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CHEMISTRY

AT THE UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL

Nuclear Magnetic Resonance Laboratory Newsletter

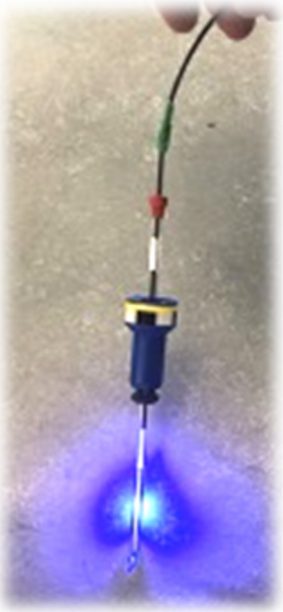
What's Inside

Now with NMR Trivia in every page!

Elucidating Photocatalysis: PhotoNMR

by Andrew Camp

Photocoupled reactions have seen explosive growth in recent years, harnessing the power of light to accomplish valuable reactions. Typically, these reactions are monitored *ex situ*, where aliquots or headspace samples are brought to instruments for characterization. While *ex situ* measurements are valuable techniques to understand reactivity, factors such as gas loss, dark reactivity, and product instability can hamper characterization of light-mediated chemistry.



Towards narrowing the timescale between reactivity and characterization, the NMR core has made *in situ* photoNMR available to the users. The system consists of a LED light source and a fiber optic line that carries light into a coaxial NMR tube. NMR has several advantages for *in situ* product characterization, including ability to determine the identity and amount of products you make. These features make NMR ...

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Assignment Service Report

The NMR Core provides a convenient mechanism to obtain chemical shift assignments as part of the "NMR Assignment Service". Think of it as a type of drop-off a sample, we run the experiments and interpret the data, providing ...

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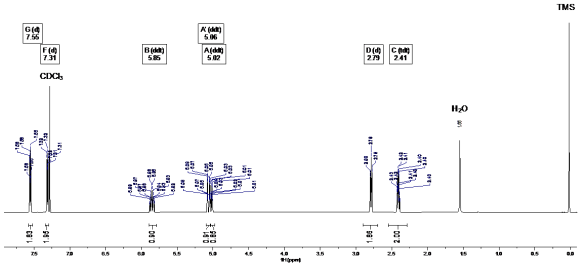

Elucidating Photocatalysis: PhotoNMR

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cont. … particularly attractive for monitoring catalytic reactions by readily quantifying various products made without requiring external calibration. These features carry over into photoNMR applications, with the added benefit that the light source intensity can be adjusted while the sample is in the instrument.

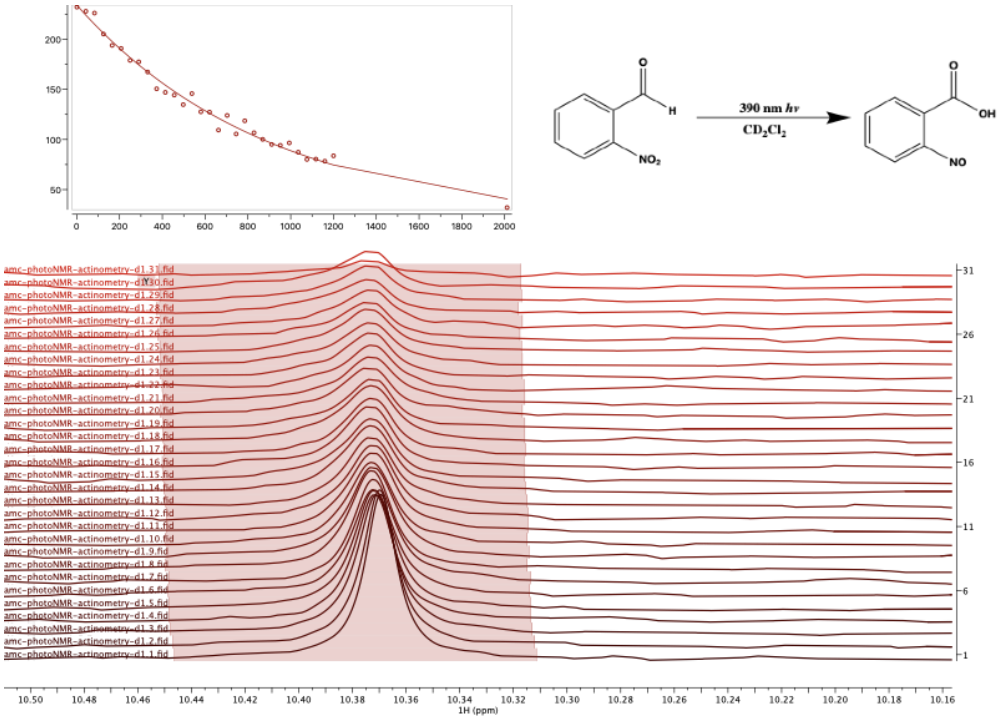


Figure 1. Kinetics of the autooxidation of 2-nitrobenzaldehyde. The aldehyde peak can be readily tracked by NMR to get kinetic data.

