively. The initial rise-time becomes more complex as the excitation intensity decreases indicating at least two competing photoionization mechanisms.

$$[A^*] = \frac{[A_0^*]}{1 + kt[A_0^*]} \quad (7)$$

or

$$[A_0^*]/[A^*] = 1 + kt[A_0^*] \quad (8)$$

Equation (8) describes the decay reported in previous photoconductivity studies of aromatic molecules in solution. These results suggest to us the possibility that the decay scheme for traditional photoconductivity measurements describes the replenishing of charge at the electrode-solution interface instead of the true relaxation of photocarriers in the solution.

As shown in Fig. 4(c), when the solution is in contact with the electrodes both a positive and negative component to the signal are seen. Figure 6 illustrates that both these components decay exponentially. Since the electrodes are not attached to a source of charge, the observation of exponential decay is not unexpected. However, the effect of solution-electrode contact is quite dramatic since the lifetime of the negative component is several orders of magnitude shorter than the lifetime of the positive component or the Dember signal.

C. Photoionization mechanisms

The Dember signal was found to vary in shape and magnitude as a function of the excitation intensity. From the peak heights, the Dember effect is shown to result from a biphotonic process. From the variation of the risetimes at least two different biphotonic mechanisms appear to be present.

Figure 7 presents a logarithmic plot of the relative peak Dember signal as a function of the relative excitation intensity. The data are taken for a $10^{-1}M$ solution of anthracene in oxygen-free THF. Similar results are obtained for an anthracene solution containing air, for anthracene powder (no THF present), and for the negative component of the photocurrent signal shown in Fig. 4(c). The straight line in Fig. 7 has the slope 2.2 ± 0.5 , indicating that the ionization of anthracene requires the absorption of two photons (biphotonic process), i. e., in all cases, the absorption of two photons is required to generate photocarriers.

Figure 8 shows oscilloscope traces of the Dember

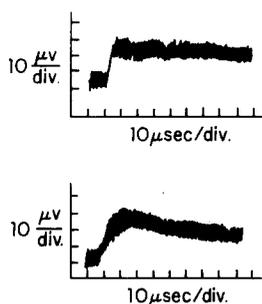


FIG. 9. Risetime behavior of the Dember signal at low excitation levels of the oxygenated sample (top) and of the oxygen-free solution (bottom). The longer component of the risetime is quenched by the dissolved oxygen and the short component is unaffected.

signals resulting from the variation of excitation intensity. At high laser intensity, the Dember signal has a short risetime followed by a long decay. As the excitation intensity decreases, the risetime becomes more complex in appearance. The early part of the risetime remains short but decreases in magnitude. A longer component of the risetime follows until the signal reaches its maximum. This behavior suggests the superposition of at least two photoionization mechanisms.

Further studies were made at low excitation levels with and without dissolved oxygen. Figure 9 shows that the longer component of the risetime is quenched by the dissolved oxygen but the short component is unaffected. From Figs. 8 and 9 we conclude that the "prompt" photoionization of anthracene corresponding to the early risetime region is caused by consecutive²⁶ photon absorption



while the "delayed" photoionization corresponding to the longer risetime component is caused by excited state annihilation



In Eqs. (9) and (10), A^* may formally be either the excited singlet or triplet or a semi-ionized state²⁷ of anthracene. The biphotonic photoionization process shown in Eq. (9) is much faster than that of Eq. (10) since the former is completed within the duration of the laser pulse while the latter is diffusion controlled. The intersystem crossing lifetime for excited singlet anthracene appears to be comparable with the duration of the laser pulse while the half-life for oxygen quenching appears to be longer.^{15,28} Thus, it would seem that the consecutive biphotonic ionization mechanism may have contributions from the singlet, triplet, and semi-ionized states of anthracene; however, the A^* species in Eq. (10) appears to be only the triplet state.

