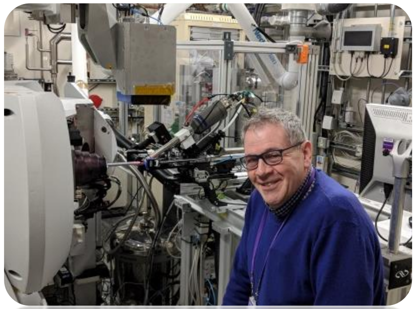
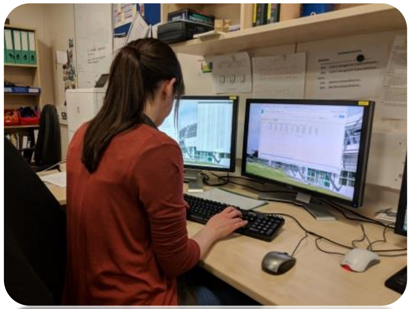
Diamond/Bath/Manchester/Cardiff Collaboration



Paul Raithby

Jonathan Skelton



Lauren Hatcher

Long term collaboration between University of Bath, University of Cardiff, University of Manchester and Diamond Light Source.

- Use pump-probe methods to investigate photo-activated chemical systems
- Jonathan has preformed all the computational studies which has been vital for this investigation

Solid-state Linkage Isomers

Simple, crystal-engineering approach:

- Use bulky, chelating ancillary fragments
- Photo-inert fragments dominate crystal packing, generating a **“reaction cavity”**
- Facilitate high conversion whilst reducing crystal strain and fatigue

***N*-bound** nitro

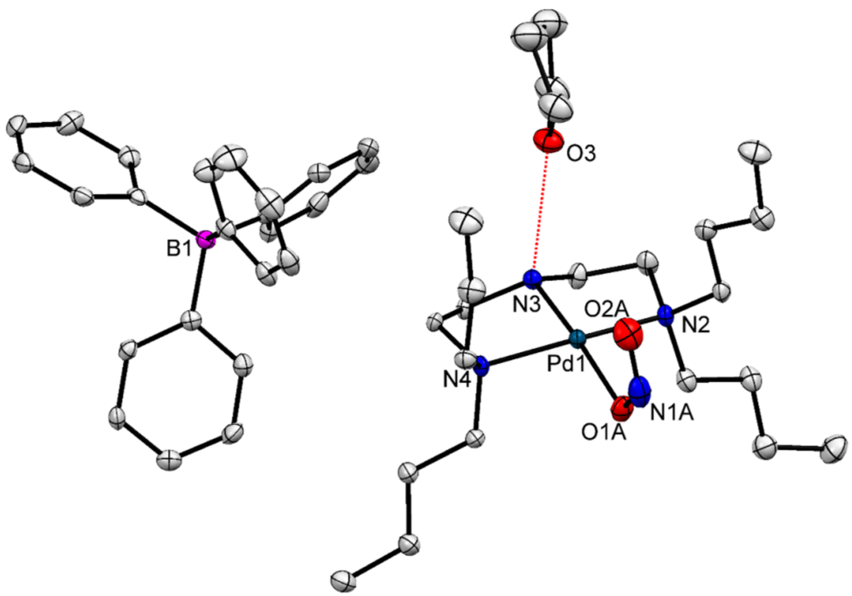
***O*-bound** nitrito

[1]

[1] *M. R. Warren, S. K. Brayshaw, A. L. Johnson, S. Schiffers, P. R. Raithby, T. L. Easun, M. W. George, J. E. Warren, S. J. Teat, Angew. Chem. Int. Ed. 2009, 48, 5711-5714.*

Pseudo-steady-state

[Pd(Bu_4dien)(NO_2)]BPh_4



- Crystal irradiated *in-situ* at λ = 400 nm
- Complete, 100% conversion to metastable nitrito-ONO isomer below 200 K

Temp / K	NO_2 Occupancy	ONO Occupancy
100	0.00	1.00
200	0.00	1.00
220	0.71	0.29
240	1.00	0.00
250	1.00	0.00
260	1.00	0.00

- Fully reversible, with reverse nitrito → nitro process induced on warming
- Very fast photoconversion MS threshold temp (“MS limit”) ~ 220 K

[1] *L. E. Hatcher, J.M. Skelton, M. R. Warren, C. Stubbs, E. L. da Silva, P. R. Raithby CrystEngComm, 2016, 18, 4180-4187*

