

# Sub-Picosecond Injection of Electrons from Excited {Ru(2,2'-bipy-4,4'-dicarboxy)<sub>2</sub>(SCN)<sub>2</sub>} into TiO<sub>2</sub> Using Transient Mid-Infrared Spectroscopy

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# Sub-picosecond Injection of Electrons from Excited [Ru (2,2'-bipy-4,4'-dicarboxy)<sub>2</sub>(SCN)<sub>2</sub>] into TiO<sub>2</sub> Using Transient Mid-Infrared Spectroscopy \*

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## Abstract

We have used femtosecond pump-probe spectroscopy to time resolve the injection of electrons into nanocrystalline TiO<sub>2</sub> film electrodes under ambient conditions following photoexcitation of the adsorbed dye, [Ru(4,4'-dicarboxy-2,2'-bipyridine)<sub>2</sub>(NCS)<sub>2</sub>] (N3). Pumping at one of the metal-to-ligand charge transfer absorption peaks and probing the absorption of electrons injected into the TiO<sub>2</sub> conduction band at 1.52 μm and in the range of 4.1 to 7.0 μm, we have directly observed the arrival of the injected electrons. Our measurements indicate an instrument-limited ~50-fs upper limit on the electron injection time under ambient conditions in air. We have compared the infrared transient absorption for noninjecting (blank) systems consisting of N3 in ethanol and N3 adsorbed to films of nanocrystalline Al<sub>2</sub>O<sub>3</sub> and ZrO<sub>2</sub>, and found no indication of electron injection at probe wavelengths in the mid-IR (4.1 to 7.0 μm). At 1.52 μm interferences exist in the observed transient absorption signal for the blanks.

**Key words:** dynamics of dye injection, N3, nanocrystalline TiO<sub>2</sub>

## Introduction

Extensive efforts have been directed toward understanding the photoelectrochemical properties and charge transfer dynamics of dye-sensitized nanocrystalline semiconductor films. Such films used in photovoltaic cells have demonstrated highly efficient solar energy conversion (>10%) in recent years,<sup>1-3</sup>. Dye-sensitized photoelectrochemical solar cells based on [Ru(4,4'-dicarboxy-2,2'-bipyridine)<sub>2</sub>(NCS)<sub>2</sub>] (N3) adsorbed to nanocrystalline TiO<sub>2</sub> rely on efficient charge-separation at the dye-TiO<sub>2</sub> interface, and fast electron injection from the excited state of the adsorbed dye molecule into the TiO<sub>2</sub> nanoparticle. Injection must be fast to compete with processes such as relaxation and degradation of the excited dye molecule. Several groups studying the transient absorption of the excited and oxidized states of the dye in the visible and near-IR, to determine the electron injection time in the N3-sensitized TiO<sub>2</sub> (N3-TiO<sub>2</sub>) and similar systems, have reported evidence for ultrafast (≤1 ps) charge separation and electron injection<sup>4-10</sup>. Tachibana *et al.* reported transient absorption measurements at 750 nm which were ascribed to the formation of oxidized N3 (pumped at 605 nm); analysis of the rise time of the 750 nm absorption indicated biphasic electron injection with injection times of 150 fs (instrument limited) and 1.2 ps.<sup>4</sup> Hannappel *et al.*<sup>5</sup> measured the rise of the near-infrared absorption of conduction band electrons at 1100 nm following photoexcitation of N3 at the lower-energy metal-to-ligand charge transfer (MLCT) absorption peak (550 nm); the near-infrared absorption signal was attributed to free or trapped electrons following injection. However, these authors believe that to obtain unambiguous results, it was necessary for these experiments to be conducted under ultra-high vacuum (UHV) conditions. These authors also challenged the assignment by Tachibana *et al.* of the 750 nm absorption band to oxidized N3<sup>4</sup>; this challenge

