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RELAXATION OF POLAR ORIENTATIONAL ORDER IN NONLINEAR OPTICAL POLYMERS BY SECOND HARMONIC GENERATION

C. H. Wang, H. W. Guan and S. H. Gu
Department of Chemistry
University of Nebraska-Lincoln
Lincoln, NE 68588-0304
USA

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ABSTRACT

An investigation of the decay of the second harmonic generation (SHG) signals from a main chain accordion and a guest/host nonlinear optical (NLO) polymer has been carried out. The shape of the decay of the SHG signal from the main chain polymer is stretched exponential with the width parameter, β , increasing with increasing temperature. The increase in β indicates a narrowing of the distribution of relaxation times. On the other hand, the SHG decay signal from the guest/host system is found to be better described by the sum of two single exponential functions with the first short time component affected strongly by the surface change effect and the second slow component associated with the relaxation of the macroscopic polarization. The time constant of the slow component is found to be successively increasing with the poling-decay cycle and it reaches a steady state value after several cycles. The relaxation time lengthening effect is obtained both above and below T_g ; however, the effect rapidly diminishes as the temperature is increased above T_g . The temperature dependence of the steady state relaxation time is not Arrhenius; the Vogel-Fulcher-Tamann equation gives a satisfactory fit to the temperature dependence data.

INTRODUCTION

Because of their potential applications in integrated optics, interest in polymeric nonlinear optical materials has grown rapidly during the past decade.¹ It is now well established that molecules containing an electron donor-acceptor substituted conjugated system exhibit large quadratic hyperpolarizabilities², β . To obtain bulk quadratic nonlinear optical (NLO) effects, non-centrosymmetric materials are required. By incorporating these molecules into the polymer system and then polarizing them with a strong dc electric field to remove the centrosymmetric environment, one can prepare a second order NLO material. The electric field polarizing process is known as poling. For application in frequency doubling or electro-optic devices, the poled polymer must maintain the polar order that has been created near the glass transition temperature of the NLO polymer. Therefore, an understanding of the underlying mechanism responsible for the relaxation of polar orientational order is of great interest.

In this paper we report recent results from our laboratory concerning the investigation of the relaxation behavior of two types of NLO polymers. One type involves NLO chromophores dissolved in the polymer hosts as guests and the other has the NLO chromophores covalently attached to the polymer to form a main chain polymer.

Experimental

The synthesis of the main chain accordion polymer used in this work has been described elsewhere by Lindsay et al.³. The synthesis of nitroaminostilbene (NAS) was carried out in our laboratory. NAS serves as the NLO chromophore, and the host polymer used in this work is polymethylmethacrylate (PMMA) ($M_w > 100$ K, Aldrich).

The NLO polymers were dissolved in appropriate solvents. For the main accordion chain polymer system, the solution was cleaned by centrifugation at 9,000 G for three hours to remove

undissolved particulates. In the guest host systems, various amounts of NAS were dissolved in the polymer solution to obtain different NAS concentrations. The solutions were filtered to remove undissolved particulates; thin, optically clear films (about 1 μm thickness) were prepared by spin coating the solution onto transparent conducting substrates (indium tin oxide, ITO, coated soda lime glass slides). The film thickness was measured with an α -stepper. The ITO coated slides containing polymer films were first placed in a vacuum oven at about 50°C for over 24 hrs and then baked for another 24 hrs at higher temperature (slightly above T_g) to obtain solvent free films. The glass transition temperatures, T_g , of all films were determined by a differential scanning calorimeter (DSC, Perkin Elmer, delta series). The variation of T_g of the NAS/PMMA system with the NAS concentration is shown in Fig. 1. In the NAS/PMMA system no evidence of phase separation was observed at the beginning for the sample containing up to 30 wt. % of NAS; however, after cycling the poling-cooling steps several times, phase separation occurs for films containing more than 15 wt. % of NAS. The concentration of the chromophores was monitored by UV-visible absorption spectroscopy. To complete the assembly of the guest/host sample for the optical experiment, two identical glass slides coated with NLO polymer films were then placed in a vacuum oven at a temperature higher than T_g to fuse them in a sandwich configuration for contact electrode poling. The corona poling technique was used to pole the main chain accordion polymer. For corona poling, a positive voltage potential of 3 KV was applied to a sharp tungsten needle located 1 cm in front of the polymer film surface. The contact poling or corona poling was conducted in dry air in an oven which housed the sample. Establishment of polar order as a result of poling and subsequent relaxation of the polar order were monitored by measuring the second harmonic generation (SHG) signal. The optical measurements were carried out at the same temperature as the poling process. The setup for SHG measurement was similar to that used in our previous work⁴. Basically it consisted of a Q-

switched Nd:YAG laser operated at 10 Hz. The fundamental beam at 1.064 μm was incident on the sample with the polarization in the plane of incidence. The SHG intensity of each sample was referenced to quartz. The intensity was detected with a PM tube and processed with a boxcar integrator which was interfaced to a personal computer.

