Conf. 910406--14

SAND--91-1000C

DE91 013262

Measurements of Photo-Induced Changes in Conjugated Polymers

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ABSTRACT

We have used the highly sensitive technique of Photothermal Deflection Spectroscopy (PDS) to measure changes in the infra-red absorption spectra of MEHPPV, P3HT and Polydiacetylene-4BCMU induced by pumping these polymers with light above the π - π^* transition energy. In contrast to previous chopped light transmission measurements of these effects, the PDS technique can directly measure the buildup or decay of the absorption coefficient, α, on the time scale of seconds to days. In the case of MEHPPV we observe that above-gap light causes the appearance of a broad infra-red peak in α, which continues to grow-in hours after the pump light is first applied. For this polymer the general shape of the absorption spectra in the unpumped state mimics the photo-induced changes, suggesting that remnant photo-induced states determine the maximum transparency observed under normal experimental conditions. For P3HT and to a lesser extent, MEHPPV, we also observe irreversible photo-induced absorption components which we tentatively identfy with photo-induced oxidation of the polymer matrix.

DISCLAIMER

INTRODUCTION

Long chain conjugated polymers have come under recent scrutiny because of their interesting electrical and optical properties [1,2]. In particular, their potential use in waveguide structures and optical switching elements [3] has focussed attention on their optical properties at wavelengths longer than the π - π^* transition [4,5], which is typically in the 2.0 - 2.5 eV range. In order for polymer waveguides to be practical, the attenuation must be a few db/cm or less at the wavelength of interest. Several sources of residual absorption in the subgap region can determine the ultimate transparency of such materials. These include: 1. broad, Urbach-like tails on the π - π^* edge due to disorder, strain, internal electric fields, or other causes. 2. Overtones of localized vibrational modes. 3. Residual absorptions induced by exciting the polymer with light above the π - π^* excitation energy. A number of recent observations of these induced absorptions have been made which indicate that their spectral character is consistent with that expected for trapped bipolarons [6]. Most of these observations have been made in a chopped mode in the 5 to 10 Hz range. In the present study we have used Photothermal Deflection Spectroscopy (PDS) to study the long time behavior of these induced absorptions as they grow in during excitation and as they decay when the pump light is removed. We find that the extremely slow kinetic behavior of these excitations may, in fact, cause them to become the dominant factor in the near-IR transparency.

While sub-gap absorption studies may be useful in understanding the mechanisms of charge excitation and trapping in these materials, they may also be a useful probe of their chemical stability. Small changes in local order or chemical composition due to various degradation mechanisms like photo-oxidation are likely to result in readily observable absorption changes in this spectral region as opposed to areas where π - π^* transitions dominate the spectral characteristics. Extended measurements of some of the present samples have indeed revealed shifts in the subgap absorption which have distinctly different spectral dependences from the induced absorption peaks, suggesting small chemical changes may be occuring.

EXPERIMENTAL

The samples studied here were produced by spin casting the polymers onto pre-scribed fused silica substrates from precursor/solvent solutions. After drying, these substrates were then broken into ~ 0.5 x 1.0 cm pieces in an inert gas environment and loaded into 1 cm^2 optical cuvettes containing Flourinert (FC-75). This commercial flourocarbon solvent was de-oxygenated prior to loading using a dry-Helium gas bubbling technique. After loading, the sample-containing cuvette was hermetically sealed and transferred to the optical spectrometer. Results on several polymers will be discussed here: Polydiacetylene-4BCMU (PDA-4BCMU), poly(2-methoxy,5-(2' ethyl-hexoxy)-PPV (MEHPPV), and poly(3-hexylthiophene) (P3HT).

General descriptions of the PDS technique and the specific apparatus employed here are given in the companion paper presented here [7] and elsewhere [8,9]. Except for a distinct OH overtone absorption in the quartz substrates which varies in magnitude from manufacturer to manufacturer and from sample to sample, the influence of the substrate is minimal in the present measurements. In addition to verifying this assertion by making companion measurements on substrates where the polymer had been stripped off, we note that the phase of the PDS signal is distinctly different when substrate contributions are important.

Excitation of the sample with light above the π - π^* transition was accomplished with a 200W high pressure Hg lamp/monochromator/quartz light pipe arrangement which was operated with a fairly wide (12-15 nm) spectral bandwidth. This excitation light impinged on the sample in a cw mode from the opposite side of the quartz substrate from the heating light and the HeNe deflection laser. Because the PDS absorption is monitored at the 19 Hz chopping frequncy of the heating light, the dc beam deflection caused by the π - π^* pump light does not appear as an absorption signal nor does it noticeably increase the operational noise level.

EXPERIMENTAL RESULTS

Figure 1 shows the time dependence of the induced absorption for MEHPPV (at 1.3 eV) when pumping with 2.3 eV light. This light is above the onset of the π - π^* absorption and is strongly absorbed in the thin sample (~0.1μm) studied here. Figure 2 illustrates a portion of the decay curve measured after the pump beam is extinguished. In both cases, growth and decay, the approach to a steady state value is very slow (many hours), and true saturation could not be observed on any convenient laboratory time scale. Before discussing the spectral dependence of the induced absorption, it is relevant to ask whether the method of measurement influences their growth or decay. Such effects have indeed been seen in other materials; in a-SiN_x:H PDS heating light strongly influences the growth and decay of UV-induced subgap absorption by excitation and recombination of UV-produced trapped carriers [10]. To test for this effect here, two growth and decay cycles of the pump-induced absorption were followed, as illustrated in Figure 2. In the first cycle the decay of the induced PDS signal was followed for approximately 20 minutes after the pump light was turned off. In the second cycle, the HeNe laser and the heating light were blocked for ~ ten minutes, starting just before the pump beam was turned off. When the laser and heating beam were turned back on the PDS signal is seen to have decayed to nearly the same value as it did during the first cycle, implying that the observed kinetics are not influenced by the presence of the rather intense heating beam. From these results we infer that the growth kinetics are also not influenced by the measuring process.

