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The Photodissociation of Tetramethyldioxetane.

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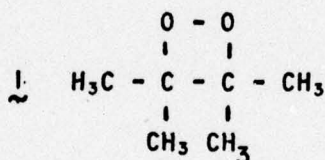
ABSTRACT

Tetramethyldioxetane was excited with a single 10 psec pulse at 264 nm. The resulting acetone fluorescence was observed and the rise time was found to be less than 10 psec. A mechanism accounting for this and previous experimental evidence is proposed.

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INTRODUCTION

Dioxetanes are an interesting class of molecules, for upon thermal decomposition an excited state product may be formed. For tetramethyl dioxetane, the electronically excited products of thermolysis have been identified as triplet and singlet acetone. When tetramethyldioxetane is excited with ultraviolet light it decomposes into either singlet or triplet excited acetone fragments [1]. The wavelength of the exciting light determines in part the ratio of singlet to triplet products. We were able to examine this reaction using picosecond spectroscopy and based upon our results we propose a mechanism which may explain both the thermal and photolytic decomposition.



EXPERIMENTAL

The experimental apparatus [see Fig. 1] uses a passively mode locked neodymium glass laser to generate a train of picosecond pulses which are separated by about 9 nsec. A single pulse is selected by use of a nitrogen spark gap which triggers a Pockels' cell, allowing a single pulse to pass through crossed polarizers. The single pulse is amplified by two additional glass rods and converted to the green with an angle tuned KDP crystal. After the remaining $1.06\ \mu$ light is filtered out, the pulse passes through an angle tuned ADP crystal producing the fourth harmonic at a wavelength of 264 nm. The U.V. light is reflected by a dichroic mirror and is transmitted through a glan air polarizer to extinguish any residual green light in the excitation beam. The U.V. beam is again reflected by another dichroic mirror followed by a quartz lens which focuses the radiation onto the sample. The majority of the green light transmitted by the first dichroic mirror is reflected by an aluminum mirror on a path shorter, but parallel to the excitation beam. This green light is used to establish a consistent time base for the short time scale experiments and allows one to monitor the exciting pulse.

The fluorescence was observed using a Hamamatsu streak camera. For short time scales the output of the streak camera was coupled into an RCA SIT camera. This camera was interfaced to a digitizer constructed by our electronics shop. The information from the digitizer was then read into a NOVA 3 computer.

The dioxetane was synthesized by the procedure of Kopecky [2] and purified by sublimation and recrystallization from pentane. Acetonitrile was

the solvent and showed negligible impurity fluorescence. No change in the absorption spectrum was seen following the picosecond experiments indicating that insignificant thermal or photochemical decomposition of the tetramethyldioxetane had occurred.

RESULTS

Photoexcitation of tetramethyldioxetane yields both triplet and singlet excited products. The singlet excited product observed in this experiment may be attributed to the formation of acetone. The fluorescence from excited dioxetane and excited singlet acetone have nearly identical lifetimes [Fig. 2], ~ 2 nsec [3]. This value is in good agreement with the accepted values for acetone [4]. Although acetone and dioxetane have quite different absorption spectra their fluorescence spectra are identical and chemical trapping experiments have shown that singlet acetone is formed upon photodecomposition of dioxetane [5]. These results demonstrate that the nanosecond luminescence from photoexcited dioxetane is due to acetone fluorescence.

If any detectable intermediates were present in the photodecomposition of dioxetane to singlet acetone, they could best be observed as a change in the rise of the resulting acetone fluorescence. At the fastest streak camera speed, the signal-to-noise ratio was so low, that no evaluation of the rise was possible. To improve the signal-to-noise ratio, signal averaging was used. To average one must first establish a reliable time base to overcome the effects of jitter in the streak camera. Owing to the weakness of the signal, the beginning of the fluorescence could not be accurately determined. The prepulse was used to insure proper addition of the signals. (See Experimental). For the measurement of the fluorescence rise, the optical path of the prepulse was adjusted so that it arrived at the photocathode of the streak camera 50 psec before the onset of the tetramethyldioxetane emission.

The conversion of the 528 nm picopulse to the 264 picopulse was carried out by a nonlinear process. Therefore the green prepulse could not be used to monitor the size of the excitation. The risetime experiments were carried out with a sweep speed of the streak camera which corresponded to 600 psec full scale. Over this period the fluorescence of acetone decays by only about 25%.

