

APPLICATION NOTE: INTRODUCTION TO TRANSIENT ABSORPTION SPECTROSCOPY

Techniques

Transient Absorption Spectroscopy

Keywords

- Pump/Probe
- Analytical Chemistry
- Flash photolysis
- Ultrafast chemistry
- Ultrafast Laser

Introduction

When a molecule absorbs a photon, it imparts energy to the molecule causing it to temporarily excite from the ground state to a higher electronic or vibrational energy level. Due to conservation of energy this can only take place when the photon energy is precisely equal to the difference between the ground and excited states can the light be absorbed. Additionally, since there is a direct correlation between the



Femtosecond laser in laboratory

number of molecules and the number of absorbed photons, it is relatively straight forward to determine the molecular density. As a result, absorption is one of the most commonly used spectroscopic techniques, particularly for concentration measurements.

Most of the excited states induced by absorption are incredibly short-lived. The spontaneous lifetime of most transient excited states are typically the order of femtoseconds or picoseconds, with the notable exception of meta-stable excited states. Based on this fact, George Porter and Ronald Norrish, while at the University of Cambridge, realized that they could use flash lamps to study these intermolecular energy transitions through a method they called flash photolysis in 1950 [1]. Even though the foundation was set in the 1950s, it wasn't until the development of the ultrafast mode-locked laser that scientists were not able to fully take advantage of Porter and Norrish's contributions. The two of them later went on to receive the Nobel prize in chemistry for this discovery in 1967, which they also shared with Manfred Eigen, who also contributed to our current understanding of ultrafast chemistry. Today ultrafast lasers have completely replaced flash lamps as the preferred excitation source for these types of experiments, and the technique is more commonly referred to as transient absorption spectroscopy (TAS).

Fundamentals of Absorption Spectroscopy

Traditionally absorption spectroscopy is discussed in terms of the Beer-Lambert Law which relates the transmitted intensity to the absorption coefficient (α) and the pathlength (z), which can be expressed as shown. While equation 1 is not the most commonly used expression of Beer's law, it is the most useful for gaining an intuitive understanding of the underlying physics.

$$I(z) = I(0)e^{-\alpha(\lambda)z}$$
Equation 1

In this form, we can clearly see that the

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absorption coefficient is wavelength dependent, therefore resulting in an absorption

excited electronic or vibrational state and the population difference (N) between the

$$\alpha_i(\lambda) = -N\phi(\lambda) = (N_1 - N_2) \frac{\lambda^2}{8\pi t_{sp}} g(\lambda)$$

spectrum. By diving deeper into the absorption coefficient for a given transition, we can [2]. Additionally, we can see that the transishow the relationship in equation 2.

Here we see that the absorption coefficient is dependent on the transition cross-section (Φ) which represents the probability of an incoming photon exciting the sample to an

ground state (N_1) and the excited state (N_2) tion cross-section is inversely proportional to the spontaneous lifetime (t_{sp}) of the excited state.

Now we can see that unlike the more simplified version of Beer's law taught in intro-

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ductory chemistry the absorption spectrum of a given analyte is not truly based on the molecular concentration but population difference. Furthermore, since the population difference is itself a time-dependent function based on the spontaneous lifetime the absorption coefficient also has a temporal dependency associated with it. All of that being said, most of the time, the population difference can be ignored because the spontaneous lifetime is so fast, and the light intensity is so week, that it never significantly depletes the ground state population.

Measuring Transition Lifetimes

While there are many different ways to use ultrafast lasers to perform TAS, on the most fundamental level they are all variations on a single technique, known as pump-probe. The procedure requires two laser beams to excite the analyte and measure absorbance determine the change in absorption. Then this process is systematically repeated for different delay times bet-

ween the pump and probe pulses to measuring the change in transmitted probe pulse energy, as shown in figure 1. From this data,



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simultaneously. First, the high intensity pump laser excites a significant percentage of the molecules in the sample to a higher energy level altering the population difference and reducing the absorption coefficient of the transition. Next, a low intensity probe laser is passed through the sample to measure the absorption. By taking the difference of the probe laser absorption with and without the pump laser, you can then one can now build a picture of the kinetics of the energy level transitions and determine spontaneous lifetime and other transient effects.