has been answered in turn.<sup>6,7</sup> Heimer *et al.*<sup>8</sup> used a system with 30 ps resolution to time resolve the electron injection into TiO<sub>2</sub> from the dye [Ru(4,4'-(COOCH<sub>2</sub>CH<sub>3</sub>)<sub>2</sub>-2,2'-bipyridine)(2,2'-bipyridine)<sub>2</sub>]<sup>2+</sup>; the instrument time response placed an upper limit on the injection time of ~20 ps.<sup>10</sup> Here we present further evidence, based on time-resolved infrared (TRIR) absorption measurements, for ultrafast electron injection times (50 fs ± 25 fs) for the N3-TiO<sub>2</sub> electrode under ambient conditions. By probing the time-resolved mid-IR absorption produced by injected electrons,<sup>9,11</sup> we are able to obtain unambiguous conclusions without the need for UHV. Probing in the mid-IR allows us to bypass the issue of the correct absorption spectrum for oxidized N3 and eliminate the possibility of any signal contributions from the cationic or excited states of the dye.<sup>9,11</sup>

### Materials and Methods

Titanium dioxide nanoparticle colloids were prepared as previously described, using Degussa P25 TiO<sub>2</sub> starting material.<sup>12</sup> The Al<sub>2</sub>O<sub>3</sub> nanoparticle colloid was prepared using a method similar to that used for TiO<sub>2</sub>. The starting material for the alumina colloid was Degussa Aluminum Oxide C (primary particle size of 13 nm). The ZrO<sub>2</sub> colloid was prepared via hydrolysis of zirconium isopropoxide and heated at 220 °C using a procedure published previously for the preparation of colloidal TiO<sub>2</sub>. Films were fired at 450 °C for 45 minutes in air. Films to be used with probe wavelengths longer than 5.5 μm were prepared on 2.0-mm-thick CaF<sub>2</sub> substrates, both sides polished. Films to be used at wavelengths shorter than 5.5 μm were prepared on either *c*-cut polished sapphire or fluorine-doped SnO<sub>2</sub> conducting glass substrates. TiO<sub>2</sub> and ZrO<sub>2</sub> films were 5 – 8 μm thick with good transparency. Al<sub>2</sub>O<sub>3</sub> films were ~15 μm thick, and showed greater scattering than the TiO<sub>2</sub> films. Immersion and storage of the TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and ZrO<sub>2</sub> films in a room temperature ethanol solution containing 200 μM N3 and 20 mM chenodeoxycholic acid<sup>14</sup> resulted in adsorption of the N3 dye to the porous film surface. The resulting dye-sensitized films showed an absorbance of ~1.0 at 400 nm and 550 nm. High purity N3 was purchased from Solaronix (Lausanne, Switzerland).

Pump-probe measurements were made using two different laser systems described previously<sup>11</sup>.

### Experimental Results

With the N3-TiO<sub>2</sub> sample exposed to air, transient absorption measurements using a visible pump and a visible or near-IR probe show a problematic long-lived absorption component. Hannappel *et al.* also observed such an accumulated signal for visible probe measurements made in a solvent environment;<sup>5</sup> only when measuring solid state samples under UHV did the accumulated signal vanish. Our initial investigations of various samples pumped at 550 nm and probed at 1.52 μm showed long-lived signals as well as signals not attributable to absorption by injected electrons. Figure 1 shows data for N3-TiO<sub>2</sub>, N3-ZrO<sub>2</sub>, and N3-ethanol samples. The N3-TiO<sub>2</sub> sample shows an ultrafast rise of absorption and subsequent initial decay, similar to that reported by Hannappel *et al.*<sup>5</sup> However, it is clear from measurements of the N3-ZrO<sub>2</sub>, where significant injection is not expected, and N3-ethanol, where no semiconductor is present, that other sources of transient absorption at 1.52 μm are present from either N3\* or N3 photoproducts in this near-IR region. To rule out nonlinear effects such as two photon (pump) absorption, we

have verified that the absorption signal is linear with pump pulse energy. The transient signal for N3-TiO<sub>2</sub> may very well be dominated by the injected electron absorption, but no clear conclusions can be drawn without well-behaved blanks to verify the absence of a signal arising from N3\* or N3<sup>+</sup>.

