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GEMINATE IONS IN NANOSECOND PULSE IRRADIATED CCl_4 DETECTED BY d.c. CONDUCTIVITY

MATTHIJS P DE HAAS and JOHN M. WARMAN
Interuniversity Reactor Institute, Mekelweg 15, 2629 JB Delft, The Netherlands

and

BORIVOJ VOJNOVIC
Gray Laboratory, Mount Vernon Hospital, Northwood, Middlesex HA6 2RN, England

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Abstract–The d c conductivity resulting from electron pulse-irradiation of liquid CCl_4 has been studied with a time resolution of approximately 10 ns At short times (< 1 μs) the transient conductivity is much larger than would be expected from free ions alone and a large contribution to the d.c. conductivity (up to at least 5 times that of the free ions) from ion pairs which eventually undergo geminate recombination is indicated

INTRODUCTION

AN INTERESTING question which has arisen in recent years is whether or not it is possible to detect geminate ion pairs using a d.c. conductivity technique and if so, what precise form the current transient would be expected to take if a d.c. conductivity experiment were carried out under conditions where a relatively large yield of geminate ion pairs were formed? For example, should the d.c. conductivity transient be simply proportional to the total concentration of all ion-pairs present at a given time as is expected to be the case for ultra high frequency, microwave conductivity measurements or should it be considerably less?

That the form of the d.c transient should be different to that obtained using microwaves would certainly be expected since it is well known that in the presence of a continuous electric field the ion pair distribution can be sufficiently distorted as to result in a significantly higher yield of escaped ions The actual form of the survival probability of ion pairs beginning with a given separation distance was in fact calculated both in the absence and presence of an applied field some time ago by Hong and Noolandi.⁽¹⁾ It is only recently, however, that attempts have been made to theoretically and experimentally study how the field-perturbed motion of these correlated ions is translated into a current impulse in the external circuitry.⁽² ³⁾

The initial experimental attack on the problem was made by Baxendale in 1981⁽³⁾ when he carried out measurements of the d c conductivity of liquid CCl_4 using the 20 ns, 10 MeV electron pulse from the Manchester Linac However, mainly because of the recovery of the detection system from overload by spurious signals due to the electron beam passing through the cell, the results were inconclusive Carbon tetrachloride was specifically chosen for the experiments because of the very rapid localisation of mobile primary charge carriers and the resulting large yield of geminate ions on a nanosecond timescale as evidenced by microwave conductivity measurements.⁽⁴, ⁵⁾

In this paper we present initial results on d.c conductivity transients in nanosecond pulse irradiated CCl_4 obtained using the technique that has been developed at the Gray Laboratory ⁽⁶⁾ This surmounts many of the "pick-up" problems associated with electron irradiation of normal d.c. conductivity cells.

EXPERIMENTAL

The d c conductivity cell used in the present experiments consisted of two parallel electrodes in an all metal container with internal dimensions of $38.5 \times 14 \times 20\ mm^3$ The electron transmission window was a 0 1 mm thick brass plate The rectangular, platinum-plated brass electrodes ($8 \times 35\ mm^2$) were 1 mm apart and positioned in the middle of the container, 1 4 mm from the electron window Each electrode was connected to a wire that was fed through the cell wall by a 50 Ω connector

The technique used for measuring conductivity transients was similar to that described by Maughan *et al.*(6) in which a passive device (wideband balanced transformer) was used to eliminate the pick-up current which is caused by the high energy electrons stopping in *or* passing through the cell. The rise time of the technique has been improved to 3.5 ns in the present experiments by replacing the balanced transformer by a 4:1 hybrid junction. The hybrid junction is an electrical circuit involving four ferrite loaded transmission lines which in the present case correspond to two input lines I_1 and I_2 connected to the electrodes of the cell and two output lines O_1 and O_2. The four lines are brought together and matched in such a way that in-phase (like polarity) signals in I_1 and I_2 are transmitted only via one of the output lines, i.e. O_1 and out-of-phase components via the other, O_2. Optimum cancellation of the pick-up current at the output O_2 will be achieved for identical pick-up currents in both inputs. In this way electron pulse interference was reduced by two orders of magnitude and conductivity changes were able to be observed within a few ns after the electron pulse. Further descriptions of hybrid junction design are to be found in Refs 7–9 and specific details of the cell and circuit used here are given in Ref. 10.

