A Stop-flow sample delivery system for TRMPS experiments

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Abstract

This report will present improvements to previously developed stop flow sample delivery systems, for use in the analysis of photosensitive reactions using different spectroscopy technologies. The results presented here will show how, by improving on the electronic systems driving such sample delivery systems, one can achieve higher speeds compared to other systems like this, and more consistent and reproducible results.

1 Introduction

In the study of fast dynamics in chemistry and biology, ultra-fast time resolved spectroscopy has been shown to be the key technology that enables scientist to observe events happening in the milli-second to pico-second timescales. These kinds of systems have been found invaluable in studying fast dynamics in photosensitive proteins, or in the reactions associated with transition metal corbonyl compounds. Usually, these types of systems use a laser or LED pulse so excite the sample and start the reaction to be analysed. Then, the reaction is observed either by continuously 'probing' the sample with a CW light source (flash photolysis) or by using a second pulsed laser source and probing from one time to an n amount of times, or by excting and probing many times at the same time. One key characteristic that these typologies have in common is that, to achieve a low SNR, they average many such events over a certain period of time.

As such, there appears the requirement for adequate sample delivery systems, that can ensure that every time the sample is excited and the reaction is started, there is new sample to be analysed. That is because the inherent nature of these pump-probe experiments requires the sample to be fully excited and observed before the next pump pulse. So far, most methods have been based on a combination of continuously flowing the sample to be analysed, since most of the samples are usually in a liquid state, and moving the sample or the laser beams such that the beam foci hit a different section of the sample cell.

One notable development in the area has been the use of microfluidic systems that use valves to control the flow of liquid trough a sample area. In a recent publication by P.Hamm et al. [1], such a system is explored, where a custom sample cell with two valves is used. In this, the system manages good results in the sub 100hz region, but certain issues still remain related to stability and speed. Whilst these systems have shown that it is indeed possible to achieve sample replacement using valves and well timed opening and closing patterns, there is no data out there on the suitability of these systems for long term use, or on the repeatability of such systems.

While the system aforementioned focuses mainly on the mechanical design of the system, and how this interacts with different fluidic effects that might introduce measurement errors and noise, very little is said about creating an electronic system that can reliably and consistently provide the desired results. Besides that, the previously developed systems offer very little control in the way the sample is replaced, whilst also not making any previsions for ensuring that electronic delays and noise do not affect the working of the system. As such, one first point where such systems can be improved is creating the appropriate electronic tools to drive and control such a system.

2 System Design

Drawing inspiration from the system described by Hamm (2020)[1], the system presented here uses SMLD Micro-valves purchased from Fritz Gyger AG (CH). According to the manufacturer's datasheet, the valves are created especially for situations where fast dispensing of small quantities of liquid is required, making them perfect for this system. The mechanical design of the system is adapted from the one described by Hamm (fig.1).

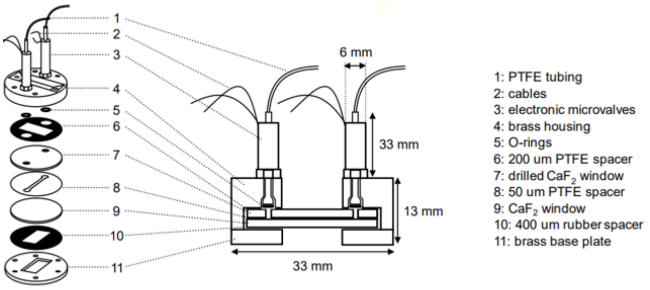

Figure 1: System mechanical design [1]

In terms of actuation and electrical connection, these use a standard solenoid and permanent magnet system to drive the plunger. As such, their working principle is relatively straight forward. The magnet is inside the valve, attached to a spring-loaded plunger. The solenoid, upon applying a current trough it, creates a magnetic field that pulls the permanent magnet towards its centre. The magnetic flux needed to actuate the valve has a non-linear time profile, and it will depend not only on the resistance imposed by the initial momentum necessary to move the sample, but also on the increasing field coming back to the solenoid from the magnet as it moves closer to its open position. In general though, one can simply assume that more flux is required in the beginning, when opening the valves, as it has to move the plunger from a stationary position, and afterwards keeping the valve open requires a minimal amount of magnetic flux. As such, care has to be taken such that the current profile applied to the valves is carefully considered, to optimise the opening and closing times, as well as the frequency at which the valves can work. Indeed, the manufacturer recommends for these units a 'peak and hold' approach, were a larger current ($\approx 1A$) is applied in the first part of the opening cycle, and then brought down to a lower level ($\approx 200mA$) for the remaining of the valve opening time (fig. 2).