Figure 3 shows the dark (no pump beam) spectra observed for MEHPPV and the quasi-steady state absorption acheived after ~45 minutes exposure to 2.3 and 3.1 eV light. The dark spectra was measured ~ 2 days after the sample was inserted and aligned in the PDS spectrometer, a procedure which involves exposure to heating light above the π - π^* edge. The small misalignments of data taken around 1.2 to 1.3 eV are due to a range change in the spectrometer operation which consumes several minutes of time; in that period the small offsets in the PDS curves develop because of the non-saturating character of the induced absorption. The large peak at 0.9 eV is due to OH in the quartz substrate; other peaks are due to C-H vibrational overtones and have been discussed in our companion paper. Figure 4 shows the difference spectra obtained by subtracting the dark data in Figure 3. In these difference spectra the overtone and substrate features vanish, leaving a prominent peak at ~ 1.35 eV which is the same spectral shape at both pump energies. Pump energies higher than 3.1 eV were avoided to reduce the possibility of any photo-dissociation of the polymer. Also plotted in this Figure are the 80K $\delta T/T$ data of Voss et al [6] which are remarkably like the present results, except for a small peak shift which could be temperature-induced. We note that while transmission measurements are more sensitive to changes in reflectivity than the PDS technique, it is unlikely that these contributed to Voss et al's data given the thickness of their samples. While our $\delta\alpha$ curves show an increase for $h\nu <$ 0.9eV, Voss et al report a second peak in $\delta T/T$ at 0.43 eV. They suggest that these two peaks are due to transitions from bipolaron gap states photo-induced by absorption in the π - π^* peak. More detailed data will be needed to improve upon this conjecture.

Dark and pumped spectra for PDA-4BCMU are shown in Figure 5. The photo-induced changes in absorption are clearly smaller than for MEHPPV and data from thicker samples will be needed to more carefully defined the exact spectral shape of the effect. As in the case of MEHPPV, the photo-induced effects take hours to fully develop and decay, and it is clear from Figure 5 that there are at least two spectral regions where marked enhancements of α are seen.

The dependence of the induced absorption on pump beam intensity is shown for MEHPPV in Figure 6 and PDA-4BCMU in Figure 7. In both cases the values of $\delta\alpha$ seen at ~1/2 hr are plotted, and, within the error of measurement, they both scale as the square root of pump light intensity. An observation such as this suggests the applicability of bimolecular recombination kinetics:

$$\partial(\delta\alpha)/\partial t = G - B\,(\delta\alpha)^2 \qquad (1)$$

where G is the creation rate of defects, proportional to the pump light intensity, and B is the volume recombination rate for the defects which are associated with the induced absorption, $\delta\alpha$. The steady state solution of Equation 1 is $\delta\alpha = (G/B)^{0.5}$. The general solution is a hyperbolic tangent function of time which is plotted in Figure 1. Clearly, the fit to the observed time dependence of $\delta\alpha$ is poor. Since the pump beam is strongly absorbed, we must account for that fact that the G value depends on position in the film; in the strong absorption limit this correction produces the somewhat slower time dependence shown in Figure 1, which does not adequately reproduce the extremely slow growth or decay (not shown) of $\delta\alpha$.

These slow kinetics raise the issue of whether even long periods in the dark leave remnants of photo-induced absorption. The α curve for a sample that has been in the dark for two days (Figure 2) does show a small peak at ~1.35 eV, very much like the photo-induced peaks.

Dark and photo-induced spectra are shown for P3HT in Figure 8. After sitting 2 days in the dark the absorption behavior has not gone back to the virgin spectra in this case, and the final spectral shape is quite different from either the virgin or the pumped curves. This suggests that irreversible chemical or structural changes may be caused by extended pump light exposure. Preliminary observations of P3HT films immersed in Flourinert that has not been de-oxygenated show more severe degradation. These data only represent scattered observations; a proper experimental approach to this issue has not been attempted. Along these lines we have also observed that there are also small remnant absortpions in MEHPPV which do not have the spectral characteristics of the data shown in Figure 4. Again, not purging O_2 from the Flourinert seems to exacerbate this problem.

SUMMARY AND CONCLUSIONS

We have established that large changes in the sub-gap absorption of all the measured polymers occur when they are exposed to light above the π -π^*

transition energy. The growth and decay of these changes requires hours to days at 300K, and true saturation or recovery cannot be observed on convenient laboratory time scales. While the excitation intensity dependence of these induced absorptions suggests bimolecular recombination, the slow growth kinetics observed are not consistent with the predictions of this simple picture. It is possible that the photo-produced charge excitations become trapped at defects on the polymer chains. A distribution of release times might then account for their slow decay. A proper treatment of this problem for motion, trapping, and recombination of excitons or polarons on a one-dimensional chain has not been attempted by us. The issue of how long one must leave these samples unexposed to pump light (room light certainly is important in this regard) before the subgap absorption is not dominated by the lingering effects of photo-induced excitations is an important question raised by our data. The 1.35 eV bump seen in the dark MEHPPV spectrum in figure 3 suggests that, in this case, photo-induced effects are still important in fixing the sub-gap transparency. This may have important consequences for waveguide operation even if no short wavelength light is available, because even long wavelength operation will produce charged excitations because of the non-negligible two-photon optical cross sections in these non-linear materials .

Finally, we have seen long term pump-induced changes in absorption which are not obviously spectrally related to the shorter term α changes. The fact that these effects seem more pronounced when no precautions are taken to minimize O_2 contamination suggests that photo-oxidation of the polymer chains may be occuring. Proper identification of these effects will require more detailed experimentation.