RESULTS AND DISCUSSION

The SHG signal is proportional to the square of the second order optical susceptibility $\chi^{(2)}$, which in the case of the electric field poled amorphous NLO polymer consists of only two elements $\chi_{33}^{(2)}$ and $\chi_{31}^{(2)}$. For a molecule with a dominant β element, one can show that if the field-dipole interaction is less than kT , $\chi_{31}^{(2)}$ is equal to $\chi_{33}^{(2)}/3$. On the other hand, $\chi_{33}^{(2)}$ is larger than $\chi_{31}^{(2)}/3$ if the poling field is large such that the field-dipole interaction is greater than kT .⁵ The study of the decay of the SHG signal provides information on the time dependence of $\chi^{(2)}$ as a result of the reorientation of the chromophore dipoles.

We show in Fig. 2 the rise and decay SHG signals for the main chain accordion polymer at 176°C with and without thermal annealing. Without annealing, the SHG signal of the fresh sample overshoots and then decreases to a steady state value after about 1 hr. On the other hand, the SHG signal of the sample with 6 hrs of annealing at 176°C increases steadily to a steady state value. In both cases the rise in the SHG signal is very rapid; the decay is, however, considerably slower and depends on thermal treatment of the sample. One notes from the expanded decay portions shown in Fig. 3 that the fresh film decays much more rapidly than the film subject to 6 hrs of annealing at 175°C. In both cases the decay behavior is not single exponential. Best fits of the $\chi^{(2)}$ (proportional to square root of the SHG intensity) data to the Kohlrausch-Williams-Watts (KWW) function (the stretched exponential) given by

$$\chi^{(2)} = a e^{-(t/\tau)^\beta} \quad (1)$$

yield the value to τ and β . Here τ is the characteristic relaxation time, and β is the width parameters whose value is $0 \leq \beta \leq 1$. Values of β and τ for the fresh and annealed films at 176°C are given in Table I. The annealed film has a much smaller β value, indicating a wider distribution of relaxation times. We have further studied the temperature dependence of the decay of the annealed film. The KWW function fit to the decay curve gives the β and τ values as a function of temperature. These results are also given in Table I. One notes that above T_g the τ value decreases rapidly with increasing temperature; on the other hand, the β parameter increases with increasing temperature.

The time dependence of $\chi^{(2)}$, as represented by the decay of the SHG signal, after the poling field is removed, is due to reorientation of the electric dipoles, which results in decreasing polar order. The KWW functional representation suggests that the decay either has a distribution of relaxation times or has a complex nonexponential single relaxation process. In any case, we can infer the relaxation process by both the characteristic relaxation time τ and the width of distribution β . The increase in β implies that the distribution of relaxation times narrows to a single exponential as temperature is increased. This result is consistent with that found in side chain NLO polymers⁶; however, the data in ref. 6 corresponds to temperatures below T_g .

It is known that when a voltage is applied to a two-layer dielectric consisting of a layer with mobile ions and an insulating layer, a space-charge layer will be built up at the interface between the two layers due to the migration of mobile ions in one of the layers⁷. The space charge will create a static electric field, which prolongs the decay of $\chi^{(2)}$.⁸ For *in situ* corona poling, positive ions continue to be deposited on the polymer films, and some of which are transported across the film, creating space charges. The decay of space charges will affect the

relaxation of the SHG signal after the corona field is turned off⁸. However, without a detailed knowledge of concentration of mobile ions, impurities, and the dynamics of the space charge decay, it is difficult to separate out the space charge contribution from the SHG intensity decay behavior. For this reason the contact electrode poling method may provide a better handle for understanding of the relaxation behavior of $\chi^{(2)}$ after the poling field is turned off, as the surface charges that are built up at the interface can be readily bled off by short-circuiting the electrodes.

In Fig. 4 we show the SHG intensity relaxation curves obtained for the 5 wt. % NAS in PMMA sample poled at 110°C under two different field strengths. At the field strength of about 7.2×10^5 V/cm, two components are clearly evident (Fig. 4a or 4b), but at a higher field strength, 9.0×10^5 V/cm, only one component is observed (4c or 4d); the short time component is nearly covered by the stronger long time component. The relaxation curve shown in (Fig. 4a or 4b) can be fit satisfactorily with the sum of two single exponentials, with a single exponential representing each relaxation component. Similarly, a single exponential is sufficient for curve (Fig. 4c or 4d) provided that the short time component is excluded. One notes the two exponential decay curve shown in (Fig. 4b) is clearly displayed when the time axis is set in the logarithmic scale, and, except for the short time portion, a single exponential decay curve fits rather satisfactorily the decay curve portrayed in Fig. 4d. On the other hand, one can also fit the whole decay curve in terms of a KWW function with a β parameters equal to about 0.26, consistent with that reported previously^{6,9}. However, a two single exponential fit gives a smaller standard deviation.