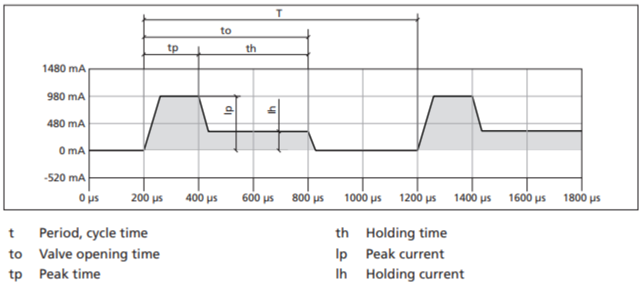

Figure 2: Current profile from datasheet

3 Valve driving topology

The usual method of creating a controllable power source is using a switch mode power supply. These work by turning on and off transistors at high frequencies (100s of kHz), with a controllable duty ratio. A synchronous buck converter configuration was chosen for this system, since it would provide the best control over the system, with a good response time and system simplicity. With this converter, the output voltage is simply the product of the input voltage and the duty ratio.

The most basic representation of the circuit required to drive one valve is presented in fig. 3. FETD and FETD1 are the two switching power MOSFETs, V-DC is a constant 15V that powers the system, R7 and L4 are used to model

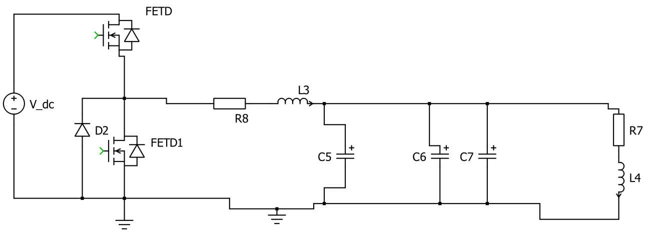

Figure 3: Simplified synchronous buck converter

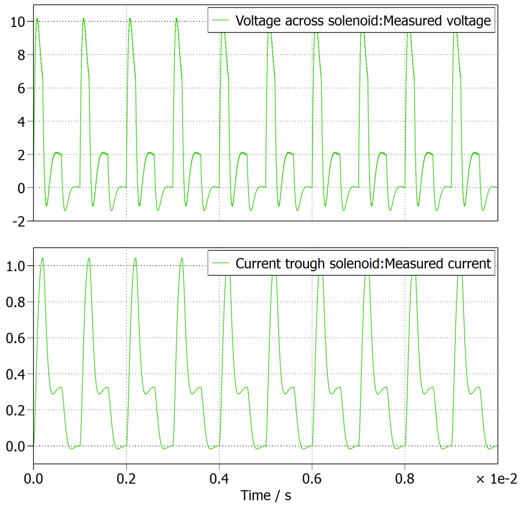

Figure 4: Simulated voltage and current curves

the solenoid, and all the other components are used for filtering the signal going into the valves. Because of the switching of the transistors, the output voltage across FETD1 will be a sum of the DC fundamental signal and the higher frequency switching component:

$$V_{out} = V_{out}^{DC} + V_{out}^{HF} \tag{1}$$

As such, the output is filtered using a LCR second-order low pass filter, designed to have a 40dB attenuation at the switching frequency of 200kHz.

Modelling of the system shows the current following the 'peak-and-hold' topology (fig.4). Since the system is driving a mostly inductive load, the voltage is not in a control loop, allowing it to overshoot to quickly charge and discharge the solenoid.

4 System testing

4.1 Methods

For the testing of the system, a classic photolysis experiment was chosen. Since in this case we only worry with the speed of each run, and not the actual analysis of the chemical and physical processes, the photolysis of $W(CO)_6$ was chosen. The behaviour of corboxyl metal compounds has been well studied and understood[2][4], so we will use existing literature to compare results and verify the behaviour of the system. In this, a sample of 0.5mM of $W(CO)_6$ in n-heptane is exposed to a pump pulse at 330nm (100μm path length), to start a reaction. Exposure to UV light causes one CO group to detach from the complex, being replaced with a haptane molecule. After some time, water impurities in the sample bond to the metal complex, replacing the heptane molecule and creating a more stable water adduct (eq. 2-4).

$$W(CO)_6 + UV \rightarrow W(CO)5 + CO \tag{2}$$

$$W(CO)_5C_7H_{16} \rightarrow W(CO)_5C_7H_{16} \tag{3}$$

$$W(CO)_5C_7H_{16} + H_2O \rightarrow W(CO)_5H_2O + C_7H_{16} \tag{4}$$

Previous literature on this kind of experiments describe the expected timescales of the reaction. The initial UV exposure and photodissociation happens in $< 300fs$, then the formation of the heptane adduct takes about 2ps, vibrational cooling over 100ps, and the replacement of the heptane ligand by water at longer timescales, depended on the amount of water impurities in the system($> 10us$)[3].

