



Experimental Considerations for Studying the Photodecomposition Kinetics of Tetrachloroaurate

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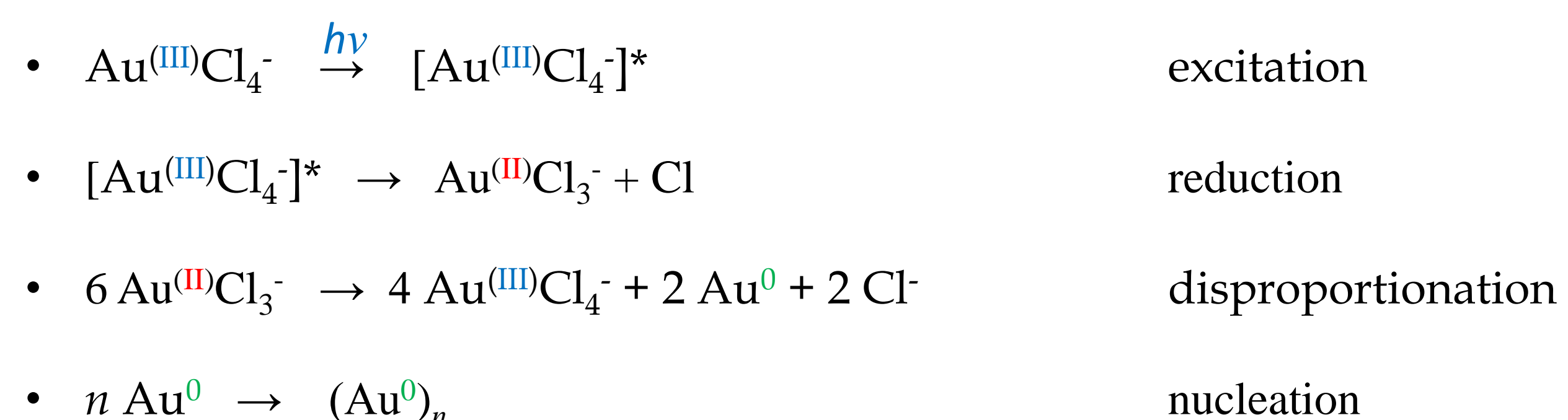
Introduction

At the most basic level, every chemical reaction involves the making and/or breaking of chemical bonds. While a great deal is known about chemical bonding, most of our understanding pertains to the intrinsic nature of bonds, or in other words, how bonds behave when the compound that they are a part of is completely isolated. Since the vast majority of chemistry does not involve such isolated species, it is of great importance to learn more about how bonds are influenced by their surroundings. Bond cleavage in the model compound, tetrachloroaurate, is studied by monitoring the rate of photodecomposition in a variety of solvents. New experiments that account for the intensity of ultraviolet radiation are beginning to produce results and potential trends are beginning to emerge.

Tetrachloroaurate Photochemistry

Tetrachloroaurate (AuCl_4^-) plays an important role across a diverse range of areas including nanotechnology, geochemistry, and photo-chemical printing. Tetrachloroaurate is common precursor for the formation of gold nanoparticles, which have widespread application in areas as diverse as chemotherapy, medical and chemical imaging, materials science, and solar cells. In geochemistry, tetrachloroaurate is important as a soluble form of gold, which aids the geochemical transport of gold through the environment. Most recently, tetrachloroaurate is being used to develop a novel process for creating microfluidic masters for devices with small features. In all cases, the ultimate fate of the molecule is highly dependent upon how Au-Cl bonds are broken.

In a series of pioneering experiments by Eustis *et al.*, the following reaction mechanism was proposed for the photodecomposition of tetrachloroaurate and subsequent formation of goldnanoparticles:



These experiments determined that the rate of the initial photoreduction steps could be greatly increased by adding glycol to the reaction mixture, but it was unclear why.

Subsequent experiments in the gas phase revealed that absorption of a UV photon does result in cleavage of the gold-chlorine bond to produce a neutral chlorine atom and charged gold fragment, and that glycol is not necessary for reduction to take place.