While the precise nature of the fast decay is still not clear at present, it is possible that it is associated with the effect of surface charges. In Fig. 5, we show a detailed "shot to shot" plot of the SHG signal for the 10% NAS/PMMA sample poled at 96°C after the poling field is turned off. In trace (a) the cathode is shorted immediately after the poling field is turned off. In

this case, the SHG takes a step decrease of almost 50%. Traces (b) and (c) correspond to decay curves with a $10^5 \Omega$ and a $10^{10} \Omega$ resistor connected to the cathode, respectively. Clearly, these curves decay gradually, with the $10^{10} \Omega$ resistor case decaying with a longer time constant. These results show that the fast component of the decay is closely, if not completely, associated with the surface charges produced at the cathode. These surface charges will polarize the dipoles of the chromophores near the surface of the film. Due to the relaxation of the surface charge, it is not difficult to see that at high voltages and at high temperatures ($T > T_g$) the SHG signal from the surface dipoles will be relaxed with a shorter time constant than that associated with the dominant macroscopic polarization in the bulk. As a result, the fast decay component that is only barely apparent in Fig. 4d is nearly covered by the dominant slower decay component.

Since the fast decay is closely associated with the surface charges, the study of the orientation of the dipoles induced near the surface will require constructing faster switching electronic circuitry that needs to turn on and off the poling field. In this work we emphasize the study of the second slower decay component associated with the relaxation of the macroscopic polarization. The relaxation of the SHG signal is associated with the fluctuations of macroscopic polarization owing to the collective dipolar reorientation of the NLO chromophores in the bulk.

In our previous work we have shown that the SHG decay associated with the macroscopic polarization is strongly affected by the pair orientational correlation.¹³ Due to the pair orientational correlation, the relaxation time of the slow component is affected by the poling field strength. In the case of NAS/PMMA system, the relaxation time increases with increasing poling field strength.¹³

We have observed an interesting memory effect associated with the establishment of the NLO macroscopic polarization. Shown in Fig. 6 is a series of SHG relaxation curves for the NAS/PMMA sample (5 wt. % NAS) at 100°C. Curve (a) is poled with a field of 8.4×10^5

V/cm. After the SHG signal decays completely, the poling field with the same strength is turned on and within a few seconds, an SHG intensity of about the same initial level is recovered. However, after the poling field is turned off, the SHG decay is found to be longer than the previous one, as shown in (b). As the process is repeated, the relaxation times become successively longer until a plateau value of the relaxation time about 4000s is obtained for the sample poled at this field strength. After the plateau value is reached, there is no longer any change in the decay curve, regardless of the number of times that the sample is repoled. These results are also observed for the sample above T_g , but the relaxation time lengthening effect above T_g is considerably reduced.

While we do not at present have a quantitative theory for the effect, we offer a qualitative explanation of the observation. By poling, the dipoles overcome the viscous barrier of the surrounding polymer to orient along the electric field direction. Since the medium is also elastic (considering the fact that the polymer system is viscoelastic), the elastic stress induced by the poling field owing to electrostriction also helps align the dipoles. This explains why the medium can be repoled rapidly after the SHG signal has decayed. The lengthening of the relaxation is presumably associated with the fact that as dipoles are polarized, the amount of space surrounding the dipoles made available as a result of the alignment is filled up by the polymer chains. The filling up of voids in effect increases local viscosity and hinders subsequent reorientation of the dipoles. As a result, the relaxation time becomes longer. Thus, as the system is repoled, more and more chromophores are surrounded by the viscoelastic polymer chains and the SHG signal will assume a progressively longer decay.

We have studied the steady state plateau relaxation as a function of temperature. The temperature dependence does not follow an Arrhenius type of behavior, but instead it displays a Vogel-Fulcher-Tamann (VFT) (or, equivalently, the Williams-Landel-Ferry (WLF)) form, as

shown in Fig. 7.

$$\tau(T) = \tau_{\infty} \exp [B/(T - T_0)], \quad T > T_0 \quad (2)$$

For the 5% NAS/PMMA system, we have found that τ_{∞} , equals 6.8×10^{-8} s and $T_0 = 193.8$ K. Two remarks are in order. Since the WLF parameter C_2 , is equal to $T_g - T_0$. We obtain for this sample a C_2 value equal to 90 K. This is consistent with $C_2 = 80$ K for PMMA reported in the literature¹⁰, as the C_2 value will increase as the polymer is plasticized. The other remark is the VFT equation appears to describe all data above and below T_g . This is in contrast to the result of ref. 6, which requires different equations to describe results above and below T_g .

Finally, we should mention that our steady state relaxation time τ in the vicinity of T_g is considerably longer by at least two orders of magnitude than that reported by Dhinojwala, et al.¹¹ using repetitive pulsed poling fields with the pulsed field spacing variable from 200 μ s to 0.5 s. In their work, they have not discussed the surface charge complication neither the relaxation time lengthening effect that we have observed. No allowance is provided to remove the surface charge in their work. On the other hand, the poling field strength used by Dhinojwala et al. is only 3.2×10^2 V/cm, which is almost four orders of magnitude less than the poling field employed in the present work. It is possible that results reported in ref. 11 correspond to the fast component. As has previously been shown, at such a weak field the slower component can not be induced¹².