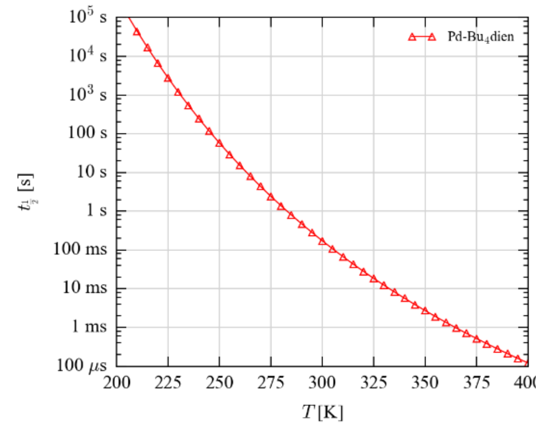
diamond

Being Predictive

- Combining Arrhenius and JMAK expressions gives expression for ES $t_{1/2}$

$$t_{\frac{1}{2}}(T) = \left[-\frac{1}{Ae^{-\frac{E_a}{RT}}}\ln\frac{1}{2}\right]^{\frac{1}{n}} = \left[-\frac{1}{A}\ln\frac{1}{2}\,e^{\frac{E_a}{RT}}\right]^{\frac{1}{n}}$$

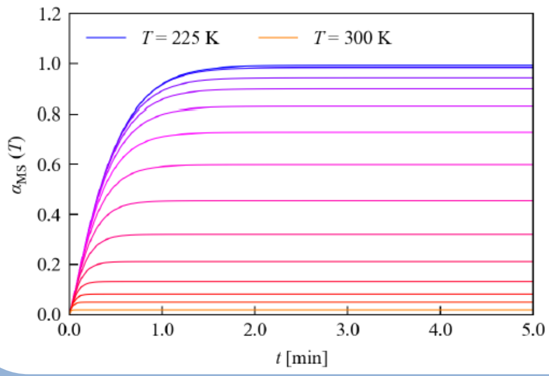
- Extrapolation allows prediction of $t_{1/2}$ (and hence lifetimes)

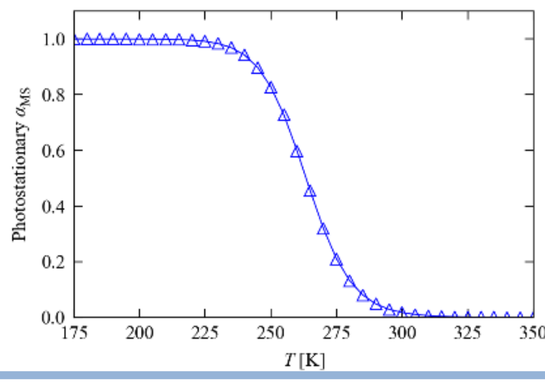


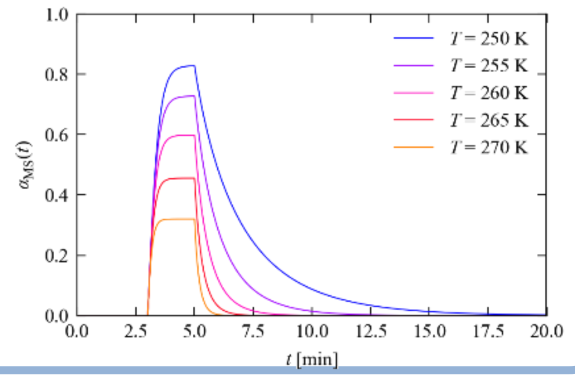
Numerical simulation: predict how isomer ratios evolve under different conditions

Input = kinetic parameters from solid-state kinetic studies

Outputs include: predicted excitation/decay, pseudo-steady-state profiles; pump-probe TR pulse sequences