Because of the 4.3 μs fall-time of the hybrid junction, for measurements at longer times either the hybrid junction was not used (Insert of Figs 1 and 2) or the signal decay was corrected by using a virtual-earth amplifier(10) (current to voltage converter) which allowed observations to be made up around 100 μs, the rise time in this case is less than 10 ns.

A × 100 GPD-460 (Avantek Limited) amplifier with a rise time of 1 ns and a decay time constant of 450 μs was used during the observation of low amplitude signals, the addition of a filter to reduce the bandwidth to 0.7 MHz reduced the noise and permitted observations on a long timescale (Insert of Figs 1 and 2). The signal was fed via a 7A15 or 7A16P plug-in to a Tektronix 7612 D transient digitizer. The digitizer was interfaced to a PDP 11–34 computer which was used to carry out signal averaging.

The cell was irradiated with 3.5 MeV electrons from a Van de Graaff accelerator, using 10 and 30 ns pulses. The dose per pulse, which is dependent on the degree of defocussing of the beam, the beam current and the pulse length, was varied from ~0.05 to 2 Gy.

The horizontal electron beam passed through the cell parallel to the electrodes and was carefully centered, so that pick-up currents on both plates of the cell are identical. All high energy electrons were stopped in the cell and return to the Van de Graaff ground via a connection to the exit port of the accelerator. In this way the electronic components connected to the cell were shielded from high frequency signals during the electron pulse.

The experimental results are the average of two transients, one transient acquired with a given polarity of polarizing voltage and plug-in, the other with the polarity of plug-in and polarizing voltage reversed. In this way any remaining spurious transient signals are further diminished.

The carbon tetrachloride (BDH) was used as received. Using a flushing system the sample in the cell was changed after a dose of approximately 1000 Gy.

RESULTS AND DISCUSSION

In the insert to Fig. 1 is shown the time dependence of the conductivity in CCl_4, at a field strength of 10 kV/cm, resulting from a 30 ns pulse (2 Gy), on a timescale of several tens of microseconds. On this timescale by far the dominant contribution to the conductivity is expected to come from "free" ions since the "escape time", τ_{fi}, given by(11)

$$\tau_{fi} = 16.7\, r_c^2/D \tag{1}$$

is less than 10 μs for molecular ions in CCl_4 (diffusion coefficient of ions, $D \simeq 2 \times 10^{-5}\,\mathrm{cm^2V^{-1}s^{-1}}$, Onsager escape distance, $r_c = 256$ Å). The escape time has been defined(11) as the time following the formation of correlated ion-pairs after which the ion-pairs remaining have less than a 10% probability of undergoing geminate recombination. Equation (1) is based on expression (2) which has been found to give a good description of the ion pair survival probability for long times(4,5,11)

$$G(t)/G_{fi} = [1 + 0.6(r_c^2/Dt)^{0.6}] \tag{2}$$

In accordance with the free ion nature of the conductivity on a timescale of tens of microseconds, the decay rate is found to be inversely proportional to the dose in the pulse due to the occurence of second order homogeneous recombination. Extrapolation of this long-time conductivity signal to zero time should then give a measure of the maximum conductivity signal to be expected from free ions alone.

In the main part of Fig. 1 the transient conductivity is shown on a much shorter timescale but using the same pulse conditions as for the data in the insert. The dashed line in the main figure represents the free ion contribution to the conductivity obtained by back extrapolation of the long time data as described above. It can clearly be seen that, at short times, a substantially larger conductivity is observed than can be ascribed to free ions alone. We are forced to conclude, therefore, that Coulomb-correlated pairs of ions, which eventually will undergo geminate recombination, can contribute significantly to the d.c. conductivity of the medium during their lifetime. This same conclusion has also been reached recently by Klaus Schmidt(2) on the basis of preliminary Monte-Carlo calculations of the perturbed motion of geminate ion pairs in the presence of an electric field.