Therefore we could select laser pulses of roughly the same intensity by averaging the data taken well after the appearance of the fluorescence and using this average as a measure of the size of the exciting pulse. This was done visually by examining a display of each digitized streak record and selecting data which differed by no more than a factor of 3. In addition, data was chosen so that the prepulse appeared in the first third of the streak record. The time base of the streak camera was calibrated with a variably spaced etalon consisting of two 90% reflectors at 528 nm. The time base was found to be uniform within about 10%. To test the averaging procedure, the lifetime of methyl salicylate was recorded with a single pulse. This was compared to the lifetime measured by averaging data from a series of much weaker excitation pulses. The agreement between the two was very good. This gave us confidence that our averaging procedure was working properly.

The results from signal averaging on the shortest time scale are shown in Figure 3. The inset peak (open circles) is a reduction of the green peak which was much more intense than the fluorescence. Examination of the prepulse shows a FWHM of 20 picoseconds. This does not indicate the true temporal width of the laser, but rather it is a convolution of the streak camera response with the green laser pulse. The rise of the fluorescence from the dioxetane was identical to the integral of the prepulse. Identical results were obtained when we studied the rise of the acetone fluorescence [3]. We feel that the risetime observed for both acetone and dioxetane are limited by the resolution of the detection system. The use of deconvolution techniques [6] show that the rise of the fluorescence must be less than 10 psec for both dioxetane and acetone.

DISCUSSION

There has been a great deal of debate involving the mechanism for thermal decomposition of dioxetane. Two different schools of thought have developed. One group contends that O-O bond cleavage precedes excited state formation while the other group favors a simultaneous break of the O-O and C-C bonds. McCapra [7] and Kearns [8] originally proposed the latter mechanism to explain the formation of excited state products from dioxetanes. Turro furthered this approach by postulating that a spin flip could occur during this cleavage allowing for the formation of triplet products [9]. MINDO/3 calculations have been carried out. They indicate a concerted reaction [10]. Substituent effects showed that variation of the β groups had little effect on the reaction rates. On the basis of these substituent effects Richardson proposed a step-wise reaction, with initial O-O bond cleavage leading to formation of a biradical [11]. In a recent study Koo and Schuster have found that there was no evidence of a secondary isotope effect upon replacing an α -hydrogen with deuterium in trans-diphenyl dioxetanes [12], indicating that there was no change in hybridization at the isotopically substituted carbon during the rate determining step. Differential quenching experiments have also indicated the formation of a biradical in the thermal decomposition [13]. These recent findings implicate a reaction passing through a biradical intermediate.

No definitive mechanism has yet been provided for the photolytic decomposition of dioxetane. Any proposed pathway must explain three experimental results. The singlet yield is much greater for the photolysis than for the thermolysis. The singlet quantum yield increases with decreasing wavelength of the exciting light. Finally, this mechanism must provide for

the fact that no intermediates were found with a lifetime greater than 10 picoseconds.

It is highly unlikely that photolysis proceeds by the same route as thermolysis. The wavelength dependence of the singlet-to-triplet ratio could not be explained if these two pathways were the same. Also it would be hard to rationalize identical mechanisms unless the biradical was formed in less than 10 picoseconds. Experiments are being performed which will measure the rate of formation of the triplet product, and provide information concerning the lifetime of any intermediates in this process.

The two dimensional representation (Figure 4) of the multidimensional reaction surface illustrates a mechanism which is consistent with all three experimental observations. Absorption of a photon excites the dioxetane to a point on the potential surface from where it may dissociate to singlet acetone with a rate k_1 . This rate is limited by the need to place sufficient energy in the reactive vibrational modes. This direct dissociation would presumably take place within a few vibrations accounting for the fact that no risetime was observed. In competition with decay of the initial excited state, the dioxetane can also undergo relaxation (k_2) to a metastable region of the potential surface. Once in the metastable region, the molecule can undergo a radiationless transition resulting in biradical.