As was eluded to in the previous section, most of the time, we are not interested in only measuring one transition, but instead, we want to see the effects on the entire

spectrum. To accomplish this goal with a monochromatic probe would be impractical, but utilizing a nonlinear optics process known as supercontinuum generation overcomes this issue. An explanation of how supercontinuum light is generated is far beyond the scope of this application note, but it should be understood that this process allows an ultra-short pulse laser to be converted into a white light source while



still maintaining most of the laser properties. As a result, one can now measure the entire absorption spectra with a single probe pulse. Figure 2 shows a simplified schematic representation of a typical TAS set-up In some TAS set-ups, a chopper and a lock-in amplifier are added into the system to improve the signal-to-noise ratio. Figure 3 shows a simulated transient absorption spectrum showing the subtle differences in absorption resulting from the population difference induced by the absorption of the pump pulse.



Figure 1: Simulated pump-probe TAS kinetic decay data.courtesy of Wang, Zhe, et al.



typical pump-probe TAS set-up.

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spectrum



Spectrometer Requirements



AvaSpec-ULS2048CL-EVO

The spectrometer parameters of a typical TAS measurement are very similar to those required for traditional absorption spectroscopy with the exception of speed and dynamic range. First, it should be noted that the speed of data acquisition is in no way correlated to the lasers pulse width or pulse repletion rate. Each spectral integration will contain a large number of individual laser pulses. Instead, the speed requirements are solely dependent on the number of data points that are required to be able to capture the transient kinetics, and how well it can be triggered with the delay line. Additionally, the dynamic range of the spectrometer is so crucial because transient absorption is measured as difference spectra, and the differences can be extremely subtle. As a result, CMOS detec-

sd

Time / I

Application Examples

N-H bond fission in aqueous adenine The scientific community has widely used Avantes spectrometers for measuring TAS. An excellent example which visually



Figure 6: TAS spectra of CNCbl in water, ethanol, and a 1:1 mixture of water and ethanol. Excited with a 266 nm pump laser [4].

tors are always preferable to due to their faster readout speeds and larger dynamic ranges than CCD detectors.

Even though the minimum integration time of most CMOS cameras is on the order graphical user interface (GUI) when using of 10 microseconds, the major bottleneck is often the spectrometers readout electronics that have to transfer the data from the detector to the computer. Avante's new dynamic store to RAM capabilities represent a major leap forward in high-speed spectral readout. Utilizing the dynamic store to RAM feature allows the user to save scans to the RAM buffer onboard the instrument, and simultaneously offload the mum of 5.6kHz when the configuration is spectra to the computer. Using the dyna-

mic store to RAM function, the AvaSpec-ULS2048CL-EVO is now capable of continually acquiring spectra at a rate of 2 kHz. Figure 4 shows an example of the new dynamic store to RAM.

This rate can be increased even further by reducing the number of active pixels being used on the detector, but this should be used with caution as it will impact the spectral resolution. The AvaSpec-FAST series of spectrometers takes advantage of this increase in the readout speed, allowing a spectral transfer rate of up to a maxireduced to 350 pixels. λ / nm



Figure 5: (a) Waterfall plot of TAS spectra of Ade[-H] in D¬2O excited with a 266 nm pump laser as a function of delay time, and (b) normalized decay kinetics at 400nm.[3]

shows the functionality of TAS data, was published by a group at the University of Bristol while studying N-H bond fission in aqueous adenine [3]. The results that are shown in figure 5 below were obtained using an Avantes, AvaSpec-FAST spectrometer, which used 750 pixels to measure a spectral range from 200 nm to 620nm. The sample was excited with a 266 nm pump laser and a supercontinuum probe laser, with a variable pulse delay from -500fs to 3ps. From this data, it is straightforward to see the time-depended nature of the changing absorption coefficient after the pump pulse. Based on the curve fit shown in figure 5b, the research team was able to determine that the spontaneous lifetime

(or time-constant as they referred to it) was 470 +/- 18 fs [3].