In order to obtain absolute yields (G-values) from the conductivity data one can make use of the fact that zero field free ions yields within the range $0.095 \pm 0.002 (100\,\mathrm{eV})^{-1}$ have been measured previously.(5,12,13) The free ion yield in the present experiments will in fact be somewhat higher than this value due to the applied field but, for the relatively low field strengths used, $G_{fi}(E)$ can be estimated using the low field linear relationship(14,15)

$$G_{fi}(E) = G_{fi}(o)(1 + E/E_d) \tag{3}$$

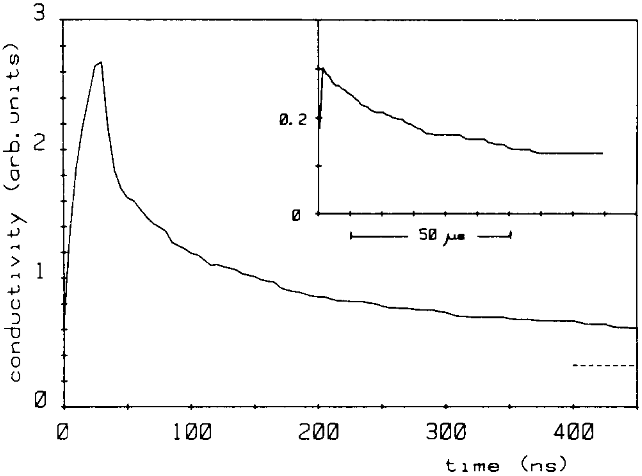

Fig 1 Time dependence of the conductivity in CCl_4 at 20°C and 10 kV/cm following a 30 ns pulse of 3 5 MeV electrons (total dose ~ 2 Gy). The dashed line represents the conductivity as derived from back extrapolating the zero time the conductivity transient observed on a timescale of 10 μs per division shown in the insert

In (3), E_d is the field strength required to double the free ion yield and is given by the expression

$$E_d = \frac{8\pi\epsilon_0\epsilon_r k^2 T^2}{e^3} \tag{4}$$

In (4), ϵ_0 is the permittivity of free space, ϵ_r is the relative dielectric constant, k the Boltzmann constant, T the absolute temperature and e the electronic charge. For CCl_4 at room temperature $\epsilon_r = 2.23$ hence E_d is expected to be 20 kV/cm.

In order to check the value of E_d under the present conditions, conductivity measurements have been carried out at field strengths of 2.5 and 12.5 kV/cm for a low dose pulse (0.05 Gy). For this total dose the lifetime of free ions towards recombination should be approximately 1 ms and hence negligible decay should occur over a timescale of a few tens of microseconds. The conductivity transients are shown in Fig 2 after being corrected for a slight droop due to the fall time of 450 μs of the circuit used for these measurements. The ratio of the plateau conductivity values for 12 5 and 2.5 kV/cm is found to be 1.42 From this a value of $E_d = 21$ kV/cm can be estimated using equation (5) which is readily derived from equation (3) and applies for measurements made at any two different values of the field strength E_1 and E_2

$$E_d = \left[\frac{G_{fi}(E_1)}{G_{fi}(E_2)} E_2 - E_1\right] \Big/ \left[1 - \frac{G_{fi}(E_1)}{G_{fi}(E_2)}\right]. \tag{5}$$

This value for E_d is in good agreement with that expected on the basis of equation (4) and is identical with the value found by Casanovas[16] within the errors of the measurements

Using this value of E_d the actual $G_{fi}(E)$ values at 2 5 and 12.5 kV/cm are determined to be 0.105 and 0 152 $(100\,\mathrm{eV})^{-1}$, respectively. The conductivity data in Fig. 2 are in fact presented in terms of G-values with the plateaus equal to the corresponding $G_{fi}(E)$-values.

The extremely long tail of the geminate decay can be clearly seen during the first 10 μs in Fig. 2 for the lowest field strength. For comparison the time dependence expected on the basis of equation (2) for zero applied field is plotted in Fig 2. The form of the curves can be said to be in at least qualitative agreement with the predictions of the field strength effect on the survival probability calculated by Hong and Noolandi.[1]

