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Fourier Transform EPR of Chemical Reactions

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ABSTRACT

Transient free radicals formed by laser photolysis have been measured in solution by Fourier Transform Electron Paramagnetic Resonance. The high resolution spectra positively identify the initial free radicals formed from the quenching of triplet duroquinone by triethylamine in solution. The spectra were used to follow the kinetics of the free radicals from less than 10^{-8} s to 10^{-2} s. The kinetics are well described by a model based on simple chemical reactions and triplet mechanism chemically-induced dynamic electron polarization. Numerical estimates are obtained for ratios of the rates of various reaction steps.

INTRODUCTION

Direct-detection Electron Paramagnetic Resonance (EPR) and electron spin echo techniques are often used for the study of photo-initiated, free-radical reactions in liquid solution[1]. While magnetic resonance is uniquely sensitive to free radicals, these two techniques have serious limitations. 1) At short times after the radicals are formed, the direct-detection EPR signal depends as strongly on instrumental parameters and spin relaxation parameters as on the electron spin magnetization. 2) At long times, the continuous microwaves present in the direct-detection techniques drives the electron spin magnetization and alters the measured signal. 3) The spin echo technique, because of poor spectral resolution, has difficult, in identifying and quantifying free radicals with overlapping or closely-spaced lines. 4) The sensitivity and signal amplitudes depend strongly on relaxation times and sample dielectric properties, making comparison between samples of different polar liquids difficult. These problems are eliminated by the use of Fourier transform (FT) EPR methods[2].

We describe here the application of FT-EPR to the measurement of the kinetics of the duroquinone radical anion formed from the excited triplet state of duroquinone by electron transfer. The sample magnetization, M_0, is produced by laser photolysis in our experiments and is aligned initially along the direction of the external magnetic field $\hat{z}$. The microwave pulse rotates M_0 into the plane perpendicular to $\hat{z}$ where it produces a free induction decay (FID) which is the observable in the experiment. The FID, which persists for about 1 μs, reports the frequencies, amplitudes and phases of every component of M_0 present at the time of the microwave pulse. The FID completely describes the EPR spectrum of the free radicals present at the instant of the microwave pulse. Thus, the FID contains the desired information about the free radicals and is free of the experimental artifacts described above.

EXPERIMENTAL

Our FT-EPR spectrometer uses 6 ns, 1 KW microwave pulses to generate FIDs from a sample volume of about 20 mm^3. Both quadrature components of every FID are digitized at 10 ns intervals and summed with the corresponding values from previous FIDs. A total of 512 points is measured for each quadrature component. The CYCLOPS phase cycling scheme is implemented to remove experimental artifacts. EPR spectra are obtained from the FIDs by Fourier transformation. The FT-EPR spectrometer[2a] will be described in detail in a later publication.

The triplet state of duroquinone is generated by photolysis of duroquinone (DQ) with the focused 308 nm output of a Lambda Physik EMG-50E excimer laser using XeCl. The laser pulse repetition rate varied between 40 and 100 Hz. FIDs were recorded with the time, t_d, between the laser trigger pulse and the microwave pulse held constant.

Duroquinone (DQ) was purified by recrystallization to remove the hydroquinone, further purification produced no detectable changes in the kinetics or yields. Solutions of 10 mM DQ in methanol containing from 0.01 to 3.0 M TEA were recirculated through a 4 mm O.D. spectrosil tube in the FT-EPR resonator. The solutions were bubbled with high-purity nitrogen to eliminate oxygen. Reagent grade methanol and triethylamine (TEA) were used as received.