In summary, we have carried out a rather detailed investigation of the decay of the SHG signals of a main chain accordion NLO polymer and a guest host NLO polymer system. The decay of the SHG signal from the main chain polymer is KWW, with the width distribution parameter β increasing with increasing temperature, thus indicating that the distribution of relaxation times narrows as the temperature increases. In the case of the guest/host system, the

exponentials, with the fast component arising from the orientation of dipoles near the surface, and the slower component associated with the decay of macroscopic polarization. Our experimental results show that the amplitude of the slower component increases with increasing strength of the poling field. If the fast component is subtracted from the data, the single exponential function gives an excellent fit to the decay of the SHG signal. However, the time constant of the slow component is found to successively increase with the poling-decay cycle, reaching a plateau value after several cycles. The memory effect is present in the sample above and below T_g , with the memory effect gradually diminishing as the temperature is raised above T_g . The temperature dependence of the steady state relaxation time is not Arrhenius; however, the Vogel-Fulcher-Tamann equation gives a satisfactory fit to temperature dependence relaxation time data.

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FIGURE CAPTIONS

- Fig. 1:** Glass transition temperature of NAS in PMMA plotted as a function of a NAS concentration.
- Fig. 2:** Rise and decay curves of two main chain accordion NLO polymer films with and without thermal annealing. Trace associated with the lower horizontal axis corresponds to a fresh film, and that with the upper horizontal axis corresponds to an annealed film.
- Fig. 3:** Decay curves of the corona poled main chain accordion NLO polymer films with (solid circles) and without (empty circles) thermal annealing.
- Fig. 4:** SHG intensity relaxation curves for 5 wt. % NAS in PMMA poled at 100°C obtained with two field strengths. The abscissa for curves (a) and (c) are in linear scale and those for (b) and (d) are in logarithmic scale. The field strength is 7.2×10^5 V/cm for (a) or (b), and is 9.0×10^5 V/cm for (c) or (d).
- Fig. 5:** Detailed shot to shot SHG intensity curves with different values of resistor connected to the cathode. Resistance for (a) is 0 ohm, for (b) is 10^5 ohm and for (c) is 10^{10} ohm.
- Fig. 6:** Lengthening of the relaxation curves as the sample is progressively poled at a constant temperature.
- Fig. 7:** Temperature dependence of the steady state relaxation time displayed in terms of Vogel-Fulcher-Tamann plot.

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TABLE I

KWW parameters associated with the decay portion of the dynamic SHG intensity curve.

Temperature (° C)	τ (s)	β
175		
a. Fresh film	19.5	0.42
b. Annealed film	3276.8	0.36
198	2097.1	0.52
204	884.7	0.73
210	395.4	0.88