Increasing the energy of the photons populates portions of the initial surface in which the gap between the initial surface and the metastable one is much larger. Therefore the rate of relaxation is decreased. One would not expect the rate of dissociation to be slowed as one excites higher and higher on the initial surface. Therefore the yield of singlets formed by this mechanism would be expected to increase with respect to the metastable intermediates. This change in relative yield will be reflected in the increase of singlet products with respect to triplet products as

the wavelength of the exciting light is decreased. Since the potential surface is actually multidimensional, additional data may require modification of our simple reaction scheme. However, at present it can account for all of the experimental observations.

The experiment has shown that photodissociation of dioxetane leads to acetone fluorescence in less than 10 picoseconds. A proposed reaction surface predicting concerted bond cleavage for singlet formation and stepwise dissociation for thermolysis explains these facts. This surface shows photolysis and thermolysis to proceed by parallel but separate pathways.

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FIGURE CAPTIONS

- Fig (1) Block diagram of laser apparatus; S = sample, F = filters.
- Fig (2) Fluorescence decay from photoexcited acetone (A) and from photoexcited dioxetane (B).
- Fig (3) Rise time of acetone fluorescence from the excitation of dioxetane. The intense pulse on the left is the green synchronization pulse. The open circles represent the reference pulse normalized so that it may be displayed on the same scale as the fluorescence.
- Fig (4) Reaction coordinate diagram for the thermal and photochemical reactions of dioxetane \sim .