RESULTS AND DISCUSSION

FT-EPR spectra of the duroquinone radical anion taken with $t_d = 0.60$ μs and 200 μs are shown in Figure 1. For small t_d, the DQ radical anion EPR spectrum is strongly spin polarized in emission, a result of triplet mechanism chemically induced dynamic electron polarization (CIDEP)[1,3]. At longer t_d, the spectrum inverts and approaches Boltzmann equilibrium. EPR lines with EPR frequencies greater than the central line of the spectrum are more intense than the corresponding lines with frequencies less than the central line for long t_d. This polarization effect is due to the radical pair mechanism (RPM) CIDEP. More pronounced RPM polarization is prevented by electron transfer from the DQ radical anion to a neutral DQ molecule. The electron transfer rate measured in a FT-EPR multiple pulse experiment[4] during laser photolysis is $2.4 \times 10^6\ s^{-1}$.

Even when the microwave pulse overlapped the laser pulse, no durosemiquinone radical (DQH·) is observed even though it is easily observed under identical conditions in solutions of isopropanol and DQ. This means that either the quenching of the DQ triplet state by TEA takes place via a charge transfer reaction or that hydrogen atom transfer produces DQH· followed by rapid deprotonation within the 6 ns deadtime of the measurement. In the absence of a strong base, deprotonation requires a second TEA molecule to act as a proton acceptor. At the lowest TEA concentrations used, a second order rate constant in excess of $10^{10}\ M^{-1}s^{-1}$ for deprotonation of DQH· is required to prevent its observation. This rate exceeds the diffusion controlled rate constant, indicating that the quenching of triplet DQ by TEA in methanol proceeds via a charge transfer mechanism.

Triplet quenching by a charge transfer mechanism leads to the following scheme for DQ radical anion production:

$$\mathrm{DQ} \xrightarrow{h\nu} {}^{1}\mathrm{DQ} \longrightarrow {}^{3}\mathrm{DQ}^{*} \qquad [1]$$

$$ {}^{3}\mathrm{DQ}^{*} \xrightarrow{k_3} {}^{3}\mathrm{DQ} \qquad [2]$$

$$ {}^{3}\mathrm{DQ}^{x} \xrightarrow{k_\theta} \mathrm{DQ} \qquad [3]$$

$$^3DQ^x + TEA \xrightarrow{k_Q} DQ^{\cdot - x} + TEA^{\cdot + x} \qquad [4]$$

$$DQ^{\cdot - *} \xrightarrow{k_1} DQ^{\cdot -} \qquad [5]$$

$$2DQ^{\cdot -} \xrightarrow{k_r} DQ + DQH_2 \qquad [6]$$

$$TEA^{\cdot + x} + DQ \xrightarrow{k_d} DQ^{\cdot - x} + TEA\ \mathrm{product} \qquad [7]$$

The * superscript denotes a spin polarized species and the ^{x} superscript denotes either a spin polarized or unpolarized species. Reaction 3 includes self-quenching and triplet-triplet annihilation processes as well as unimolecular intersystem crossing. Radicals derived from the TEA are not observed here because of their rapid reaction with ground state DQ by reaction 7 and because of their rapid spin-spin relaxation[3]. This scheme is similar to that used in previous studies[3] except for the inclusion of reaction 3.

The intensity of the central EPR line is plotted in Figure 2 as a function of t_d for TEA concentrations of 2.4 M and 0.15 M. The central line is used since it is unaffected by radical pair mechanism CIDEP from the disproportionation of the DQ radical anion. The solid lines through the data points are a least-squares fit to the data of the reaction yields based on reactions 1-7:

$$S(t_d) = a_0 \{\exp(-a_1 t_d) - \exp(-a_3 t_d)\} + a_4 \{1 - \exp(-a_3 t_d)\} / (1 + a_2 a_4 t_d) \qquad [8]$$

where a_0 and a_4 are the intensities of the spin polarized and the equilibrium signals respectively, a_1 is the DQ radical anion spin-lattice relaxation rate, a_2 is the disproportionation rate and a_3 and a_5 are the rates of the rise of the signals. Even though the TEA concentrations differ by a factor of 16, the rates for the two samples shown in Figure 2 are virtually identical (a_3 = 22.4 and 22.9 MHz, a_1 = 0.27 and 0.28 MHz. The risetime of the strongly polarized EPR signal is not determined by the reaction rate, but rather, by the loss of polarization within the triplet state with a time constant $^3T_{1e}$, the triplet spin-lattice relaxation time and the time profile of the laser pulse. The decay of the strongly polarized signal within 10 μs is the result of spin-lattice relaxation of the DQ radical anion with a time constant $^2T_{1e}$. The very slow decay of the signal at times longer than 100 μs is the result of the disproportionation of the DQ radical anions.