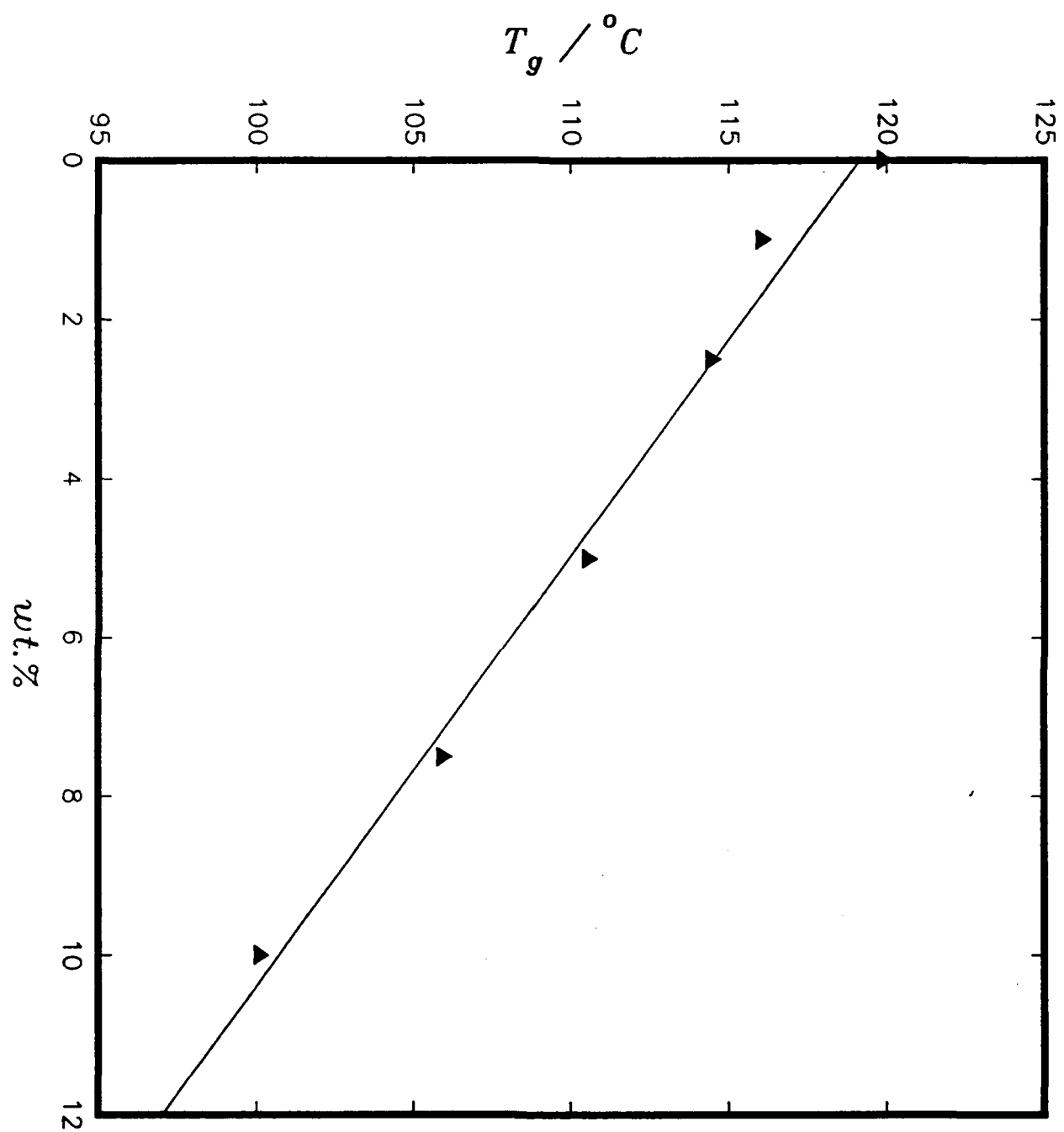


Fig. 1