Due to a long-lived absorption we observed when probing at 1.52  $\mu\text{m}$ , we made additional transient absorption measurements at longer IR-wavelengths. The samples were measured in air, and the linear absorbance at 2110  $\text{cm}^{-1}$  (4.74  $\mu\text{m}$ ) was 30 mO.D. for the N3-TiO<sub>2</sub> sample and 70 mO.D. for the N3-Al<sub>2</sub>O<sub>3</sub> sample. Using the 1 kHz system, we used a pump pulse energy of 1.1  $\mu\text{J}$  at 400 nm and 100 fs pulsewidth to excite samples of N3-TiO<sub>2</sub>, N3-Al<sub>2</sub>O<sub>3</sub>, N3-ZrO<sub>2</sub>, and unsensitized TiO<sub>2</sub>. Probing the resultant absorption at 4.63  $\mu\text{m}$  and 4.9  $\mu\text{m}$ , we find no transient absorbance for either the N3-Al<sub>2</sub>O<sub>3</sub> or N3-ZrO<sub>2</sub> samples, and only a small absorbance for the unsensitized TiO<sub>2</sub>. N3-TiO<sub>2</sub> shows a transient absorbance maximum of  $\sim 3$  mO.D. at 4.63  $\mu\text{m}$  and  $\sim 6$  mO.D. for 4.9  $\mu\text{m}$ . Results are shown in Figure 2. The transient mid-IR signals can be well fit by a single exponential rise convoluted with the instrument response function. The best fits yield time constants of 50 fs  $\pm$  25 fs, as shown by the solid lines in Fig. 2 (a) and (b). The risetime of 100 fs does not produce as satisfactory a fit of the data, as shown by the dashed line. The instrument response function was determined in a thin silicon wafer right before or after a kinetics scan at each wavelength. A typical response in silicon is shown in Fig. 2 (b); this signal can be well represented by the integration of a gaussian function with FWHM of 185 fs. The transient absorbance for the unsensitized TiO<sub>2</sub> is  $\sim 0.6$  mO.D.,  $\sim 10\%$  of the absorbance for N3-TiO<sub>2</sub> at 4.9  $\mu\text{m}$ . These results show conclusive and direct evidence of the arrival of electrons within the TiO<sub>2</sub> following photoexcitation of adsorbed molecules of N3.

As shown in Figure 3, when probing at 6.6  $\mu\text{m}$  we obtain similar results showing electron injection for N3-TiO<sub>2</sub>, no injection for N3-Al<sub>2</sub>O<sub>3</sub>, and slight IR absorption for unsensitized TiO<sub>2</sub>. In addition, the data shows a fast initial decay following the rise; this decay occurs on a  $\sim 50$  fs timescale. The origin of the initial decay is not determined, but is consistent with either the cooling or trapping of the injected electrons. The free electron absorption cross-section is proportional to the density of states and relaxation of electrons toward the conduction band minimum is expected to result in reduced IR absorption. Trapping of electrons could also result in a reduced IR absorption. Our preliminary measurement of the spectral dependence of the IR absorption indicates an absorbance which increases with probe wavelength.

## Discussion

Using TRIR absorption spectroscopy, we have measured the electron injection time for N3-TiO<sub>2</sub>. Pumping samples of N3-ethanol, N3-TiO<sub>2</sub>, N3-Al<sub>2</sub>O<sub>3</sub>, and N3-ZrO<sub>2</sub> at 400 nm or 550 nm, we probed the absorption by injected electrons using infrared femtosecond pulses at 1.52  $\mu\text{m}$  and also in the range of 4.1 to 7.0  $\mu\text{m}$ . Our results from the 1.52  $\mu\text{m}$  TRIR experiments show the presence of long-lived absorption, as well as absorption by N3-ethanol and N3-ZrO<sub>2</sub>. Any injection from N3-ZrO<sub>2</sub> is likely quite inefficient, and N3-ethanol provides no free or trapped electrons; therefore, the absorption signals for these samples could be due to products of the photodegradation of N3 or possibly to lower-lying N3 excited state absorption. Hannappel *et al.*<sup>5</sup> reported that measurements of the visible transient absorption made in a solvent or air environment exhibited an accumulated signal which they attributed to "side reactions". To overcome this spurious accumulated signal, they made all solid state measurements in a UHV environment. We have found that probing further into the IR, in the 4.1 to 7.0  $\mu\text{m}$  range,