Even though the rates of the chemical reactions are different for the two samples in Figure 2, the shapes of the kinetic curves are the same. The major differences are the quantitative amplitudes of the two curves. Those amplitudes contain the information about the chemical rate constants of the reactions and are given by:

$$a_0 = \frac{(1-\gamma)\,[^3DQ]_0\, k_Q\,[TEA]}{k_1-k_3-k_Q[TEA]-k_\theta} \qquad [9]$$

$$a_4^{-1} = [^3DQ]_0^{-1} \quad (1 + \frac{k_\theta}{k_Q[TEA]}) \qquad [10]$$

where $[^3DQ]_0$ is the initial yield of DQ triplets and γ is the initial spin polarization of the DQ triplets. The variation of a_0 and a_4 with TEA concentration is easily quantified by FT-EPR, in contrast to direct detection EPR or electron spin echoes. The FT-EPR resonator is strongly-overcoupled and has a very low quality factor Q, making the signal intensity independent of the dielectric properties of the sample solution. Furthermore, the integral of an EPR line is independent of relaxation times. This allows direct comparison of EPR intensities from different solutions. Equations 9 and 10 show that the EPR signal intensities depend on ratios of the quenching rate k_Q with either the triplet decay rate k_θ or the triplet spin-lattice relaxation rate $k_3 = (^3T_{1e})^{-1}$. Since the triplet spin-lattice relaxation time is on the order of a nanosecond in non-viscous liquids[5] and the triplet lifetime in the absence of quencher can be as long as a millisecond for some molecules, k_Q can be measured, in principle, by FT-EPR if it lies between 10^{11} and 10^3 $M^{-1}s^{-1}$. For 10 mM solutions of DQ in methanol, we obtain values of k_3/k_Q = 5.53 M and k_θ/k_Q = 0.0899 M.

CONCLUSIONS

We find that FT-EPR has several advantages for the study of fast free-radical reactions in solution. 1) High resolution EPR spectra are obtained which can positively identify the free radicals involved and provide information about the reaction mechanisms. 2) The sample magnetization, which is measured at a well-defined time (approximately 6 ns aperture), allows the evolution of the electron spin magnetization to be followed directly. 3) Microwaves are not applied to the sample until the instant of the measurement so that spin evolution is not perturbed prior to the measurement. 4) The use of multiple-pulse sequences allows the measurement of rates which otherwise are not directly accessible. 5) The ability to compare signal amplitudes from different samples allows the measurement of reaction rates over an extremely wide range.

ACKNOWLEDGMENTS

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FIGURE CAPTIONS

1. FT-EPR spectra from the duroquinone radical anion produced by a 308 nm laser pulse in a deoxygenated solution of 10 mM duroquinone and 0.65 M triethylamine in methanol. A) Emission spectrum taken 0.60 μs after the laser. B) Absorption spectrum taken 200 μs after the laser pulse. The emissive spectrum is about 80 times more intense than the absorptive spectrum as indicated by the signal intensity scales.

2. The intensity of the central FT-EPR line as a function of time after the laser pulse. The symbols represent the data points while the solid lines are least-squares fits of equation 8 to the data. A) 10 mM duroquinone and 2.4 M triethylamine in methanol. B) Solution containing 10 mM duroquinone and 0.15 M triethylamine in methanol.