So far, the system has been used for photoinitiated catalysis, monitoring the photo-release of H_2

(which typically escapes into the headspace), and measuring photon flux though chemical actinometry.

Next time you're considering doing photochemistry, bring your sample to the NMR Core! We might just help you shine a light on the problem.

Assignment Service Report

cont. … high quality data and saving you time.

The basic service, "**Connectivity Assignment**" applies ^{1}H, ^{13}C and 2D NMR to assign ^{1}H and ^{13}C chemical shifts to a proposed structure.

"**Absolute Assignment**" adds NOESY and/or ROESY data to assign inequivalent protons.

"**Heteronuclear Assignment**" adds experiments involving ^{11}B, ^{15}N, ^{19}F, ^{29}Si and/or ^{31}P for further heteronuclear connectivity.

Take a look at the "Request Services" tab in iLab.

An example report can be found here.

Interesting NMR Acronyms

WURST!

(Wideband Uniform Rate Smooth Truncation)

A pulse that achieves broadband adiabatic inversion of magnetization for solution-state ^{13}C decoupling at high magnetic field.

INADEQUATE!

(1D Incredible Natural Abundance Double Quantum Transfer Experiment)

A pulse sequence that suppresses ^{13}C uncoupled signal and yields satellites as antiphase multiplets.

NMR TRAINING OPPORTUNITIES

Training for access to the NMR Spectrometers in the NMR Core is geared toward people who are in research groups and generating their own samples. Everyone goes through some kind of hands -on assessment of their ability to operate a spectrometer. This includes **under-graduates, graduate students, "zero year" graduate students, post-docs, faculty and visitors.** All users must have an iLab account with an associated funding source and chart field.

"**Drop-off NMR**" offers a hands-off approach to obtaining NMR data. A brief training maybe required to show the user how to navigate the software ("IconNMR") and load samples on the sample changer. Samples are run in auto-mation Monday through Friday nights on the B600 spectrometer. Sample information is submitted on a web form and clearly labeled samples should be placed on the NMR tube rack **outside of CA051 by 5pm each day**. File names must only contain letters, numbers, underscores and hyphens - NO spaces, commas or other punctuation. IconNMR will save data on the computer and email a compressed data folder for each successful run. Sample(s) should be picked up the next day. Samples left for a week or so will be moved to the hood in the Sample Prep Lab in CA051.

If you would like to run your own NMR experiments and at time other than overnight, you can request general training on the "Request Services" tab in the NMR Lab on iLab. The first step in training includes a virtual session covering basic procedures to acquire NMR data, the NMR spectrometers in the core, and using the NEO400 and NEO600 NMR Spectrometers which run in automation 24/7. The **NEO400** has a nitrogen cooled broadband cryoprobe that runs many nuclei with good sensitivity. The **NEO600** has a helium cooled cryoprobe optimized for ^{13}C and ^{31}P and very good ^{1}H sensitivity - second best in the NMR Core.

For access to the 400NB, 500 and B600 spectrometers, one must run Topspin, Bruker's NMR software, directly. Individuals schedule this training on the 500 or B600 by submitting a request in iLab. The **400NB** tends to be used for routine ^{1}H and ^{19}F spectra, the **500** for variable temperature work, longer runs (think reaction kinetics and dynamics), and photo- NMR, which are all covered in a specific training. The **B600** is equipped with a helium cooled cryoprobe optimized for ^{1}H (most sensitivity in the core) and ^{19}F and capable of high sensitivity ^{13}C spectra.

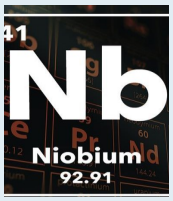
Individual training sessions are scheduled for specific experiments, like variable tempera-ture, DOSY, relaxation, etc. NMR Staff will coordinate time for direct one-on-one training on a spectrometer once requested through the "Request Services" tab in iLab.

"**Advanced NMR Training**" comprises multiple virtual and hands-on opportunities to fine tune your NMR skills to obtain high quality NMR data. Topics include advanced shimming methods, navigating 2D acquisition para-meters, speeding up 2D experiments with Non-Uniform Sampling ('NUS') and a discussion of nuclear spin relaxation. These sessions are scheduled intermittently through out the year.

NMR Trivia!

What element was used to construct the first superconducting magnet?

Ans: Niobium



Farewell Messages

Ling Xu

Dear NMR users,

I wish to let you all know that I truly enjoyed my time at the NMR Core as the NMR Graduate RA. Being able to help with different NMR applications and provide support was truly a great experience. Although I will miss working at the Core, I will be continuing my chemistry research career in China.