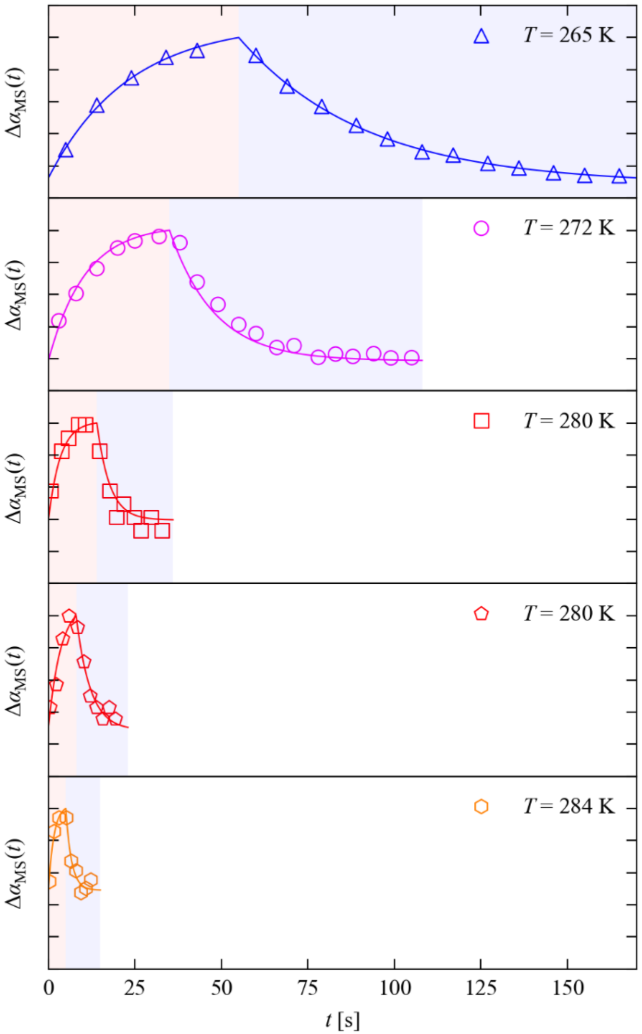


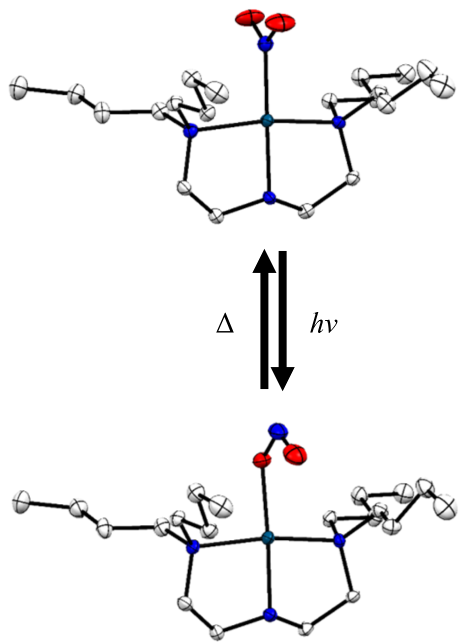


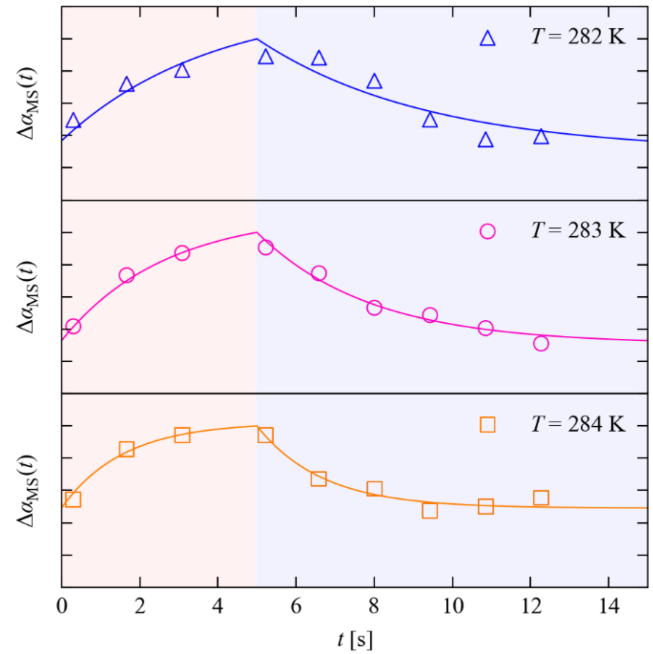
[1] *L. E. Hatcher, J.M. Skelton, M. R. Warren, C. Stubbs, E. L. da Silva, P. R. Raithby CrystEngComm, 2016, 18, 4180-4187*