Accompanying and ongoing computational investigations suggest that glycol may not directly participate in the reduction step. Instead, the presence of water is likely to hinder reduction by causing cleavage of the gold-chlorine bond to produce a charged chlorine atom. If this is true, then addition of glycol would simply reduce the hindering effects of water. Additionally, solvents other than glycol should have similar effects on tetrachloroaurate photoreduction.

Old Kinetics Experiments

- Monitor the rate of UV photodecomposition in aqueous solution using UV/Vis absorption spectroscopy.
- Every 3-5 minutes, the sample is removed from the irradiation compartment and placed into a spectrometer to measure UV absorbance.
- Measure how photodecomposition rates are affected by the addition of various alcohol co-solvents.

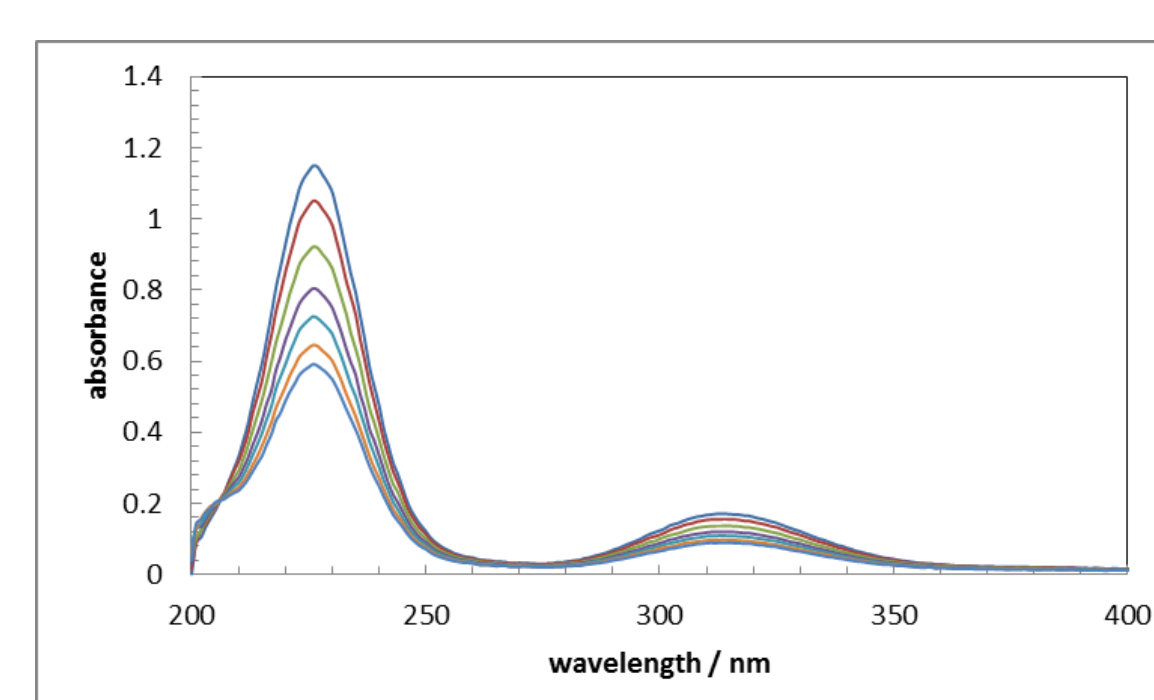


Figure 1 - UV-Vis absorption spectrum of tetrachloroaurate as a function of UV-irradiation time.