In the case of this experiment, the fast reaction times are ideal to check whether the sample is being replaced when needed. Since a change in absorption is visible on fs timescales, testing of higher repetition rates on the sample delivery system is possible.

The IR spetrometer used in this experiment is the same as the one presented by Greetham et al.[4]. The system is based on 2 Yb:KGW amplifiers. The probe amplifier (100kHz 6W 180fs, Pharos SP) drives two IR BBO/KTA

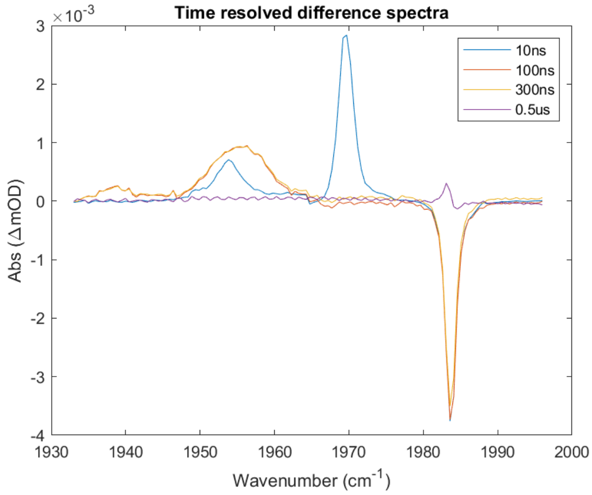

Figure 5: Test FTIR of the sample

based OPAs (Light Conversion Ltd., Orpheus ONE), providing two probe pulses. The pump amplifier (0-100kHz, 15W 260fs, Light Conversion Ltd., Pharos) drives a single BBO-based OPA set to 330nm. Data was taken in a single-UV-pump-multiple-IR-probe fashion, with different pump frequencies tested to validate the speed of the system. The sample chamber valves are frequency locked to the pump pulse trigger, with an adjustable delay time.

4.2 Results

Before running an experiment on the system, the valve driving circuit was tested separately. Fig.6 shows the voltage across one of the valves, matching the simulations from fig.4. It can be seen that it behaves as expected, the voltage being allowed to over and under shoot to rapidly adjust the current trough the solenoid.

Ensuring that the sample behaved as expected, in line with previous literature, was essential in validating the behaviour of the system. Fig 5 shows the TRIR spectra for the sample, validating its validity. One can observe a strong bleach at 1984nm, along with the vibrational excitation of the weak heptane adduct at 1968nm. The formation of the water addudct can be seen in the 1950 - 1960nm region as starting to happen after the creation of the heptane compound.

To certify the system for a wide range of repetition rates, tests were conducted in the region 10 - 400hz. Previous work shows promising results below 100hz, so this is a good addition and will exemplify the improvements made to the system. In all tests, pressure is provided from a peristaltic pump running at 23 RPM. The functionality of the system will be illustrated by following the behaviour on the strong bleach at $1984cm^{-1}$, as it's the only behaviour that stays constant during the reaction. Fig.7 shows the signal dropping, in line with excitation by the pump pulse and creation of the water adduct, and staying at around -3mOD until the valves are open, where the signal recovers to zero, showing the full replacement of the sample. This behaviour is seen to be consistent across different frequencies.

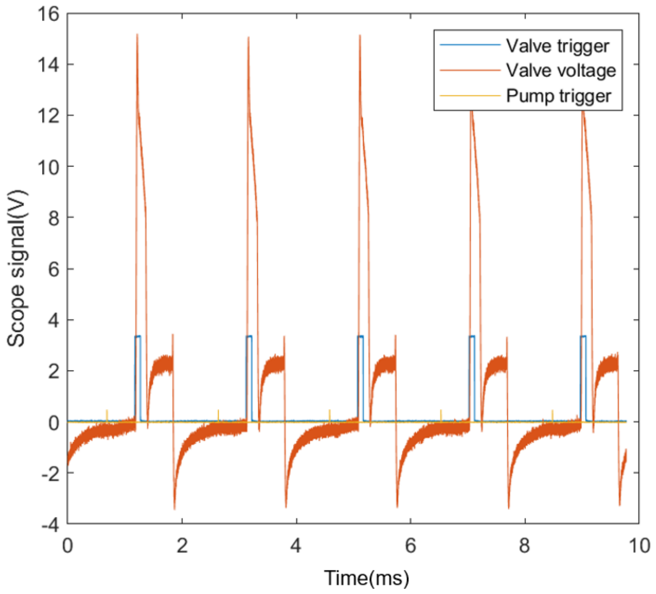

Figure 6: Measured valve voltage (500hz)

The system was also tested in a 5 hours stability test, to observe its repeatability. Fig. 8 shows that, while certain oscillatory effects are present, the sample replacement rate is very reliable, with virtually no hysteresis in the opening sequence of the valves.