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Fig 1A

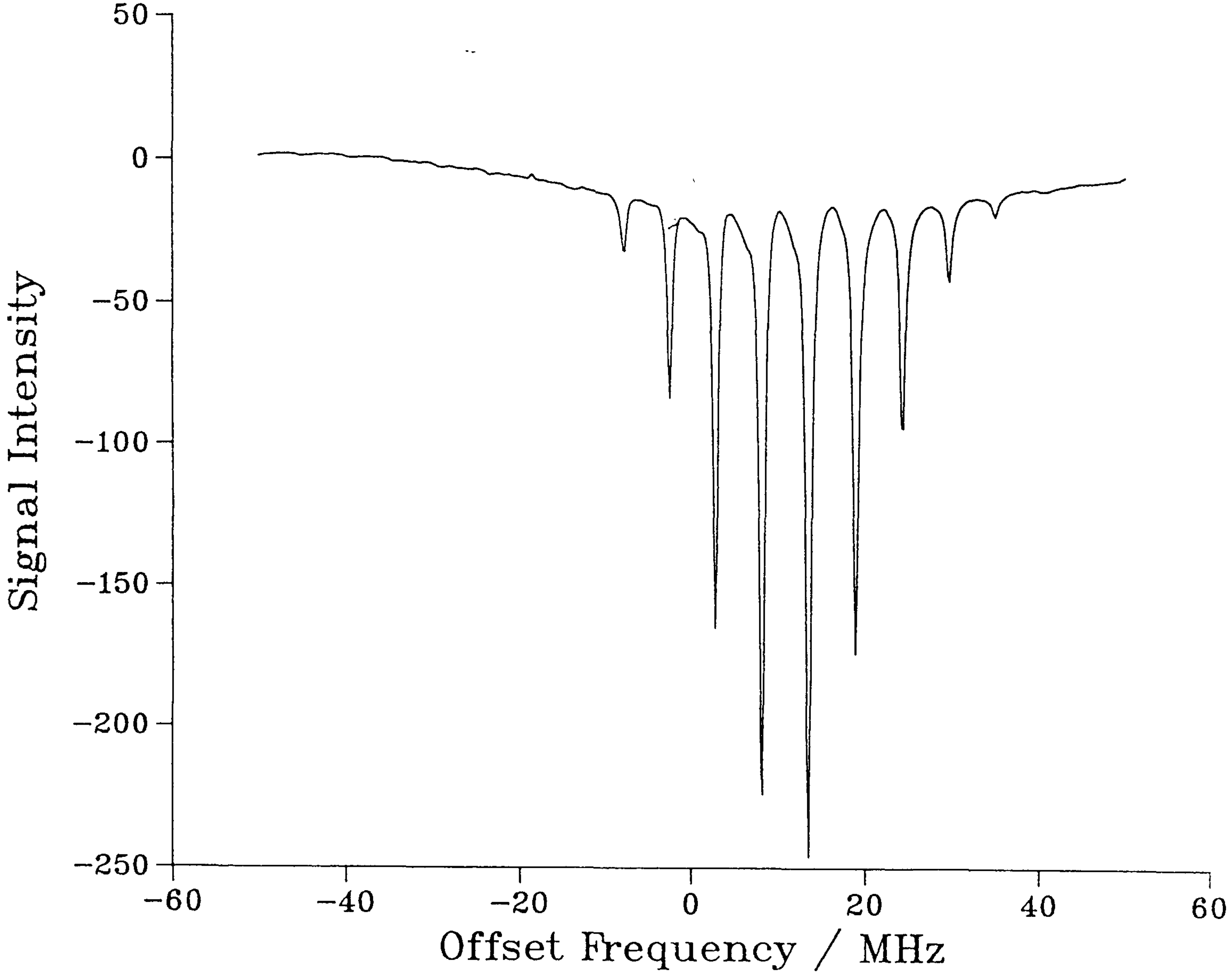