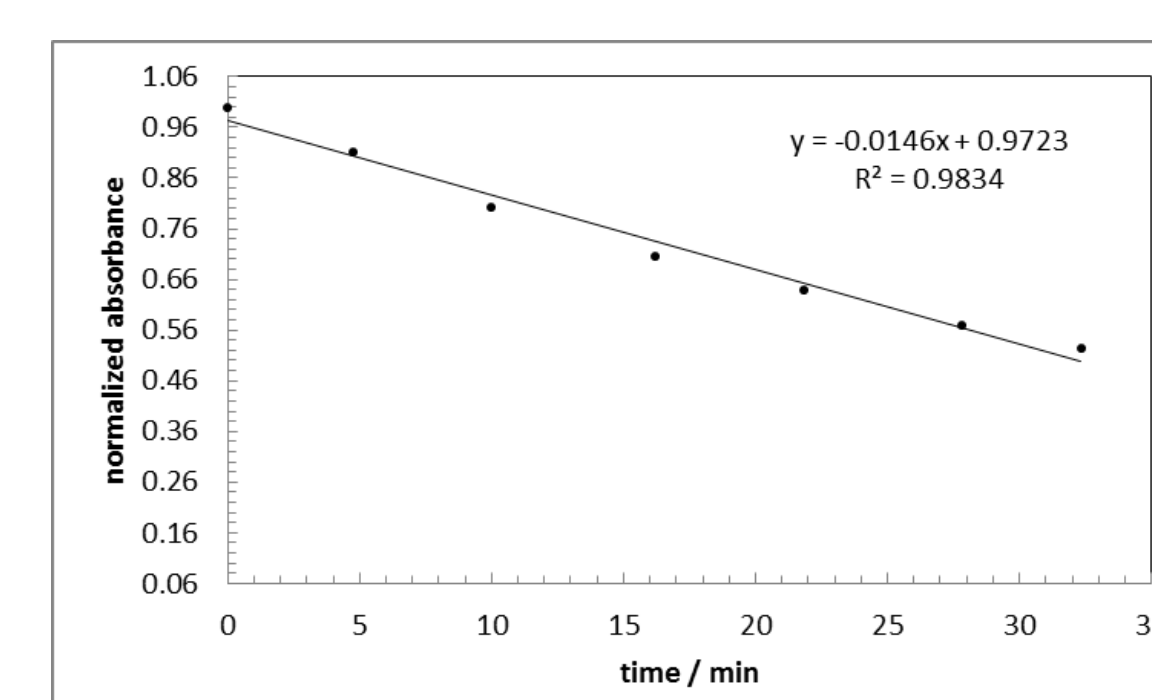


Figure 2 - Initial rate plot for the photodecomposition of tetrachloroaurate.

- Look for trends between reaction rate and various "solvent-based" solution properties.
- Reaction depends on the intensity of UV irradiation but, initially, this could not be controlled or monitored.