ACKNOWLEDGEMENTS

The authors would like to thank W. R. Bayless for assistance in making the PDS measurements.

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FIGURE CAPTIONS

Figure 1. The time dependence of photo-induced absorption measured at 1.3 eV on a ~0.1 μm film of MEHPPV pumped with 2.3 eV light. The data are shown as open triangles. The solid curve is the time dependence predicted from simple bimolecular recombination while the dashed curve incorporates the effect of a generation rate which is an exponentially decreasing function of distance in the sample.

Figure 2. Two experimental cycles where the decay of the photo-induced absorption in MEHPPV (at $h\nu = 1.3$ eV) is monitored following the turn off of the 2.3 eV pump beam. In one of these cycles (darker lines) the HeNe laser and the PDS heating light were turned off for part of the decay.

Figure 3. Dark (no pump beam) and photo-excited PDS absorption traces for a MEHPPV sample pumped at two different photon energies above the π -π^* transition. Both pumped spectra were obtained after about 30 min. of exposure to the pump beam.

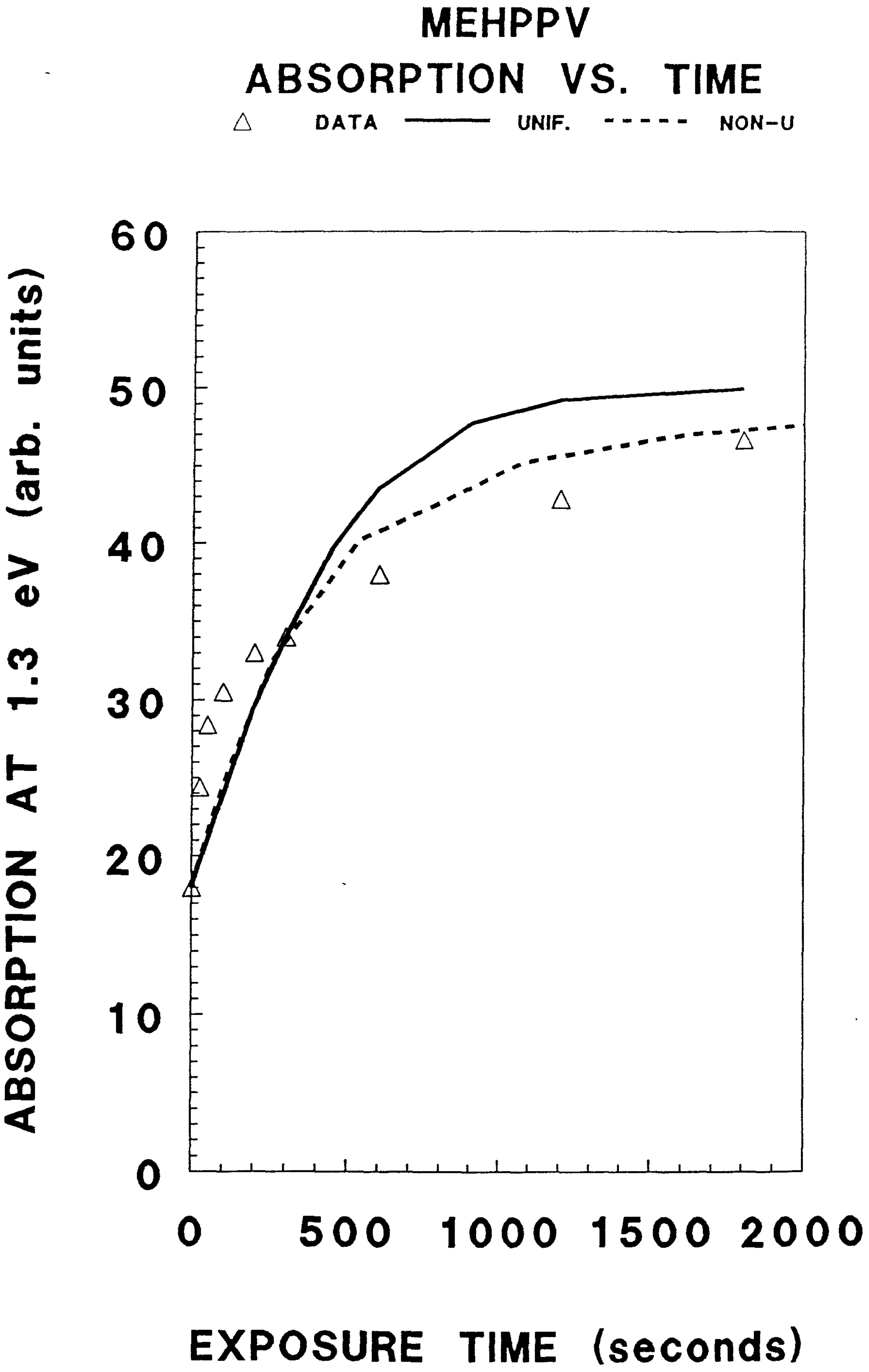
Figure 4. Difference spectra obtained by subtracting the dark curve in Figure 3. The dashed curve is for a 2.3 eV pump beam, the dotted curve is for a 3.1 eV pump beam. The solid line is the 80K $\delta T/T$ data of Voss et al.

Figure 5. Dark and photo-excited PDS spectra for PDA-4BCMU pumped with 2.3 eV light. The pumped spectra was a quasi-steady state curve obtained after ~45 min. of excitation.

Figure 6. The pump beam intensity dependence of the 2.3 eV light-induced absorption for MEHPPV. These data were obtained after ~ 30 min. exposure.