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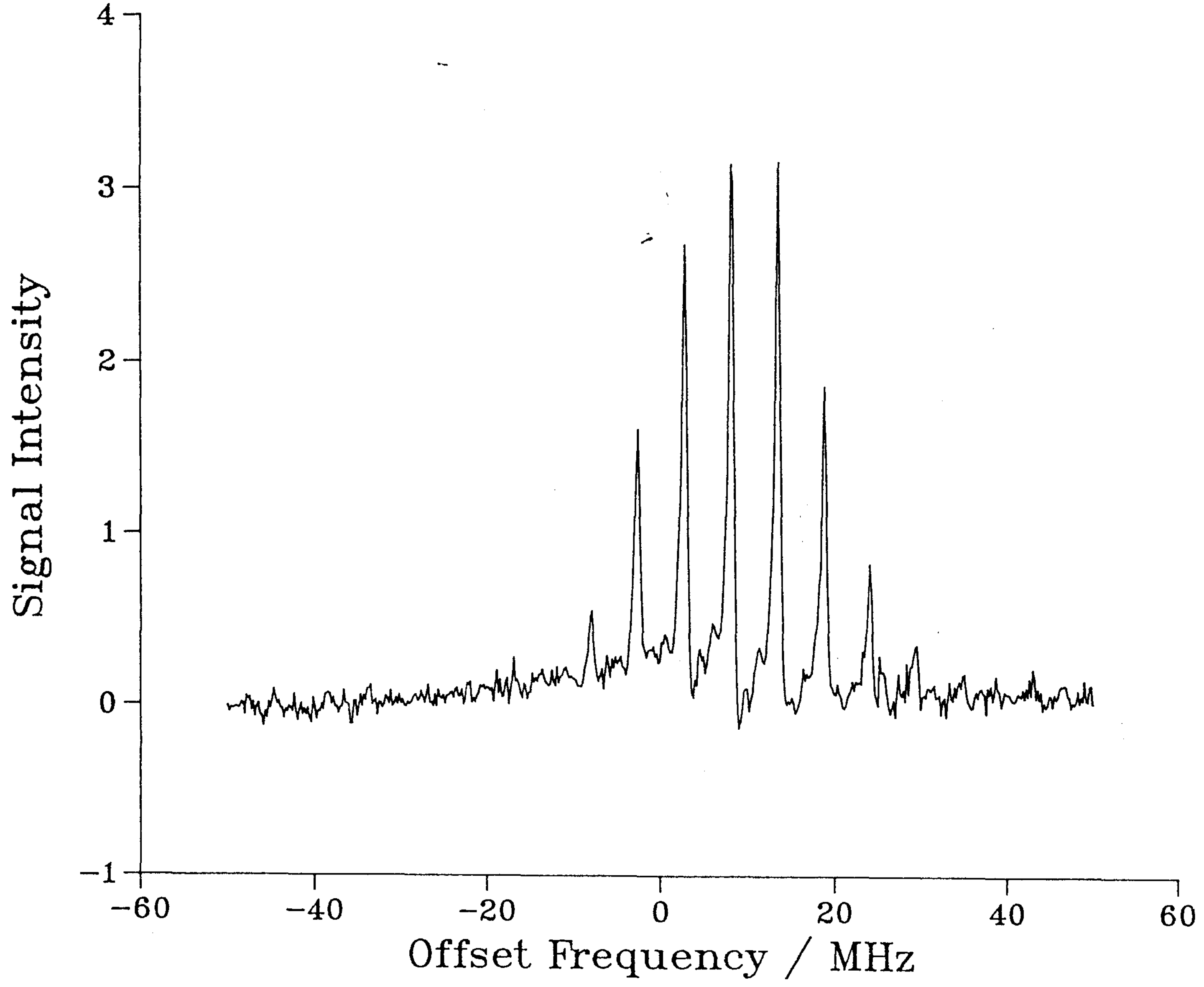
Fig 1B