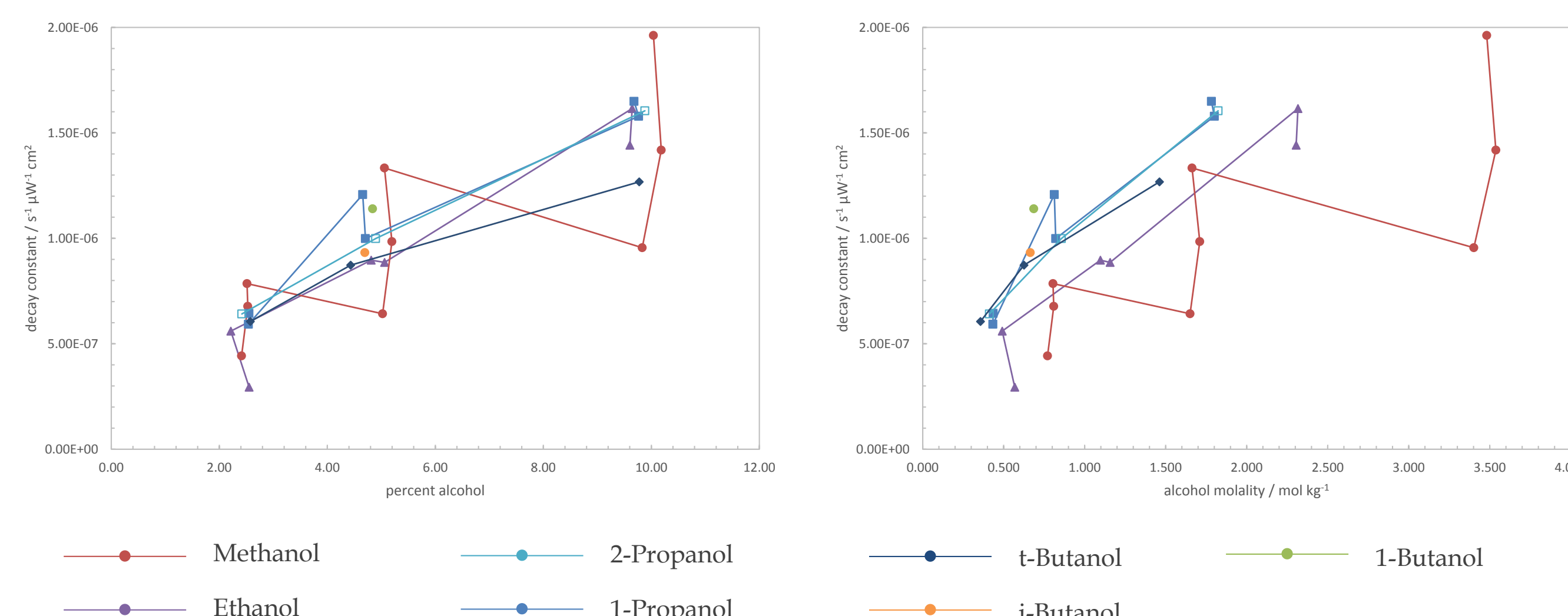


Figure 3 - Plots of photodissociation rate constants as a function of different physical properties, used to identify possible trends. Note the large variability in replicate measurements.

- Replicate measurements revealed large variability in rate constant.
- Analysis of the experimental procedure revealed large variability in the kinetic probe time.
- Depending on the time it took an individual to obtain a UV-Vis absorption spectrum, the effective duty cycle of the experiment varied between

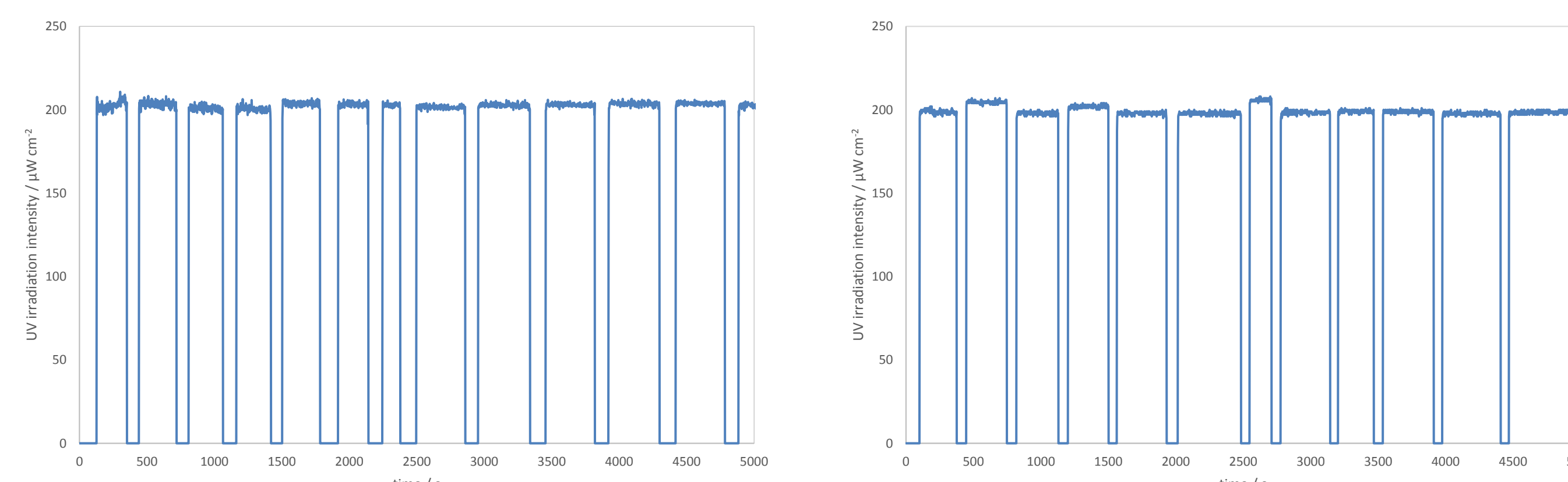


Figure 4 - UV irradiation intensity during replicate experiments with large variation in duty cycle. The experiments represented in the plots had a duty cycle of 74% (left) and 85% (right).