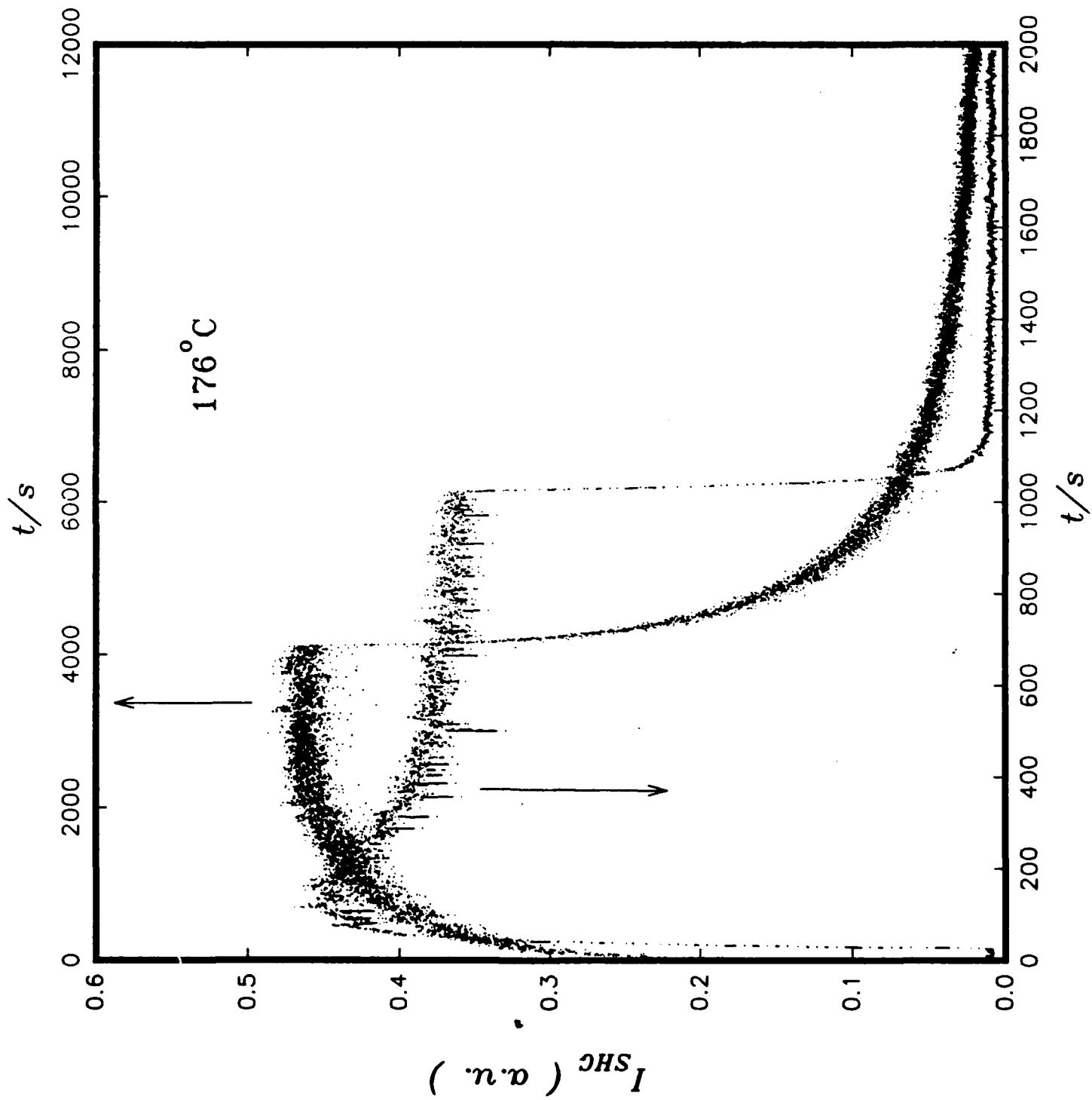
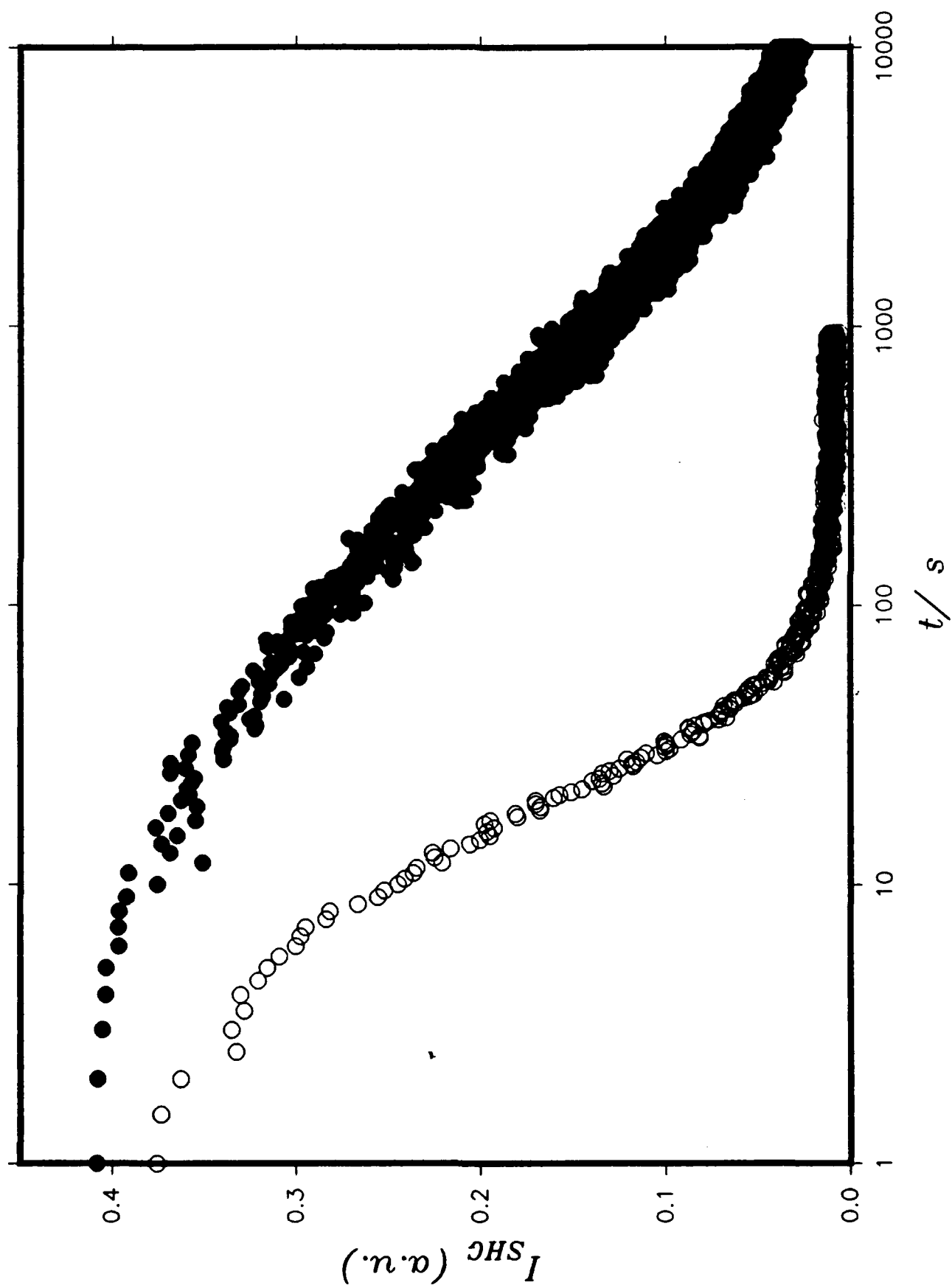