Signal Intensity
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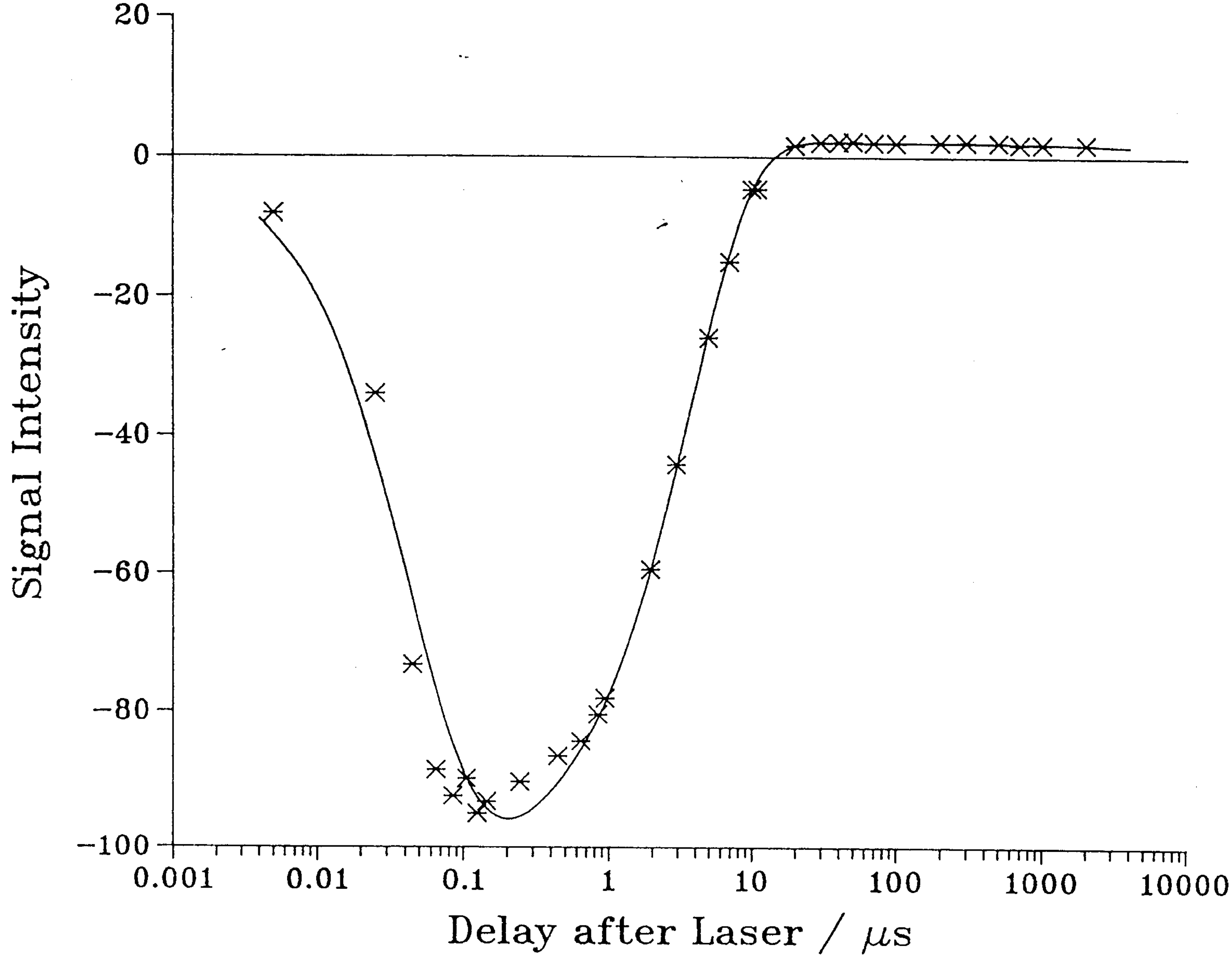
Fig. [illegible]