Further evidence for the existence of at least two photoionization mechanisms is furnished by studying the Dember signal as a function of solute concentration. At low concentration but high excitation intensity, the same behavior as displayed in Fig. 9 is observed, i.e., two components of the risetime exist and the slower one is quenched by dissolved oxygen. As the concentration increases, the Dember signal saturates as shown in Fig. 10. The photoionization schemes represented by

Eqs. (9) and (10) would be expected at low concentrations to show a linear or quadratic dependence respectively. At low concentration Fig. 10 exhibits a linear dependence on concentration. However, it would be premature to conclude that consecutive biphotonic absorption dominates because the apparent linearity may reflect partial saturation of the quadratic dependence. Moreover, at low intensity and low concentration, the risetime behavior suggests that triplet-triplet annihilation is significant.

Although the photoionization of aromatic molecules in solutions by photons whose energy is considerably below the gas-phase ionization limit is well known, the detailed nature of the photoionization mechanisms has been a subject of controversy.²⁷ Various research groups have previously reported that either Eq. (9) or Eq. (10) exclusively represents the photoionization mechanism of aromatic molecules.²⁹ Recently, Metzger and Labhart²¹ have found for pyrene in THF that low excitation intensities favor triplet-triplet annihilation, while high excitation intensities favor consecutive photon absorption. The results we find for anthracene in THF supports their view that at least two mechanisms are competing during the photoionization process.

D. Concluding remarks

We have observed the generation of a transient diffusion current (Dember effect) in liquids through the action of an incident light beam which causes the creation of a charge carrier concentration gradient along the light path. Moreover, we have demonstrated that the Dember effect in liquids may be used to determine the sign of the majority charge carrier, the nature of the photoionization mechanism, and the behavior of the subsequent ion transport dynamics. Any laboratory can perform these simple experiments with the availability of an excitation source to cause the nonequilibrium spatial distribution of photocarriers and an oscilloscope to record the Dember signal. Indeed, the cost of materials for construction of the sample cell shown in Fig. 3 is less than 15 dollars.

The Dember signal can be observed using only a flashlamp. However, the use of a pulsed laser has the

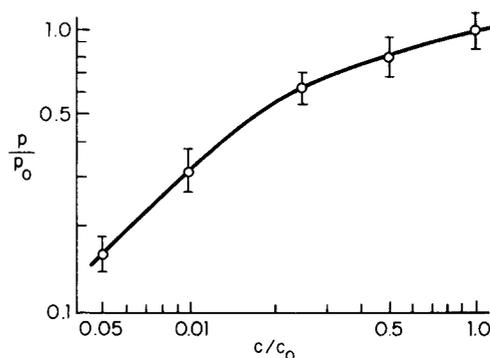


FIG. 10. A log-log plot of the relative peak Dember signal as a function of relative concentration of the anthracene in the THF solution. As concentration increases the Dember signal saturates.

advantage that it can deliver so much more power in a narrow excitation bandwidth. The present study employed a fixed wavelength pulsed laser, but a tunable pulsed laser, such as a frequency-doubled dye laser, can be used to measure the variation of the Dember signal with wavelength. For example, this would permit the determination of thresholds and give us insight into how the probability for ion pair production in liquids depends on the initial excess energy of the photoejected electron.

Previously, only solid state systems have been studied with the Dember effect. The present work shows that the Dember effect can be observed in liquids, and surely extended to gases as well. In liquid systems the addition of artificial traps or scavengers to solutions, the variation in the dielectric constant of the medium with choice of solvent, the determination of the diffusion lengths of the majority carrier, ion transport phenomena such as the diffusion of ions through interfaces or membranes, and electron injection at solution-electrode junctions as well as the nature of surface states can all be readily investigated with the Dember effect.

We wish to stress that the observation of the Dember effect does not require the radiation to cause ionization in the medium but rather to create a spatial gradient in the concentration of charge carriers. Thus the Dember effect should be observable in electrolytes or even plasmas. In particular, the Dember effect may have important applications to the study of aqueous solutions of ions since these liquids cannot be investigated by traditional photoconductivity methods. The Dember effect may also be used to convert solar to electrical energy. The above examples are not meant to be exhaustive, but they suggest that the Dember effect is worthy of much additional attention.

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