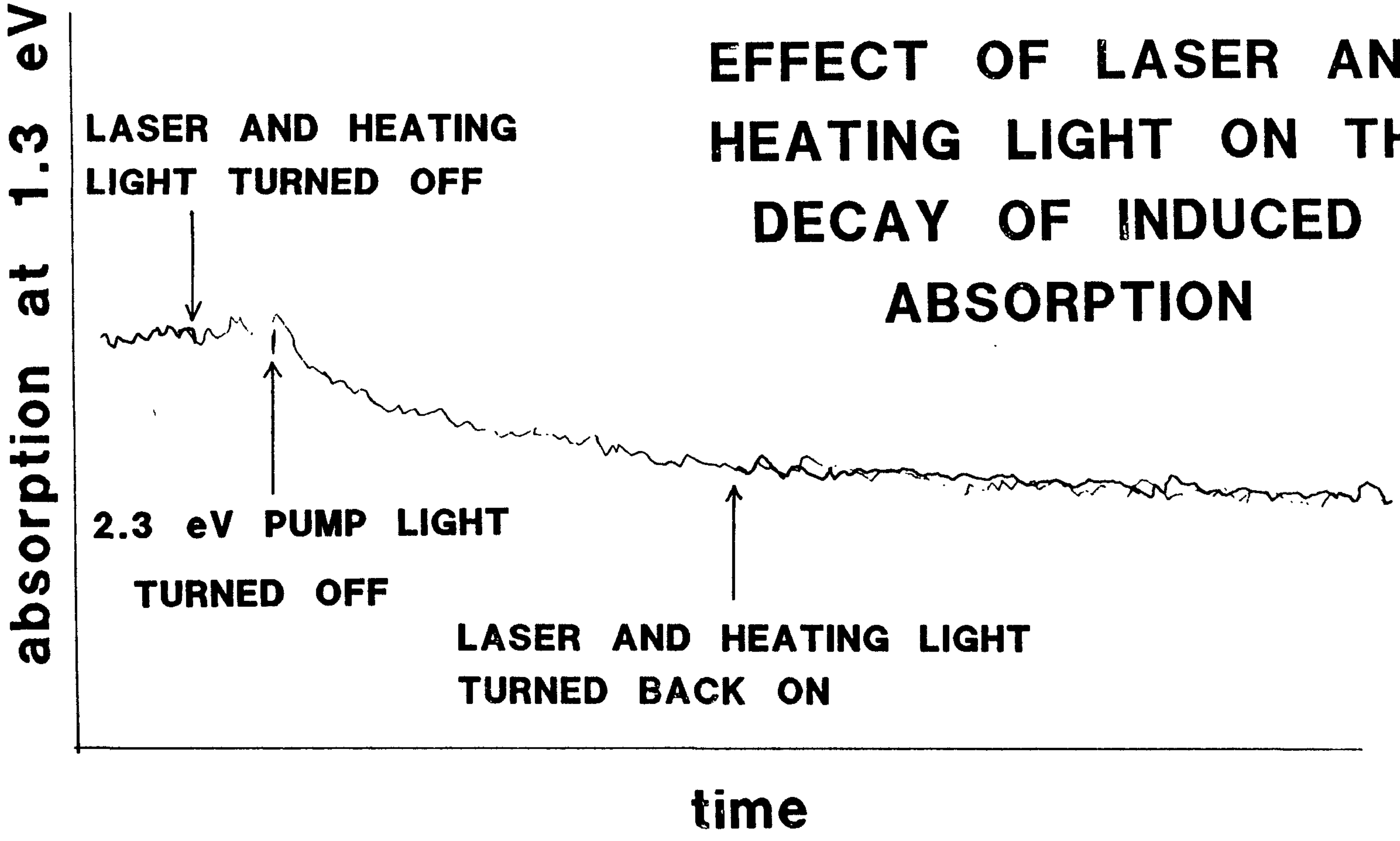
Figure 7. The pump beam intensity dependence of the 2.3 eV light-induced absorption for PDA-4BCMU. These data were obtained after ~ 30 min. exposure.