environment. We have found that probing further into the IR, in the 4.1 to 7.0  $\mu\text{m}$  range, simplifies measurement of the TRIR absorption by injected electrons by eliminating the requirement of the UHV apparatus; we observed no accumulated or long-lived absorption components in this wavelength range. In addition, our results indicate that we eliminate the possibility of any contribution to the IR absorption signal arising from the dye excited or cationic states; the former could arise from non-injecting dye molecules. Analysis of our transient absorption data for probe wavelengths of 4.63, 4.9, and 6.6  $\mu\text{m}$ , shows an instrument-limited electron injection time for N3-TiO<sub>2</sub> of  $\sim 50$  fs. For Al<sub>2</sub>O<sub>3</sub> with a bandgap of  $\sim 10$  eV, and ZrO<sub>2</sub> with a bandgap of 5 eV,<sup>15-18</sup> the conduction band edge is expected to lie too far negative to allow injection from N3\*. As expected, our TRIR absorption measurements indicate that while N3-TiO<sub>2</sub> produces an IR-absorbing electron population within the semiconductor, no such absorption is present for the non-injecting N3-Al<sub>2</sub>O<sub>3</sub> and N3-ZrO<sub>2</sub> samples. The broad IR absorption of N3-TiO<sub>2</sub> could be due to free electrons, trapped electrons, or both. Data taken at 6.6  $\mu\text{m}$  suggests a cooling or trapping of the injected electrons on the  $\sim 50$  fs timescale. Efforts to measure the time-resolved injected-electron IR absorption spectrum for N3-TiO<sub>2</sub> are underway.

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- \* The work reported here has been previously published in Ref. 11.
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**Figure 1.** TRIR absorption data for 550 nm pump and 1.52  $\mu\text{m}$  probe of N3-TiO<sub>2</sub>, N3-ZrO<sub>2</sub>, and N3-ethanol (after Ref. 11)

**Figure 2.** TRIR absorption data for probe wavelengths of (a) 4.63  $\mu\text{m}$  and (b) 4.9  $\mu\text{m}$  following photoexcitation by 400 nm, 100 fs pulses. As seen in (a), neither N3-Al<sub>2</sub>O<sub>3</sub> nor N3-ZrO<sub>2</sub> show evidence of injected electron absorption. The system response function from free-carrier absorption in silicon shown in (b) is seen to match very closely the rise of the absorption signal for N3-TiO<sub>2</sub>; unsensitized TiO<sub>2</sub> shows a small absorption due to carriers photoexcited directly within the electrode. The rise times indicate an injection time  $\sim$  50 fs (after Ref. 11)

**Figure 3.** TRIR absorption of a 6.6  $\mu\text{m}$  probe for N3-TiO<sub>2</sub>, N3-Al<sub>2</sub>O<sub>3</sub>, and unsensitized TiO<sub>2</sub> following photoexcitation by 400 nm, 100 fs pulses. The fast ( $\sim$ 50 fs) rise of absorption for N3-TiO<sub>2</sub> is followed by an equally fast initial decay. The source of this decay has not been decisively assigned, though it is believed to be due to cooling or trapping of the injected electrons (after Ref. 11).