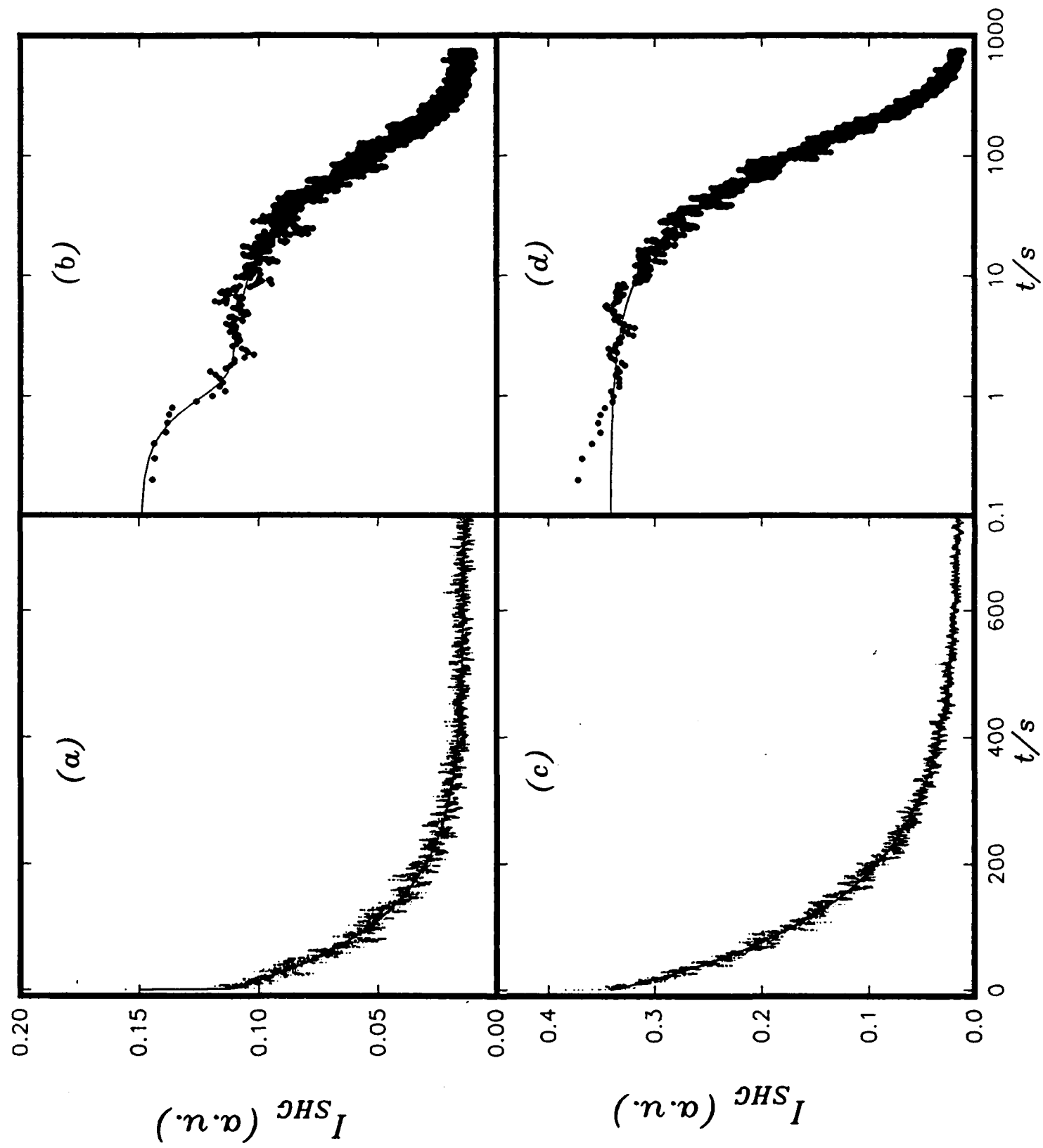
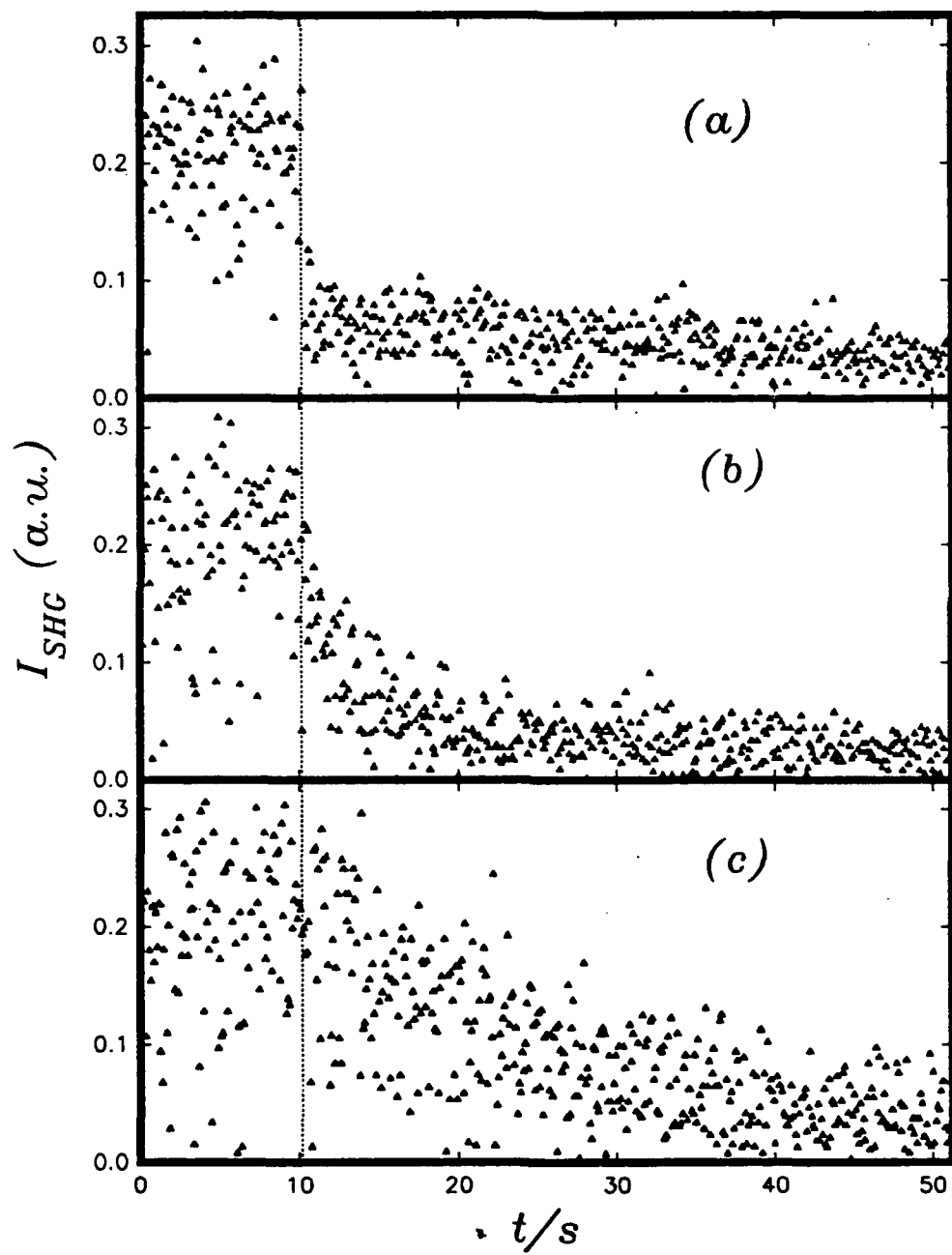