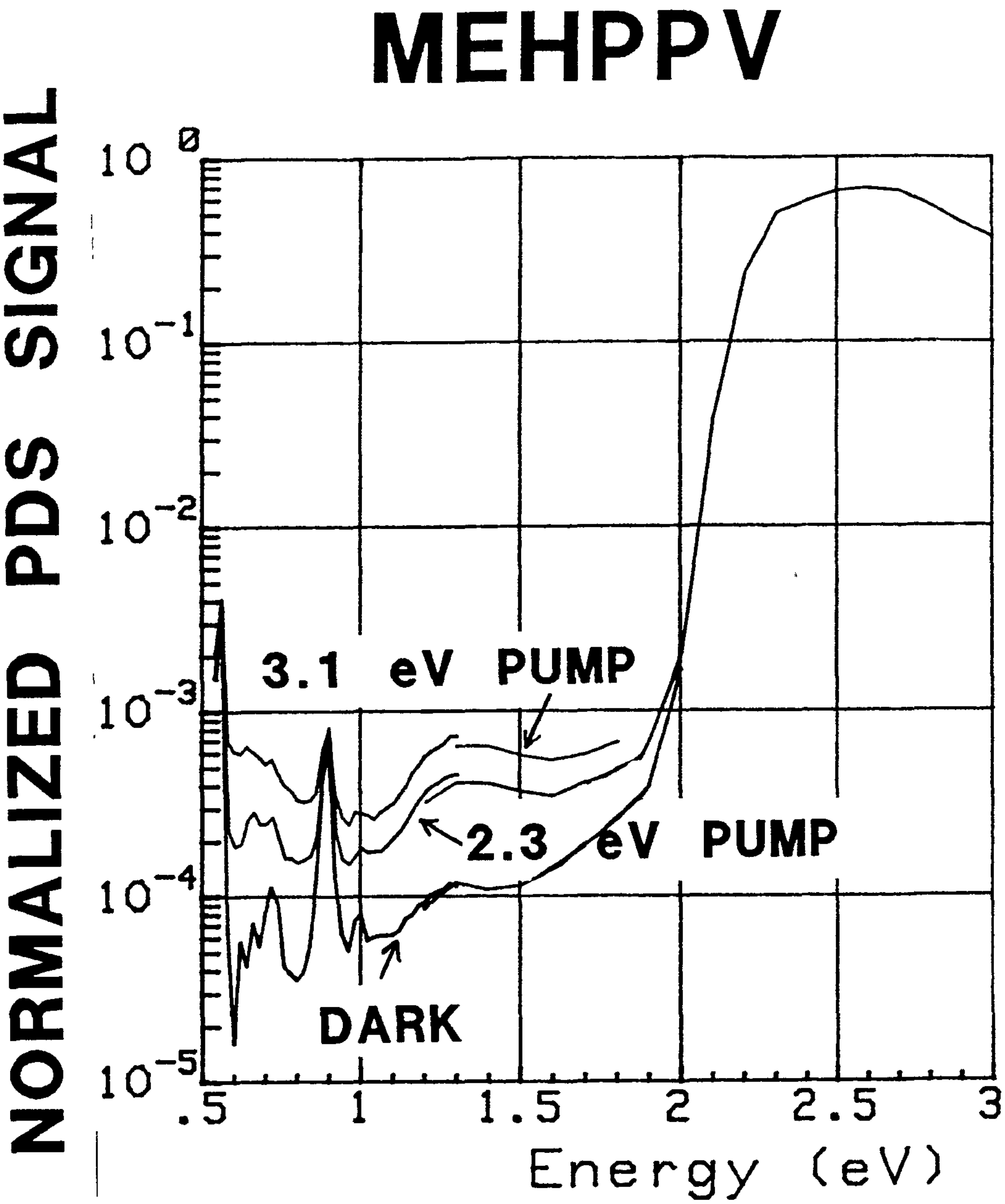
Figure 8. The dark (virgin), pumped (after ~30 min.), and remnant (after 48 hrs) PDS absorption data obtained for a sample of P3HT.

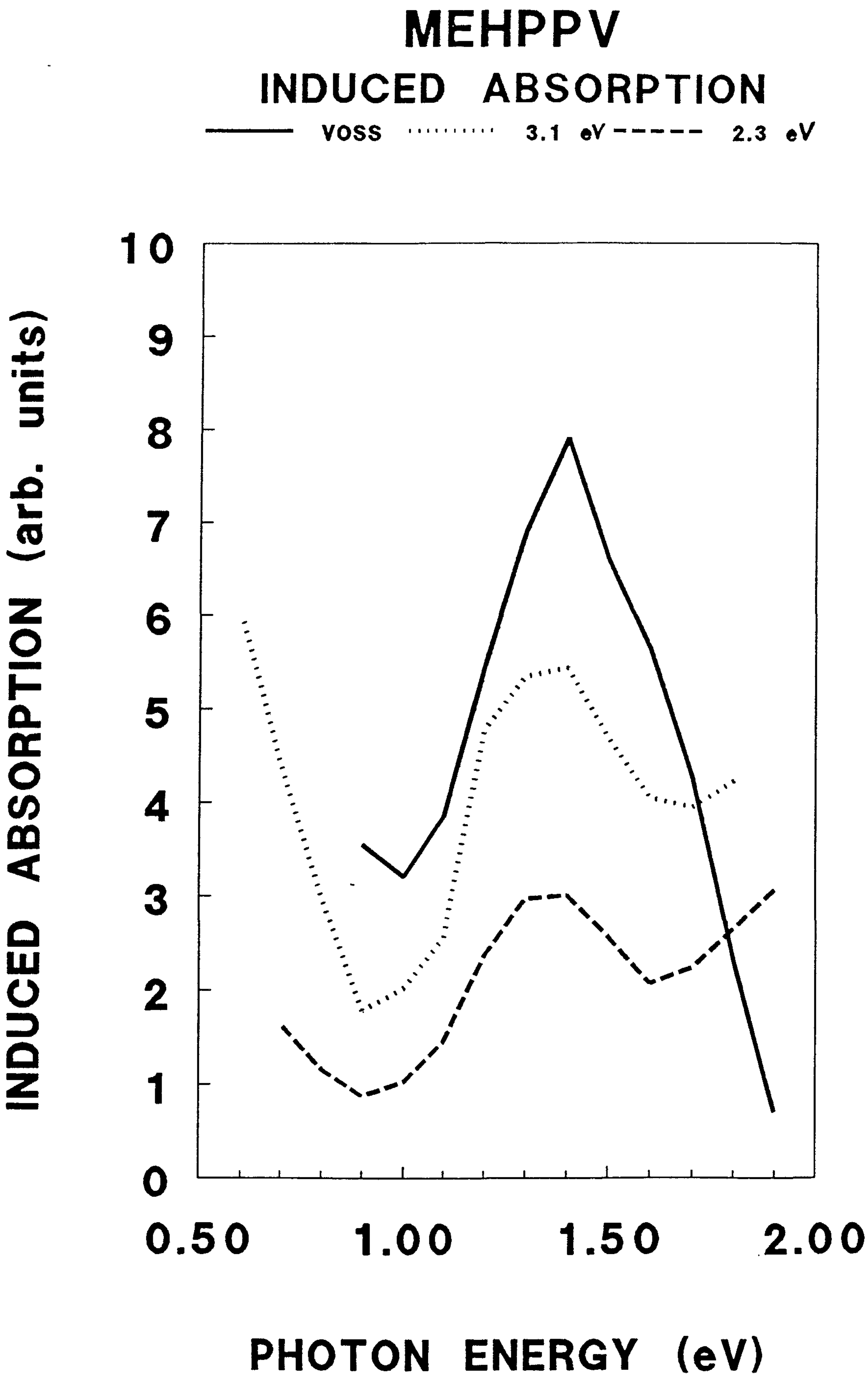

MEHPPV
ABSORPTION VS. TIME
△ DATA
UNIF.
NON-U
ABSORPTION AT 1.3 eV (arb. units)
0
10
20
30
40
50
60
0
500
1000
1500
2000
EXPOSURE TIME (seconds)