New Kinetics Experiments

- To overcome the problem of variable probe time, we have redesigned the experiment to use a flow through configuration.
- The new configuration makes use of two, separate cuvettes, one for irradiation and one for spectroscopic measurements.
- A sample solution is continuously irradiated with a UV lamp in an irradiation cuvette.
- Using a peristaltic pump, the sample solution is continuously pumped into a probe cuvette located in a spectrometer, and then returned to the irradiation cuvette.
- UV-Vis absorption spectra are recorded every 30 seconds.
- Because the system is fully automated, the kinetic probe time is no-longer affected by human variability.

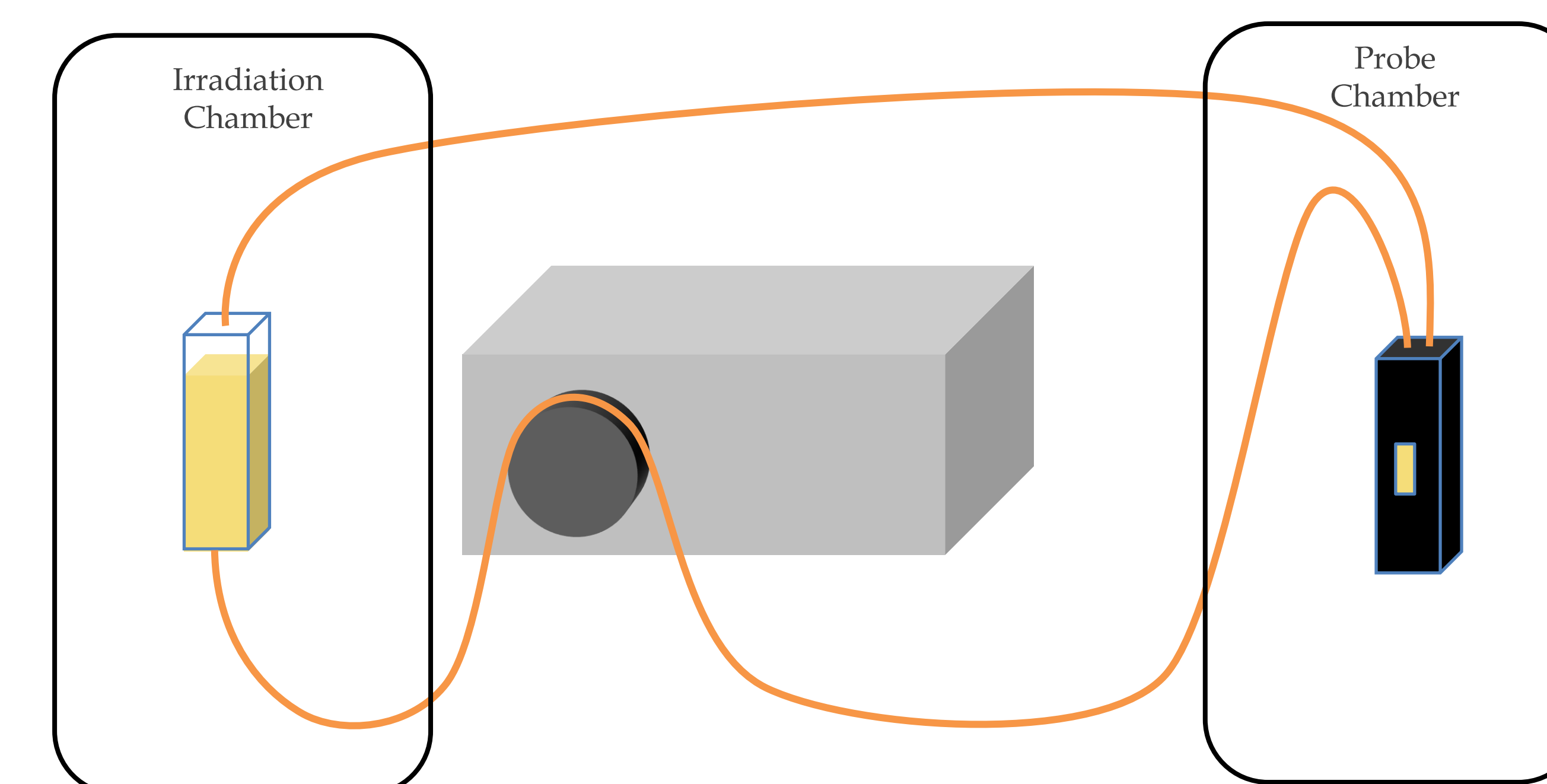