Behavior of cyanocobalamin in excited states

A second exciting usage of TAS was published by a team at the University of Michigan while studying how cyanocobalamin excited states behave in biological systems [4]. In this study, they used an Avantes spectrometer to measure how different solvents affect electron transitions, as shown in figure 6. The team then used this data to verify a complex quantum mechanical model that they developed to "lay the groundwork for detailed studies of a range of cobalamin cofactors proposed for use as anti-vitamins, photoactivated



drug delivery agents, and in situ production of hydroxyl radicals [4]." Photoreduction of graphene oxide Lastly, a joint team from the Max

Planck Institute, University of Hamburg, University of Ioannina, and University of Toronto used TAS to better understand photoreduction of graphene oxide [5]. In this research, they used TAS to show that the photoreduction process was actually a multistep process by observing that there where two overlapping decays, one which took place in under 2 picoseconds (ps) and a second taking place between 2ps and 250 ps. The fast decay correlated to the ionization of the graphene oxide and the water producing solvate electrons, which

Final Thoughts

As researchers continue to probe more in-depth into the underlying physical chemistry of complex systems like the ones mentioned, it is becoming ever more for which Gérard Mourou and Donna critical to understand the internal transition kinetics within molecules and atoms. While this application note is by no means viding the community with cutting edge a comprehensive review of all of the entire field of ultrafast transient absorption, it provides an introductory overview of the physics behind TAS as well as typical system configurations. Furthermore,



Time delay (ps) Figure 7: Short term (a) an long term (b) kinetic decay of photoreduced graphene oxide in

water using a 266nm pump and the differential absorption at 400nm[5]. then interacted with the graphene oxide

to cause the reduction during the slow decay period. The data shown in figure 7 was collected using an Avantes fiber-coupled spectrometer and excited using 266 nm pump laser.

TAS spectroscopy is currently undergoing a second renaissance with the recent invention of the attosecond pulsed laser. Strickland were awarded the Nobel prize in 2018. Avantes is excited to keep prospectrometers for the next generation of ultra-fast spectroscopy.

For more information about the full range of laboratory and OEM spectrometer options available from Avantes including our

new dynamic store to RAM capabilities, please feel free to visit the website at www.avantesusa.com or give us a call at +1 (303)-410-8668 where our knowledgeable applications specialists are standing by to help.

References

- [1] Porter, G.N., 1950. Flash photolysis and spectroscopy. A new method for the study of free radical reactions. Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences, 200(1061), pp.284-300.
- [2] Saleh, B.E. and Teich, M.C., 2019. Fundamentals of photonics. john Wiley & sons.
- [3] Roberts, G.M., Marroux, H.J., Grubb, M.P., Ashfold, M.N. and Orr-Ewing, A.J., 2014. On the participation of photoinduced N-H bond fission in aqueous adenine at 266 and 220 nm: a combined ultrafast transient electronic and vibrational absorption spectroscopy study. The Journal of Physical

Chemistry A, 118(47), pp.11211-11225.

- [4] Wiley, T.E., Arruda, B.C., Miller, N.A., Lenard, M. and Sension, R.J., 2015. Excited electronic states and internal conversion in cyanocobalamin. Chinese Chemical Letters, 26(4), pp.439-443.
- [5] Gengler, R.Y., Badali, D.S., Zhang, D., Dimos, K., Spyrou, K., Gournis, D. and Miller, R.D., 2013. Revealing the ultrafast process behind the photoreduction of graphene oxide. Nature communications, 4(1), pp.1-5.