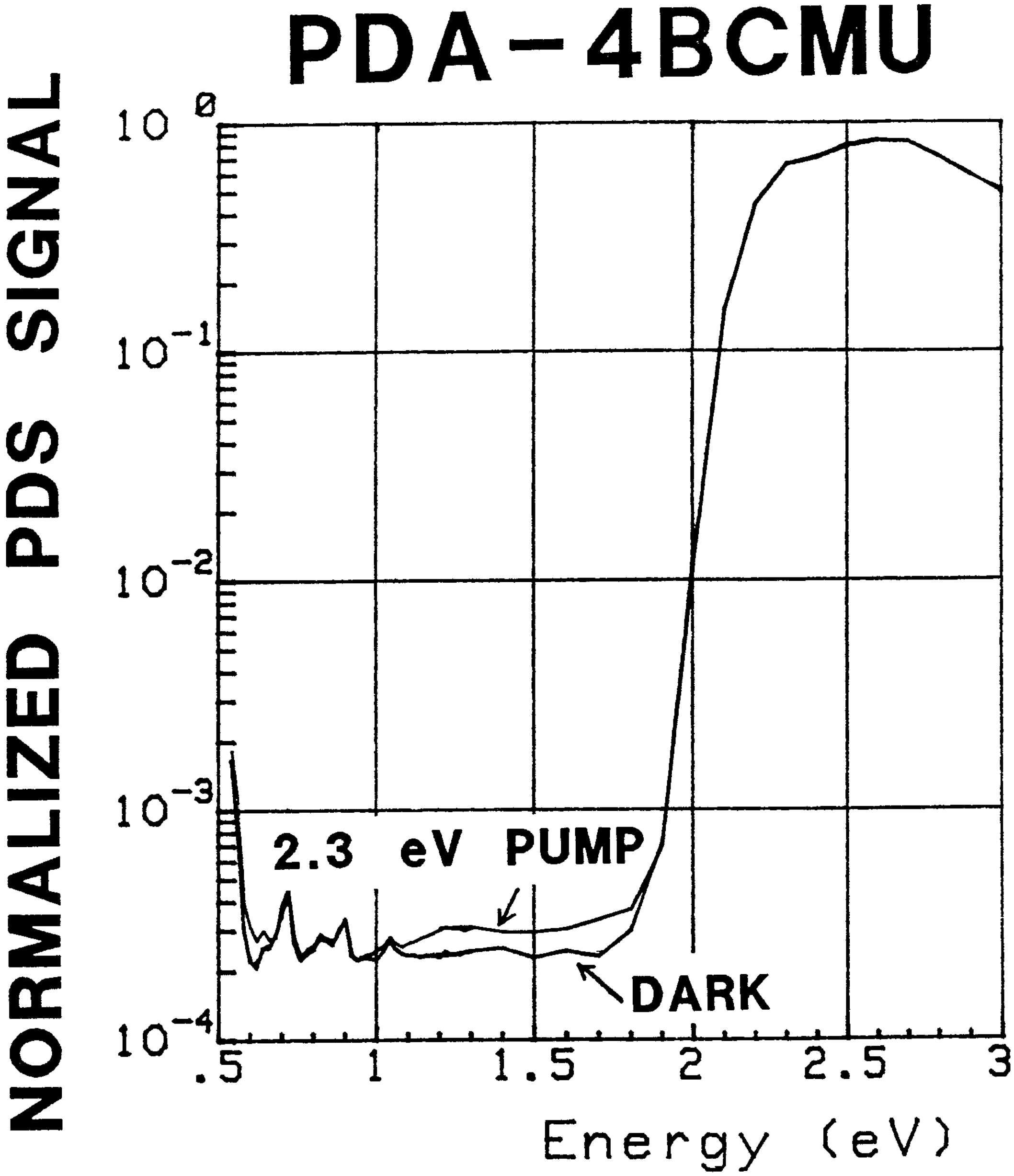
MEHPPV

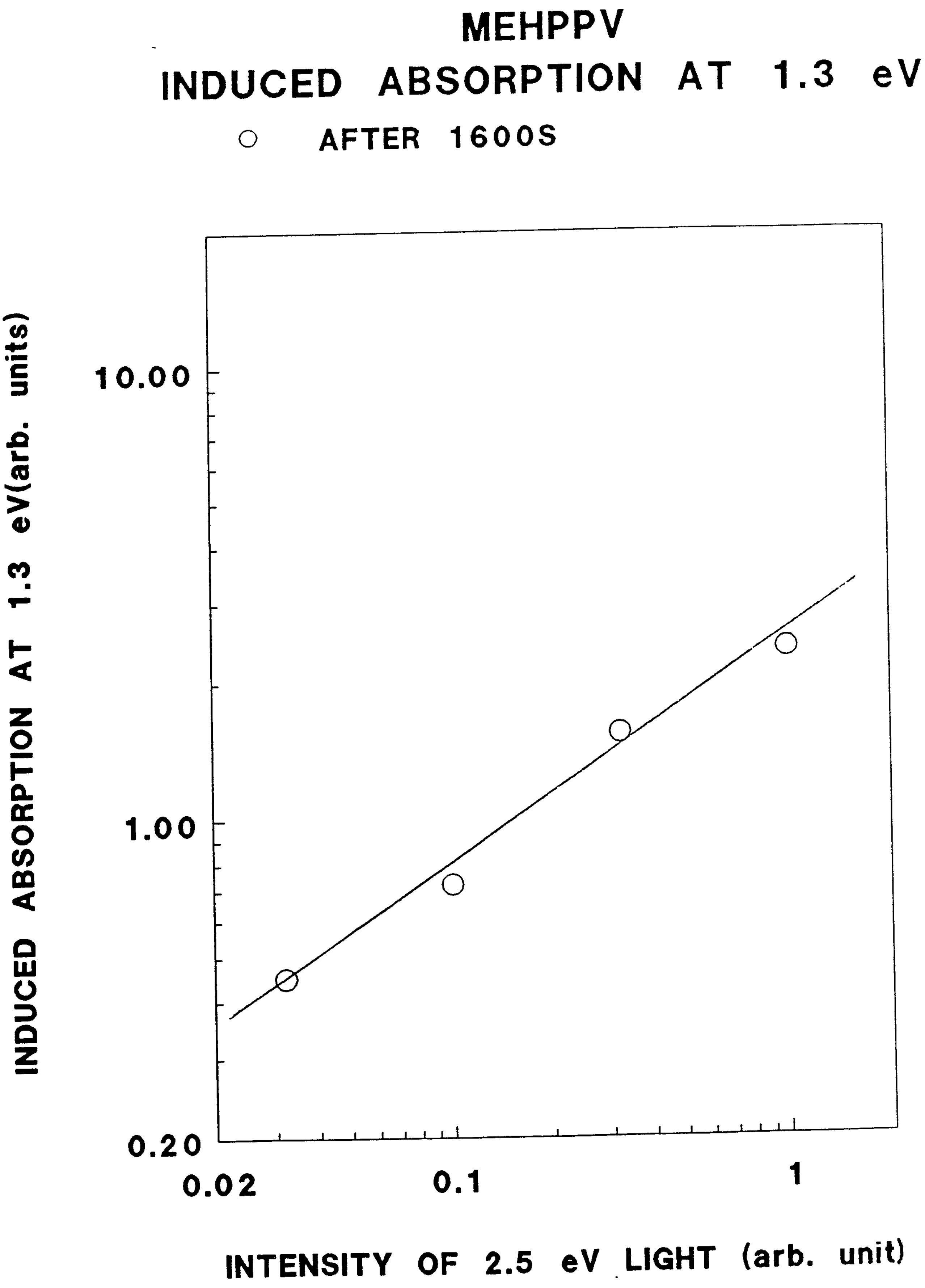
EFFECT OF LASER AND HEATING LIGHT ON THE DECAY OF INDUCED ABSORPTION

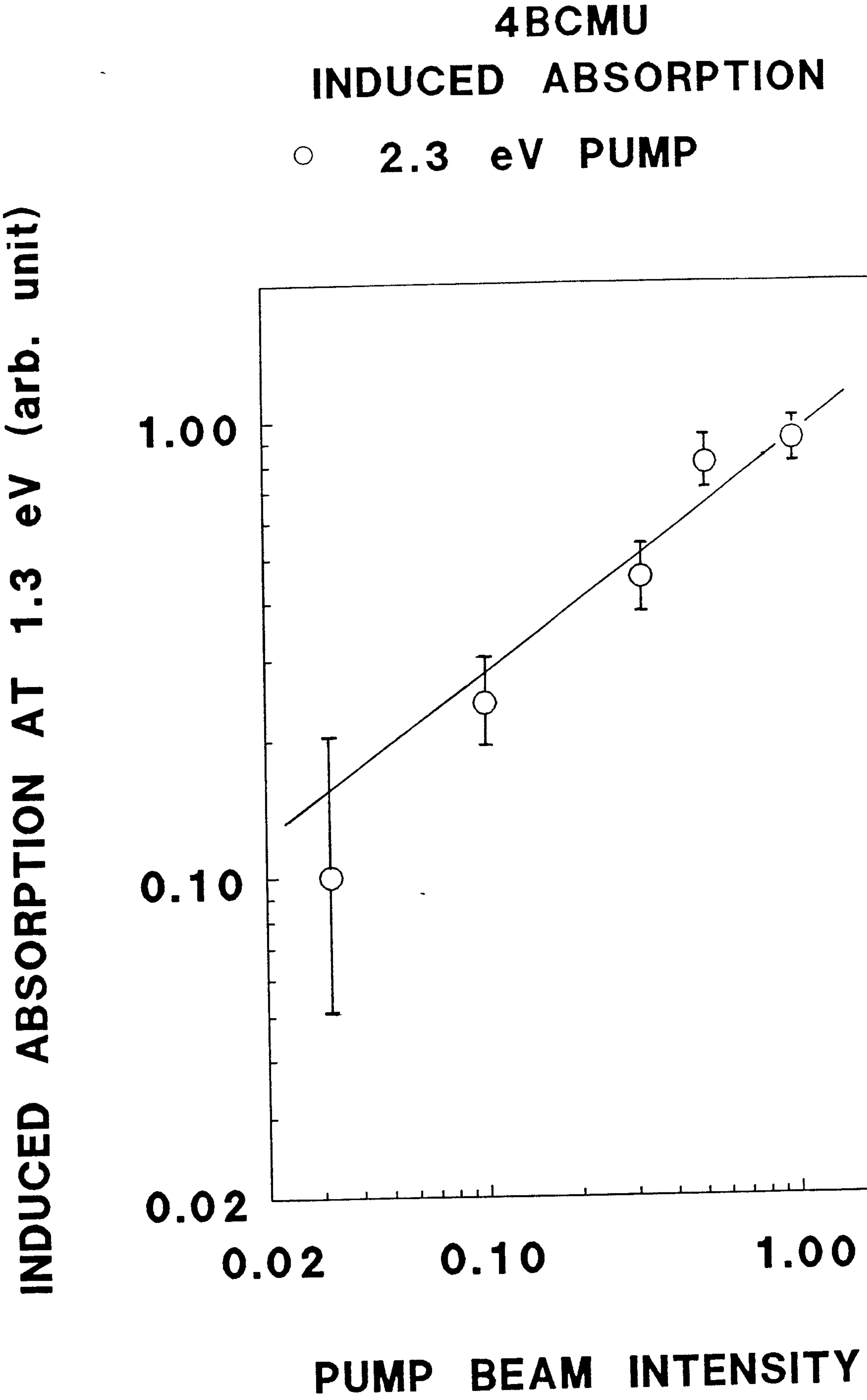



MEHPPV
NORMALIZED PDS SIGNAL
10^0
10^-1
10^-2
10^-3
10^-4
10^-5
.5
1
1.5
2
2.5
3
Energy (eV)
3.1 eV PUMP
2.3 eV PUMP
DARK