Finally in Fig. 3 are shown the fastest time resolution data that we have been able to measure using the present d.c technique. The results were obtained using a 10 ns pulse (0.7 Gy) The data are plotted as an effective G-value of ion pairs at a given time and for a given field strength, "$G(Et)$", which is derived from the conductivity data using

$$\text{“}G(Et)\text{”} = \frac{\sigma(Et)}{\sigma_{fi}(E)} G_{fi}(E) \tag{6}$$

In (6) $\sigma_{fi}(E)$ is the conductivity which would result from the free ions in the absence of second order recombination and which can be obtained by back extrapolation of low dose, long-time data It is appar-

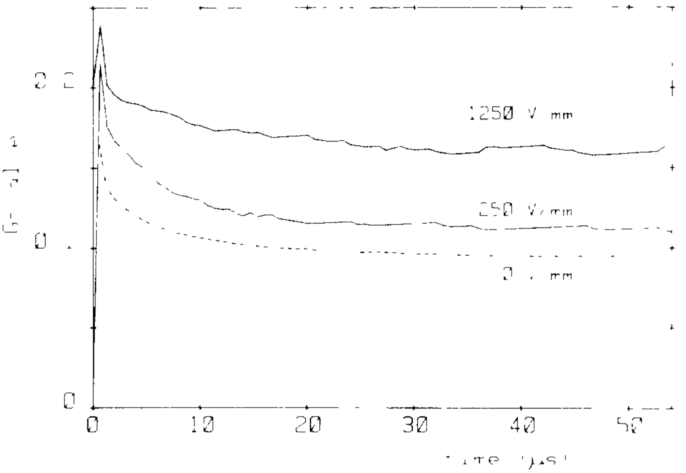

FIG. 2. Effect of the applied field on the time dependence of the yield of ions in CCl_4 at 20°C. A 10 ns pulse of 3.5 MeV electrons with a total dose of approximately 0.05 Gy was used. The dashed curve was calculated using the free ion yield of 0.095 $(100\,eV)^{-1}$, (see Refs 5, 12, 13) and the $t^{-0.6}$ relation which has been found to describe the ion pair survival probability at long times (see Refs 4, 5) in the absence of an applied field.

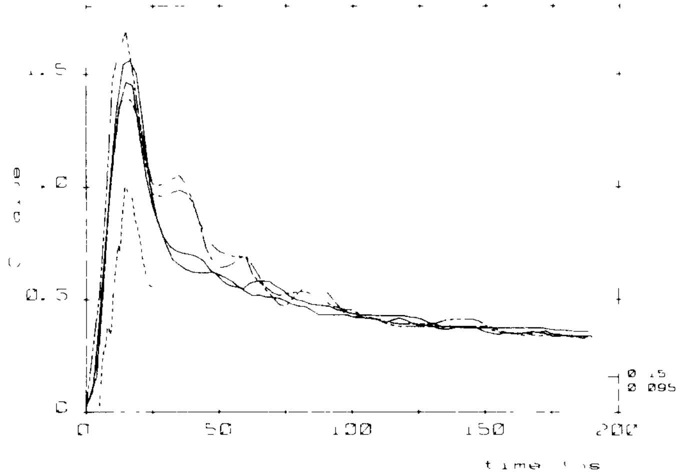

FIG. 3. The time dependence of the yield of ions in CCl_4 at 20°C following a 10 ns electron pulse. The upper curves were obtained using the d.c. technique (total dose ~0.7 Gy). For the upper full curves the hybrid junction was used together with the virtual earth amplifier (t_{10-90} ~ 10 ns), while for the upper dashed curves the hybrid alone was used (t_{10-90} ~ 3.5 ns). The lower dashed curve was obtained with the microwave technique (total dose ~ 100 Gy, t_{10-90} ~ 1 ns) (see Refs 4, 5). The horizontal dashed and full lines at the right represent the free ion yield for zero field and 12 kV/cm, respectively.

ent that effective yields of approximately one, corresponding to six times the free ion yield for the field strength of 12.5 kV/cm, can be detected. The yields observed using the d.c. conductivity technique appear in fact to be even larger than the yields observed at short times by microwave measurements as is shown by the comparison with the microwave transient[4, 5] in Fig. 3. It is the intention to carry out a more thorough quantitative analysis of the data obtained check this point. The comparison in Fig. 3 should, therefore, be considered to be provisional and only semiquantitative at the present time. It is to be hoped that a more quantitative comparison with theoretical calculations can be presented in a future publication.

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