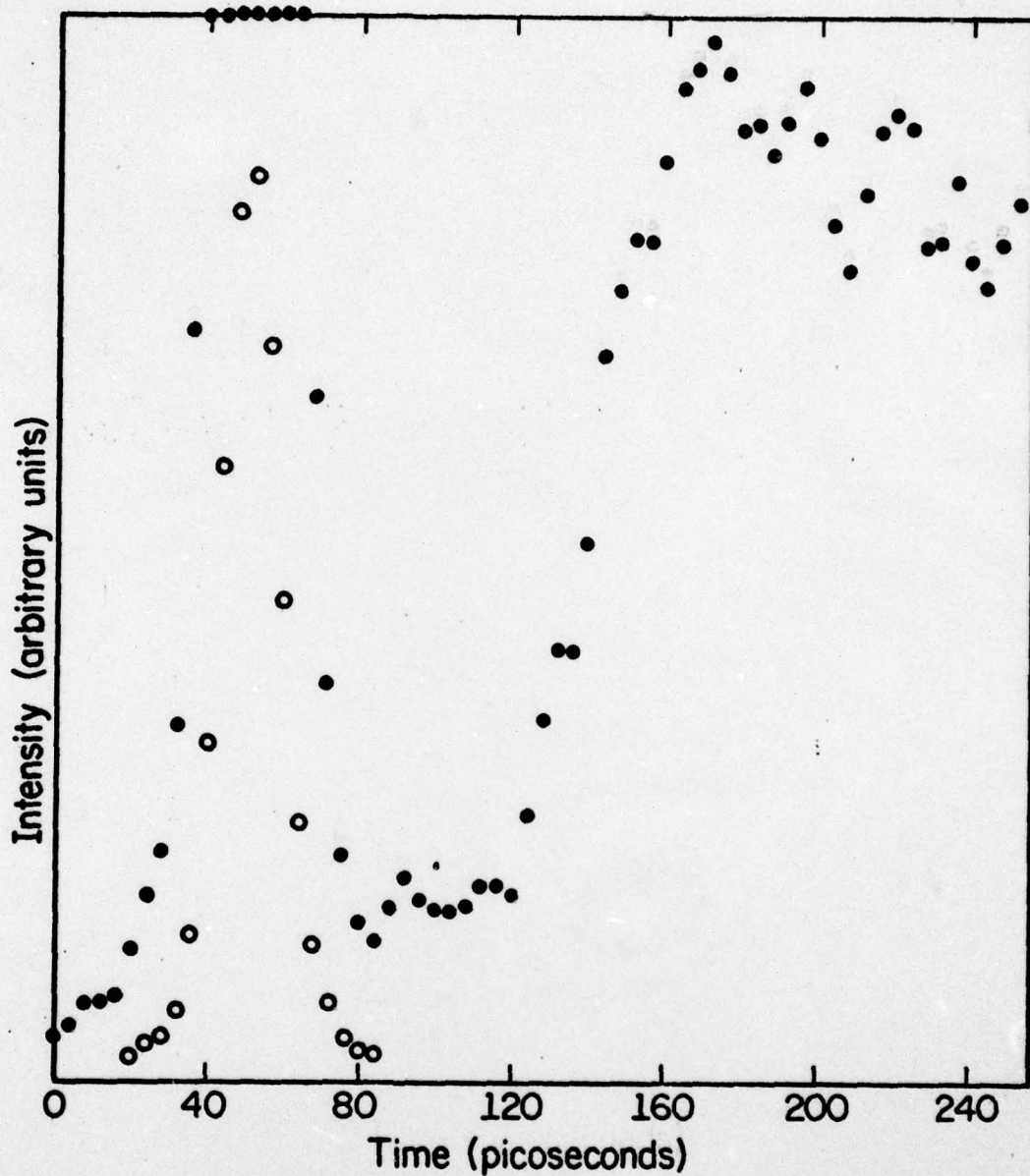


Figure 3.