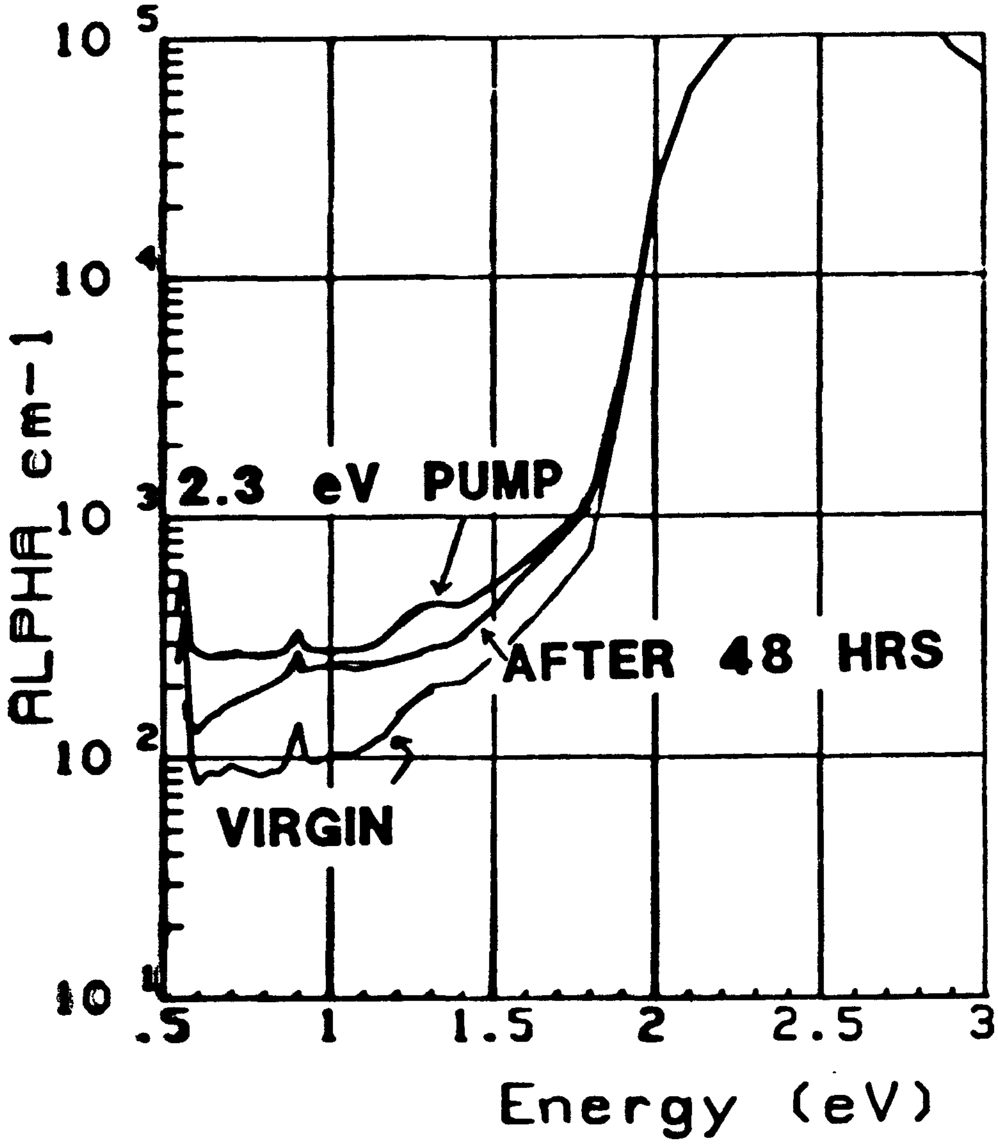

MEHPPV
INDUCED ABSORPTION
VOSS
3.1 eV
2.3 eV
INDUCED ABSORPTION (arb. units)
0
1
2
3
4
5
6
7
8
9
10
0.50
1.00
1.50
2.00
PHOTON ENERGY (eV)


PDA-4BCMU
NORMALIZED PDS SIGNAL
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
.5
1
1.5
2
2.5
3
Energy (eV)
2.3 eV PUMP
DARK


MEHPPV
INDUCED ABSORPTION AT 1.3 eV
○ AFTER 1600S
10.00
1.00
0.20
0.02
0.1
1
INDUCED ABSORPTION AT 1.3 eV(arb. units)
INTENSITY OF 2.5 eV LIGHT (arb. unit)


4BCMU
INDUCED ABSORPTION
○ 2.3 eV PUMP
INDUCED ABSORPTION AT 1.3 eV (arb. unit)
1.00
0.10
0.02
0.02
0.10
1.00
PUMP BEAM INTENSITY

P3HT



10 5
10 4
10 3
10 2
10 1
ALPHA cm-1
2.3 eV PUMP
AFTER 48 HRS
VIRGIN
.5
1
1.5
2
2.5
3
Energy (eV)