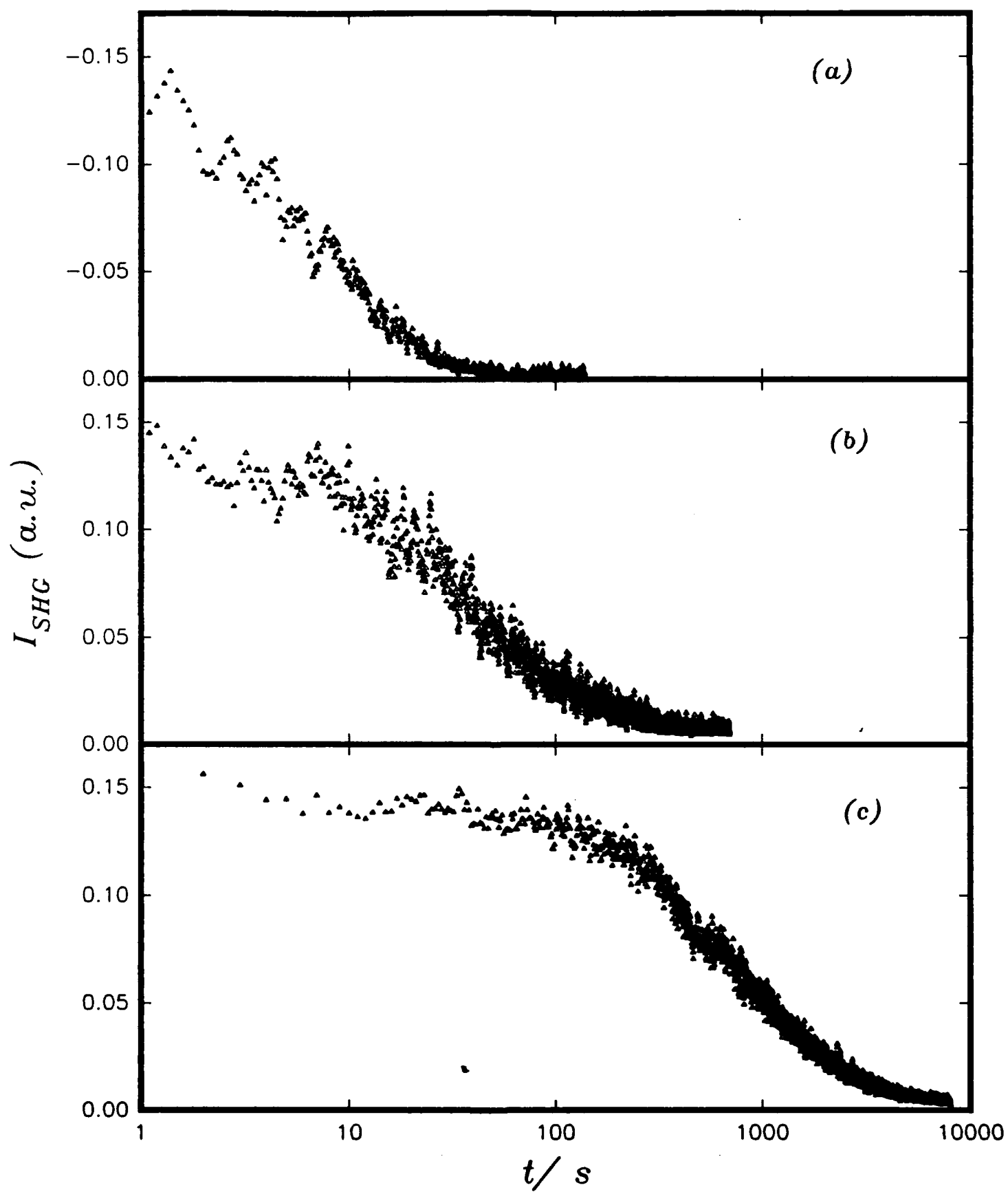


Fig 2.









F. J. 1