Figure 5 - Schematic of the new flow-through system

- Flow system characteristics:
 - Total volume: 4-5 mL
 - Irradiation cuvette volume: 3.2 mL
 - Probe cuvette volume: 0.110 mL
 - Flow rate: 6-7 mL min⁻¹
 - Flushable with dilute nitric and hydrochloric acids (separately)

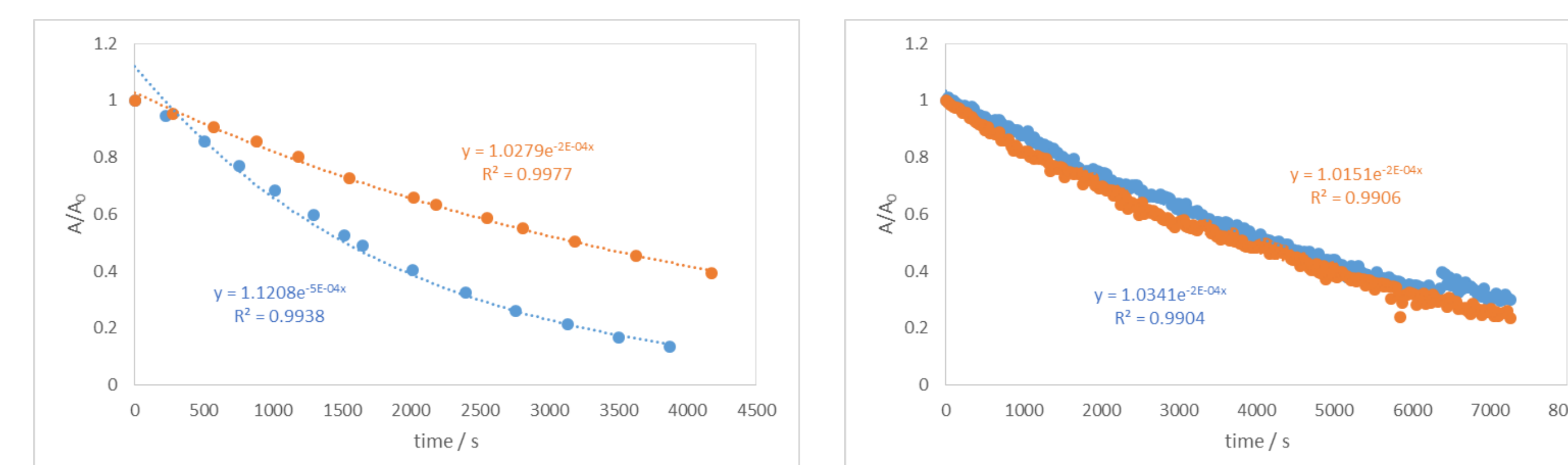


Figure 6 - Replicate experiments for ~10% methanol solutions conducted with the old setup (left) and the new setup (right).

- The new, flow-through experimental setup allows for more frequent data collection and greatly improves precision.
- New variables, such as dead-time, lag-time, and effective irradiation volume must be further characterized before obtaining further data.