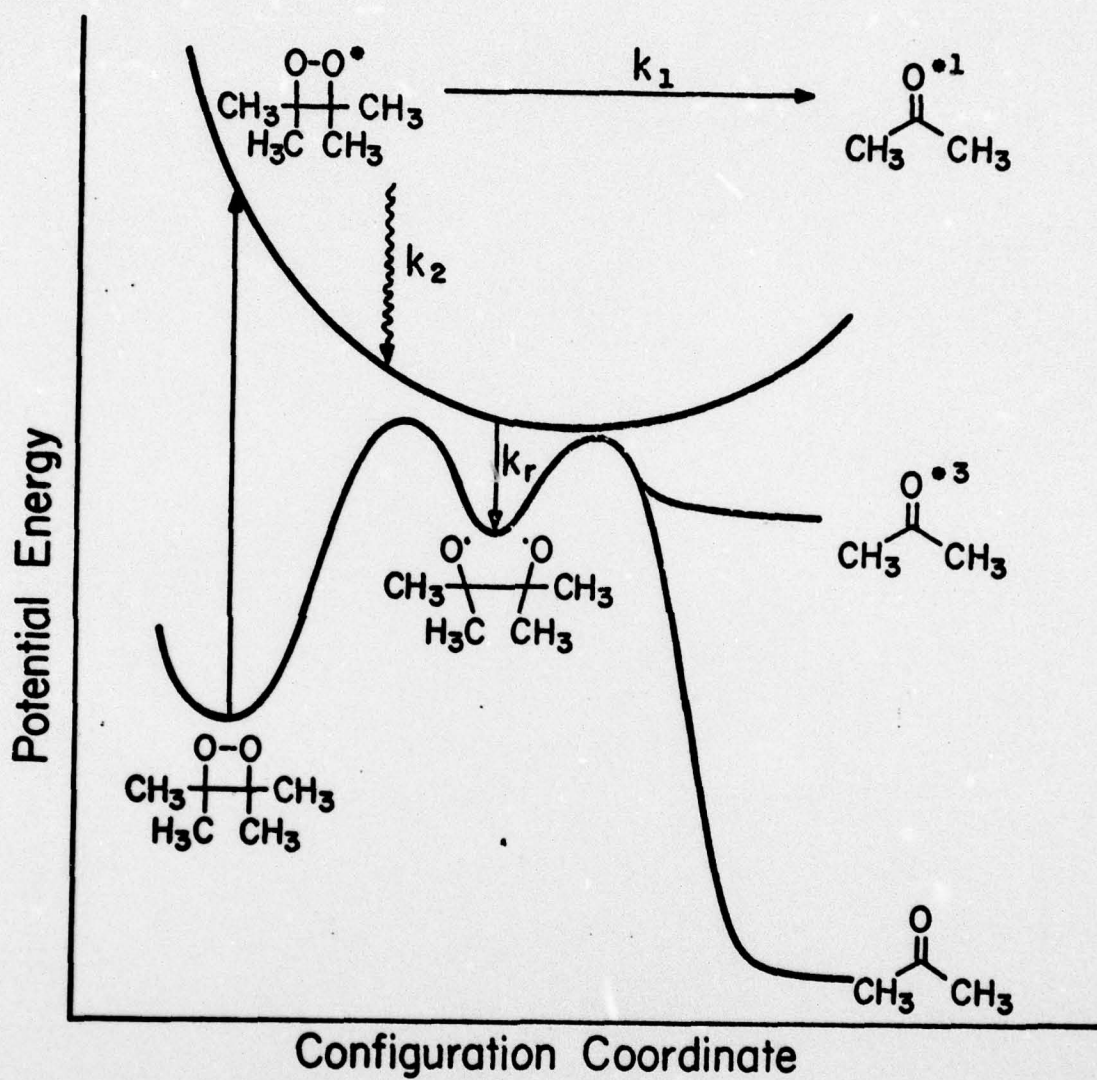


Figure 4

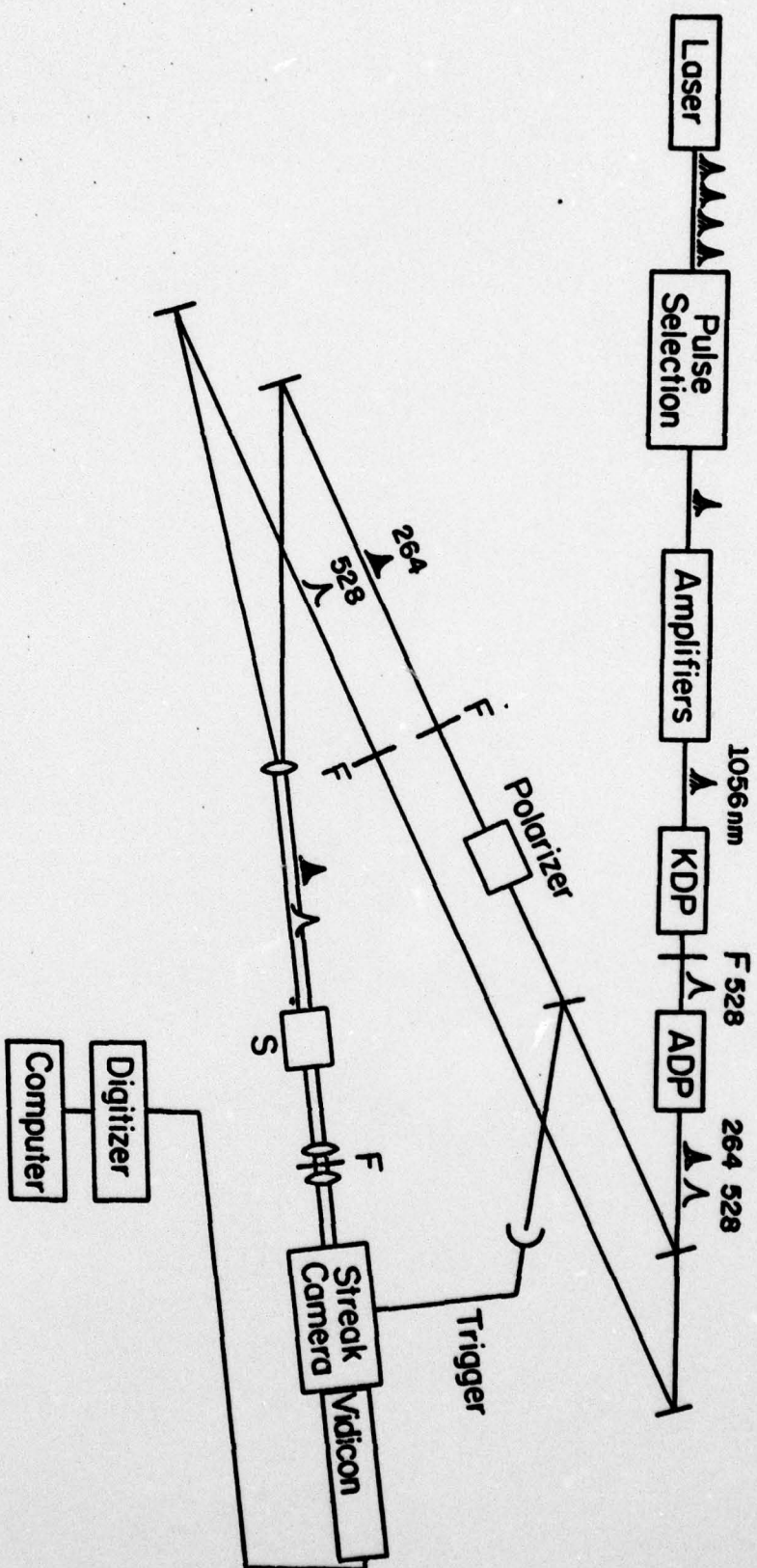


Figure 1.