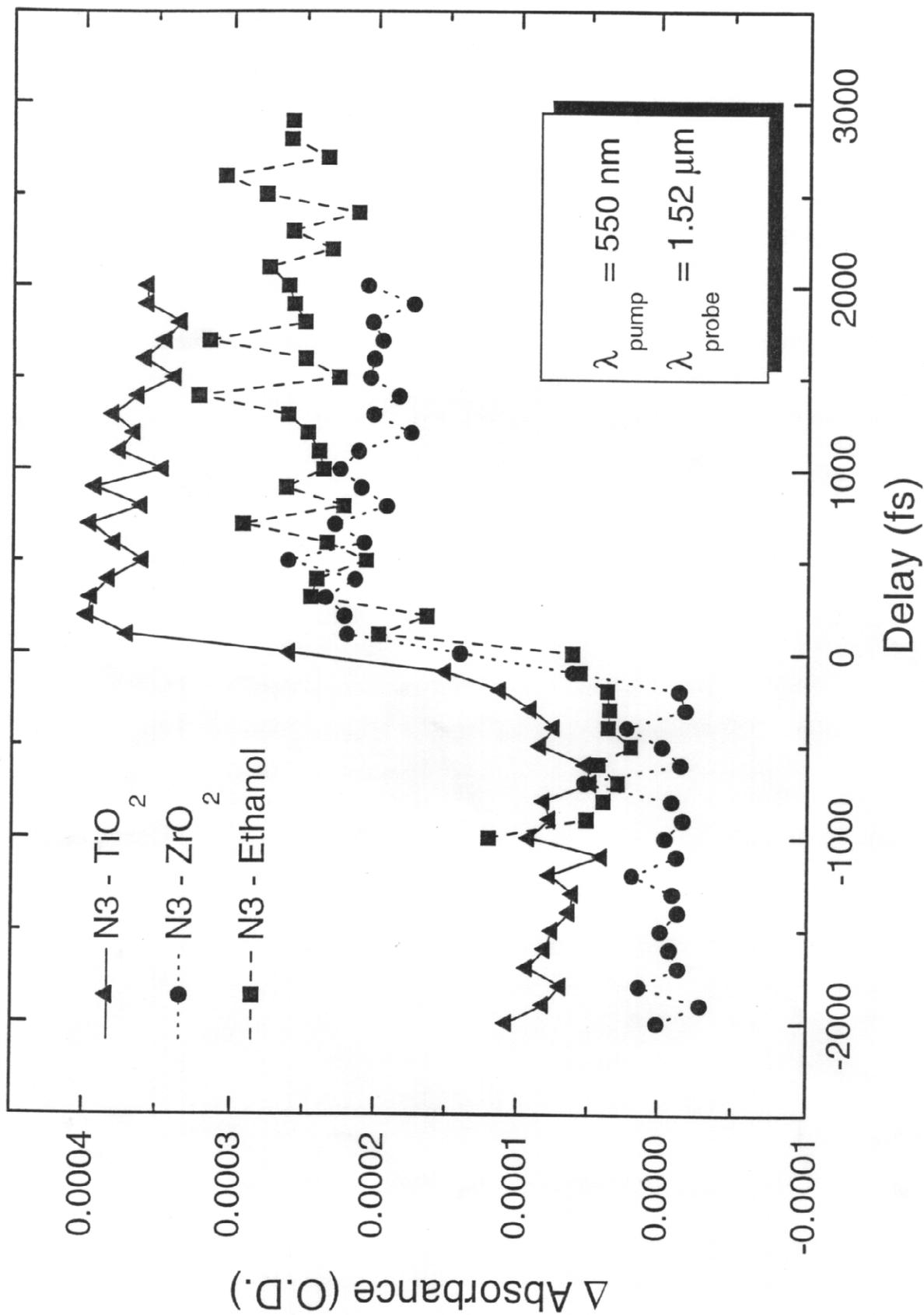


Figure 1.