As an NMR Core RA, my daily duty is to help with instrument troubleshooting and training new users. Though they might sound trivial, I actually master the NMR acquisition procedures and I am able to identify any minor mistakes that lead to faulty results, such as parameter adjustments and NMR samples' conditions. Meanwhile, additional projects also introduced me to explore more NMR techniques to accommodate assignments from small molecules to polymers. Especially adjustment of relaxation delays and pulse width in 1D and 2D experiments could achieve better peak shape, and DOSY experiments could resolve different molecules in an NMR sample.

Again, NMR is an amazing technique to cooperate with chemistry research, and I appreciate my time working at the Core!

Jobel Barcoma

As my time at the NMR Core Laboratory winds down, I can't help but reflect on all the awesome people I have worked with. Marc, Andrew, and Ling (and Josh) have been so helpful and supportive that they created a good working environment for everyone.

Even though I was only a workstudy student, I have grown and learned so much while working at the NMR lab. I initially performed tasks such as weekly spectrometer maintenance, working in the prep room, and doing general lab maintenance. I always wanted to help in any way that I can, so next thing I know, I was not only learning about NMR or anything Chemistry related, but I was also making the CRITCL core's website, submission forms, NMR newsletters, posters, and virtual tours. I also had the opportunity to learn the fundamentals of different 2D NMR experiments and gained experience analyzing spectral data. It has been a blast collaborating with them on so many projects.

Moving forward, I will be taking a gap year, but I am still interested in furthering my education. I will greatly miss working with everyone, including the other core facility directors and grad students. I will never forget our uncoordinated lunch sessions with Josh and Diane or the problems that happen in lab whenever Marc is not around. It was a great decision for me to step out of my comfort zone and experience something new. Working at the NMR Core has been the highlight of my journey at UNC as a Chemistry major.

It has been a pleasure working with each one of you, and I wish you all nothing but the best!

Spectrometer Selection

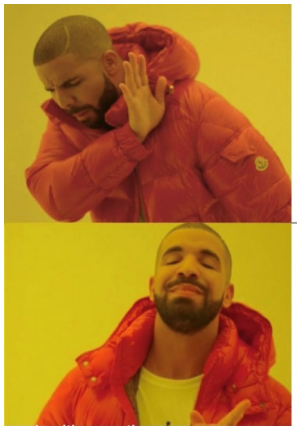
	^{1}H	^{31}P	^{13}C	^{19}F	^{11}B, ^{29}Si and other nuclei	Variable Temp	COSY, HSQC, HMBC, NOESY	5mm tubes with the following exceptions
400NB	Yes	Yes	Yes (conc.)	Yes	some are possible	N.A.	Yes	greater than 6 inches
NEO400 ("Prodigy")	Yes (low conc.)	Yes (low conc.)	Yes	Yes, no 1H decoupling	Yes	~ -40 to +120	Yes (low conc.)	special spinners for variable temperature
NEO600 (cryoQNP)	Yes (low conc.)	Yes (low conc.)	Yes (low conc.)	No	No	0 to 60 Celsius	Yes (low conc.)	short J-Young tubes
B600 (cryoQCI)	Yes (low conc.)	No	Yes (low conc.)	Yes (low conc.)	No	0 to 60 Celsius	Yes (low conc.)	
500 (bbo or bbi probe)	Yes	Yes (best on bbo)	Yes (conc., bbo)	No	Yes (bbo)	**-120 to +120**	Yes	special spinners for variable temperature

Yes (conc.): requires concentrated samples
Yes (low conc.): good for dilute samples

Some NMR History...

- NMR in bulk materials was simultaneously and separately discovered by Bloch and Purcell in 1946. They were awarded the Nobel Prize in Physics in 1952
- The first study of ^{13}C in organic compounds was published by Lauterbur in 1957.
- Ernst and Anderson reported the first use of pulsed or FT-NMR (NMR as we know it today) in 1966. The Fourier Transform took forever!!!
- Ernst likened the way in which the new process identifies nuclei to listening to a piano. "Imagine you want to find out which strings are broken in an old piano, and how time consuming it would be to strike one key after the other," said Ernst. "FT NMR is like striking all 88 keys at once and immediately identifying which keys are still functioning."

https://www.nobelprize.org/prizes/chemistry/1991/perspectives/



Retrieving NMR test tubes that were dropped-off to be reused by my lab

Using new NMR test tubes and not picking up the ones left from drop-off

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Who discovered NMR?

Isidor Rabi received the Nobel Prize in Physics in 1944 for the discovery of NMR (in a molecular beam). Cornelius Gorter originally proposed the idea in 1936 but was unable to demonstrate the phenomenon due to limitations in his experimental setup. Gorter is sometimes referred to as "the man who *almost* discovered NMR".

More at: http://mriquestions.com/who-discovered-nmr.html

NMR Quiz!

Which of the following is *not* a real NMR experiment?

A. DOSY
B. TOCSY
C. NOESY
D. MOSEY

Ans: D. MOSEY