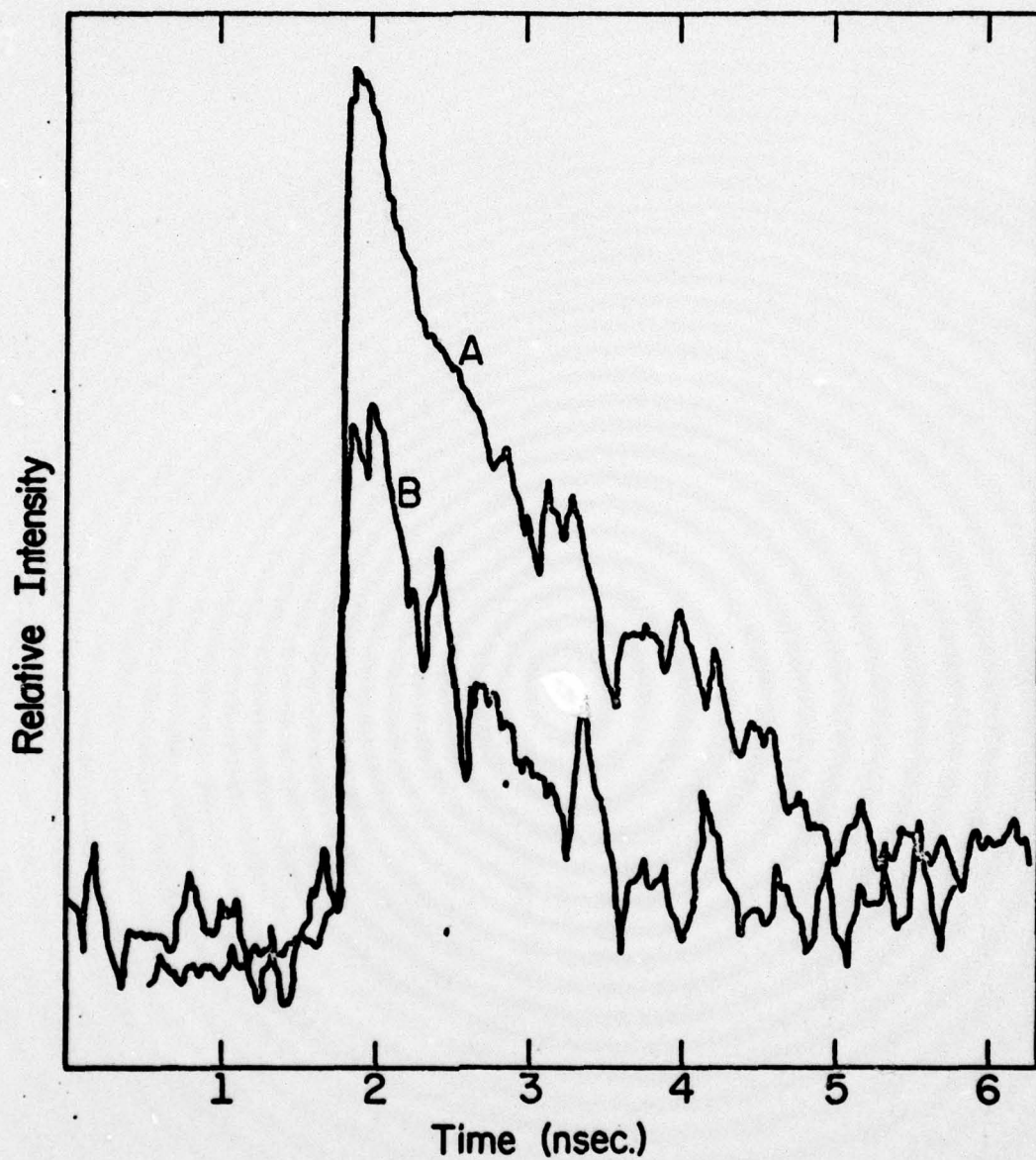


Figure 2.

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