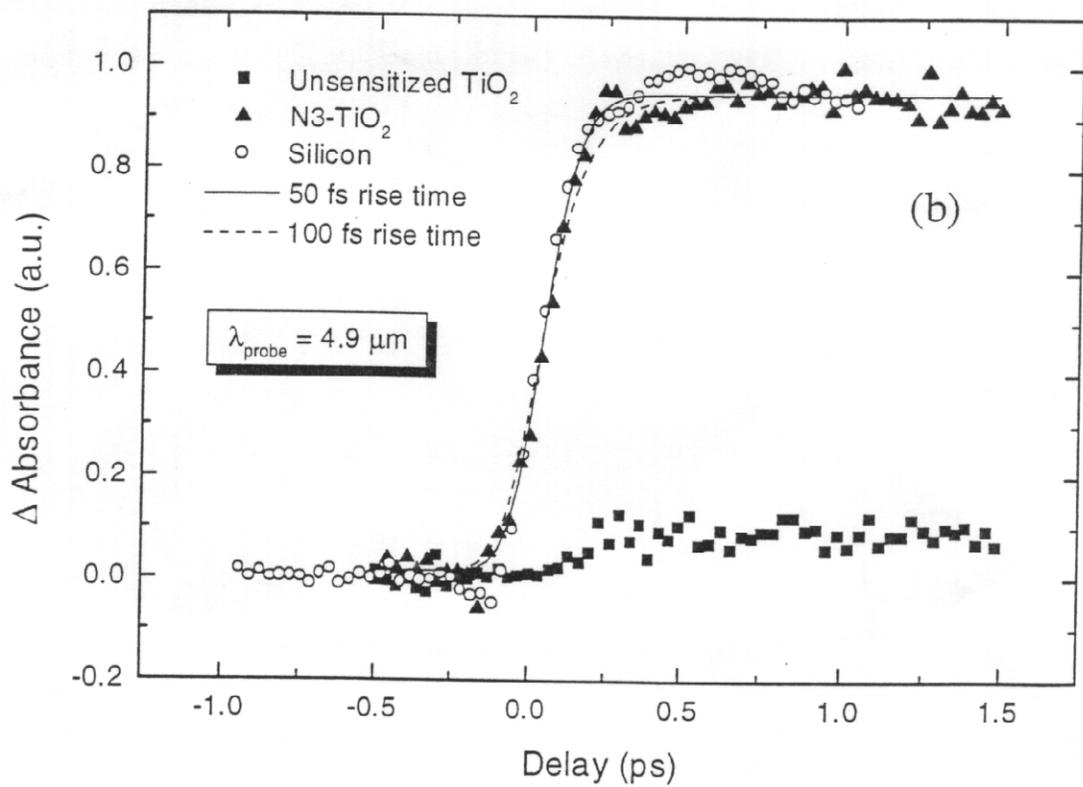
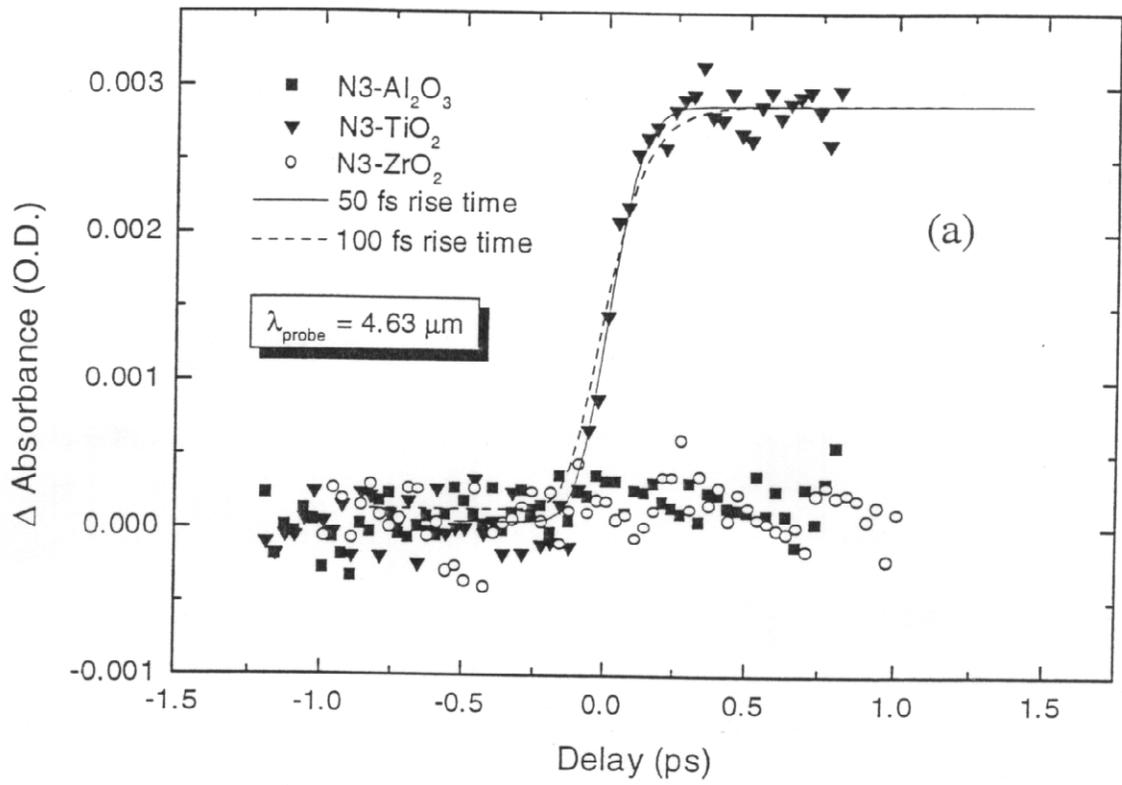


Figure 2.