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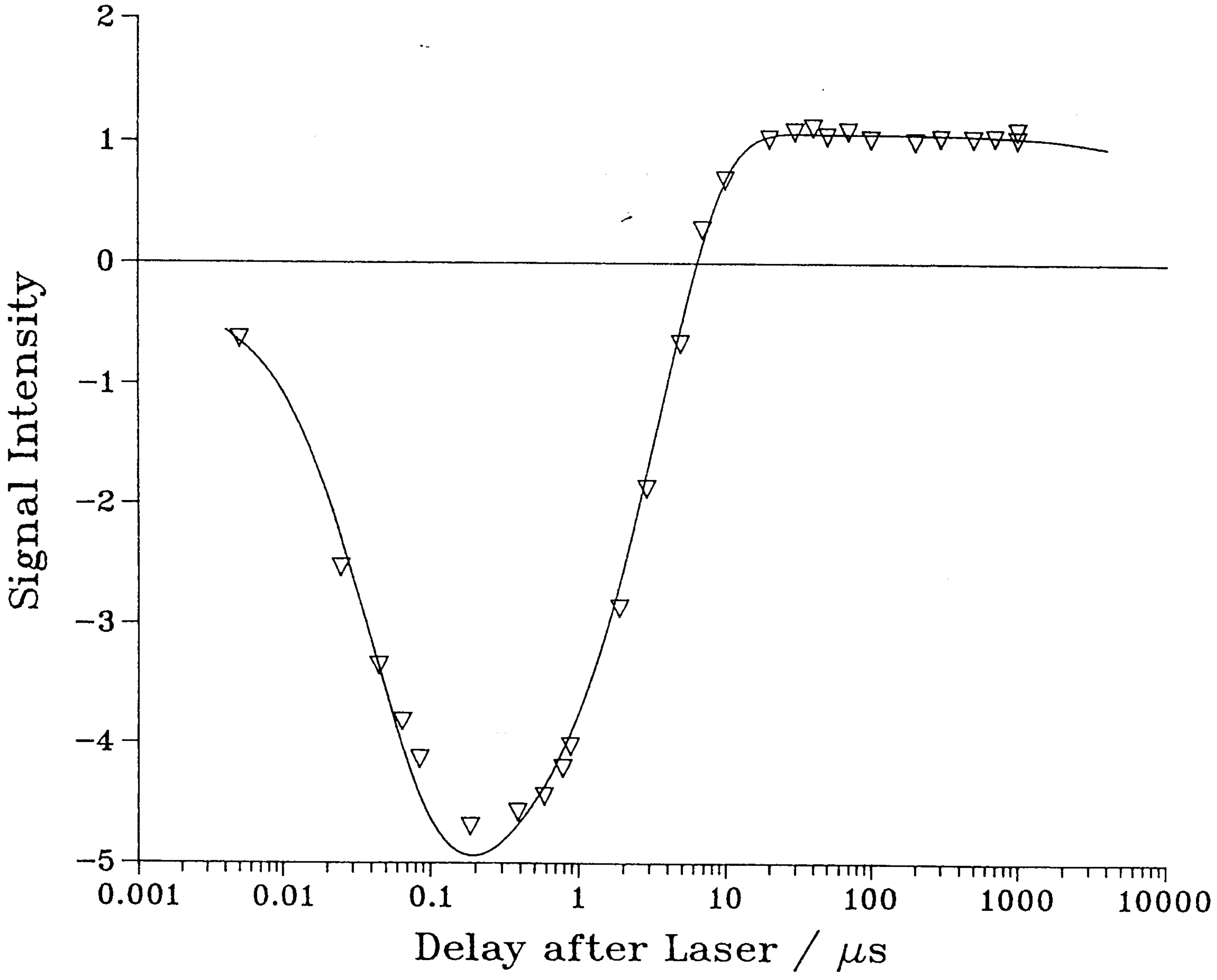
Delay after Laser / μs

Fig. 13



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Delay after Laser / μs