One notable aspect that needs to be take into account when using these systems is the oscillatory component observed in most experiments conducted. Present in most readings but really visible in fig. 8, this oscillation patter is attributed to the continued movement of the liquid inside the sample chamber following valve closure. Since the sample is in a heptane solution, and the internal pressure of the system was measured at around 2.1atm, the speed of sound is $c \approx 1100m \cdot s^{-1}$ [5]. As such, with the length of the sample channel being $l = 15.5mm$, the period of a wave travelling trough it would be $T = 2l/c = 39us$, which is in line with the wave observed in fig.8. This behaviour was seen to be decreased when over-tightening the screws holding the assembly together. Nonetheless this is not desirable, as the CaF_2 windows used are particularly brittle, making the assembly unstable, and posing the risk of contamination from the sample leaking. Knowing the period of the oscillation, another set of tests can be ran with a delay of $T/2$, and the measurements subtracted, to eliminate the oscillation.

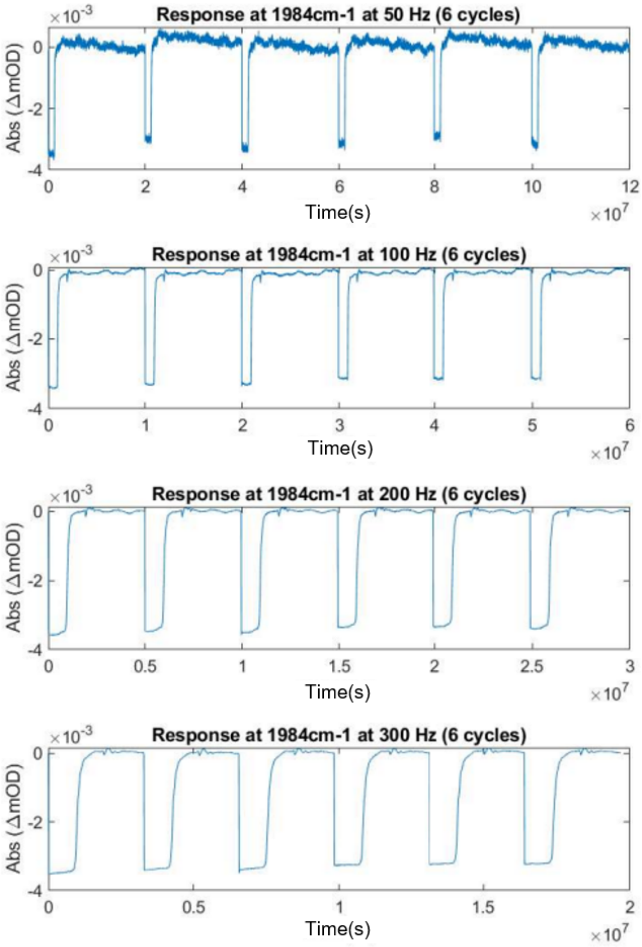

Figure 7: Response of the sample at $1984cm^{-1}$

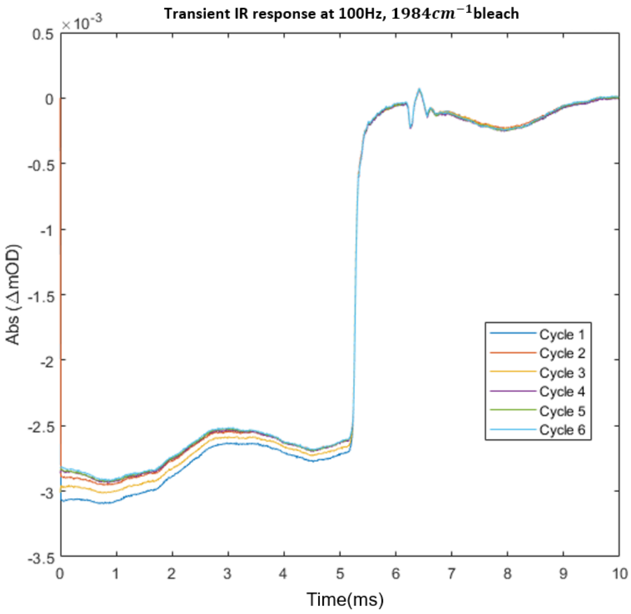

Figure 8: Stability test over 5 hours

5 Conclusion

Improvements have been presented in support of using a stop-flow system for time resolved spectroscopy applications. With these kinds of experiments becoming more available in the study of complex molecular dynamics, sample solutions that keep up with the ever-increasing demand for higher speeds and resolutions are required. The miniaturisation of such systems, as well as the limiting of moving parts, both an the sample stage as well as on the actual optical system, allows for more robust systems.

References

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