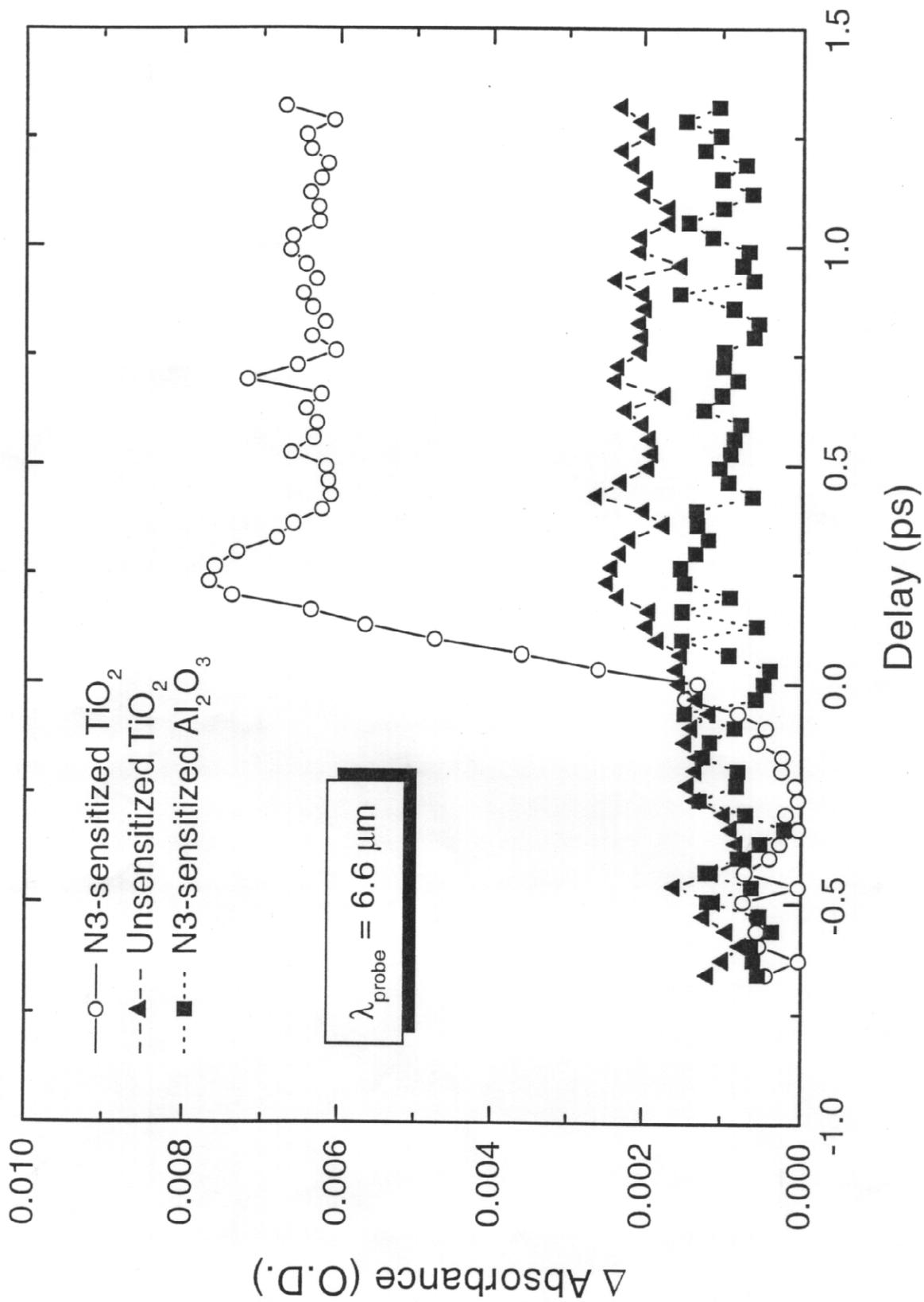


Figure 3.

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