diamond

Time-resolved Results







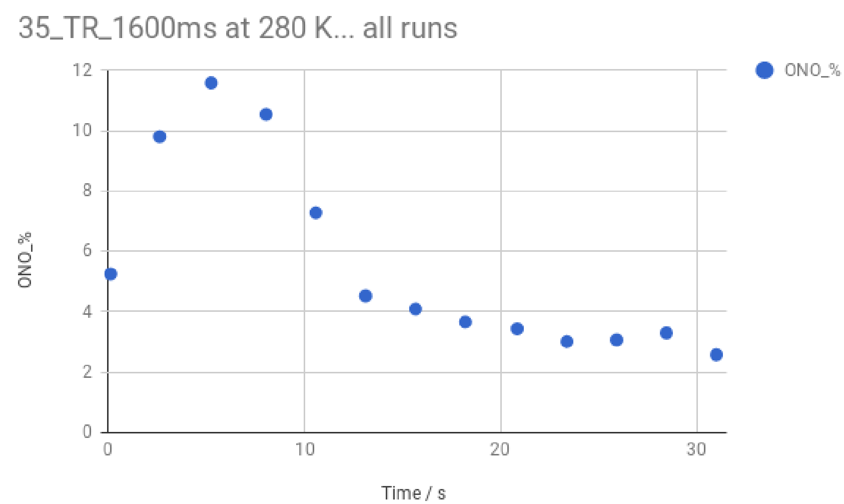
diamond

Automatic processing

Quick analysis to determine the photo-conversion of each time-bin is crucial to guide the next set of experiment

- Images are sorted into time-bins during data collection
- Diamonds computer cluster was utilised to auto-processed all time-bin simultaneously using xia2/DIALS (peak finding, indexing, integration and scaling)
- A series of structure refinement was then automatically completed and statistical information output

Plot produced 5 minutes after end of collection from the auto-processing:

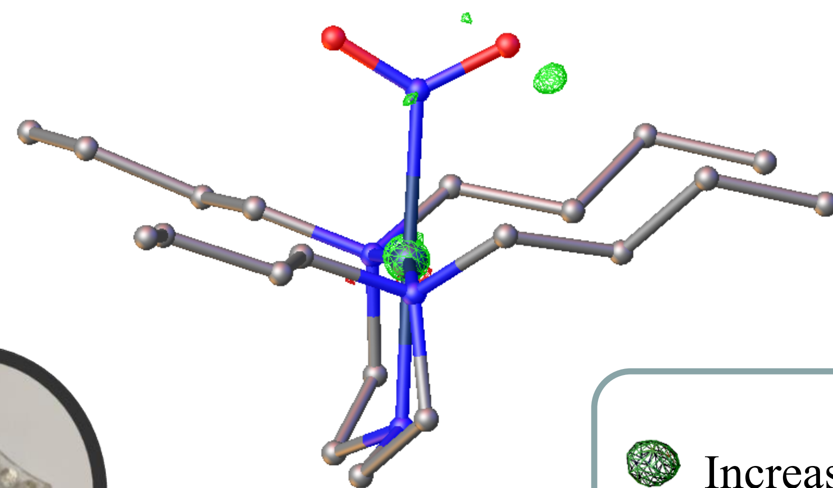


diamond

Molecular Movie

Current level: 0.7

Dataset 0
Ground State
LEDs OFF

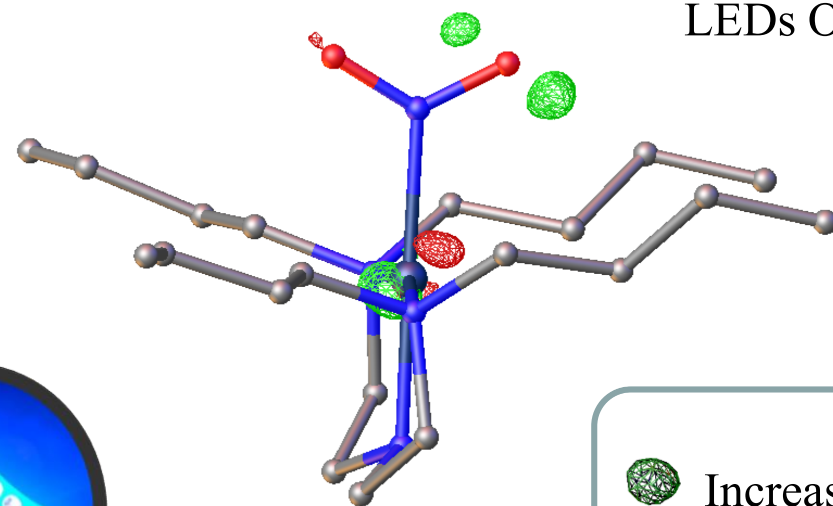


KEY

Increase in electron density

Decrease in electron density

Molecular Movie



Dataset 1
Excitation time
4s
LEDs ON

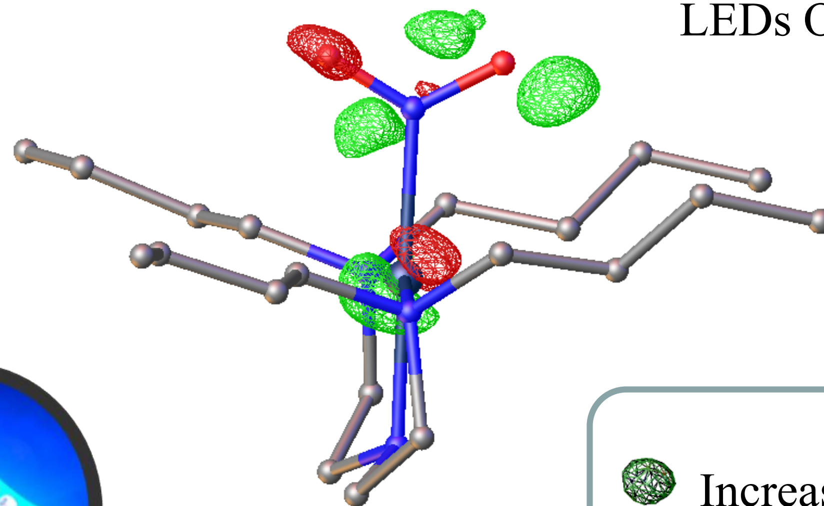
KEY

Increase in electron density

Decrease in electron density

diamond

Molecular Movie



Dataset 2
Excitation time
13s
LEDs ON

KEY

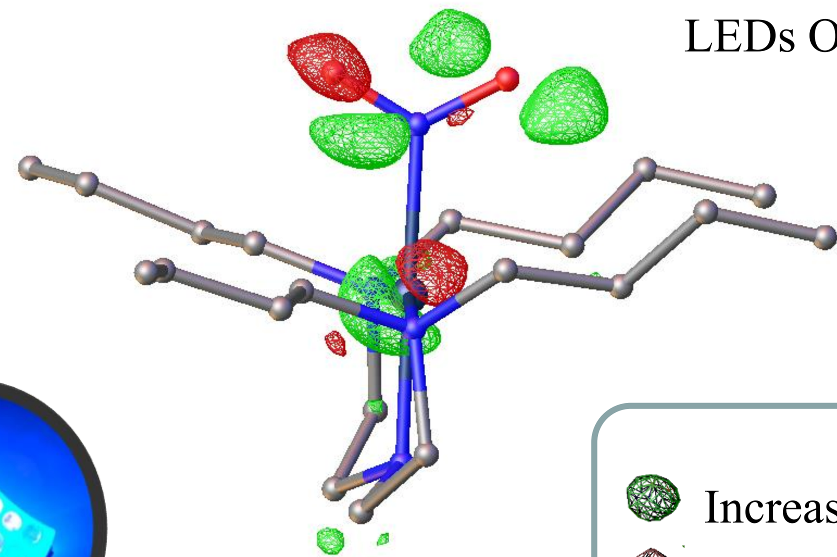
Increase in electron density

Decrease in electron density

diamond

Molecular Movie

Dataset 3
Excitation time
23s
LEDs ON



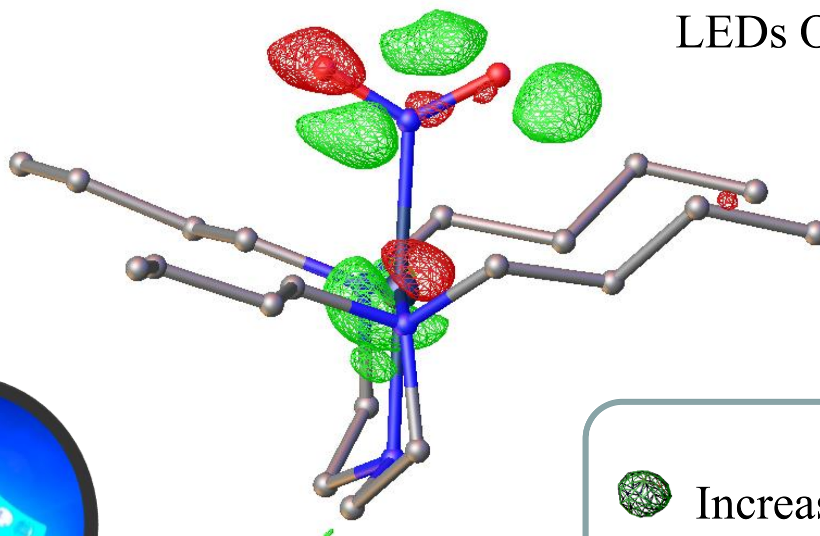
KEY

Increase in electron density

Decrease in electron density

Molecular Movie

Dataset 4
Excitation time
32s
LEDs ON



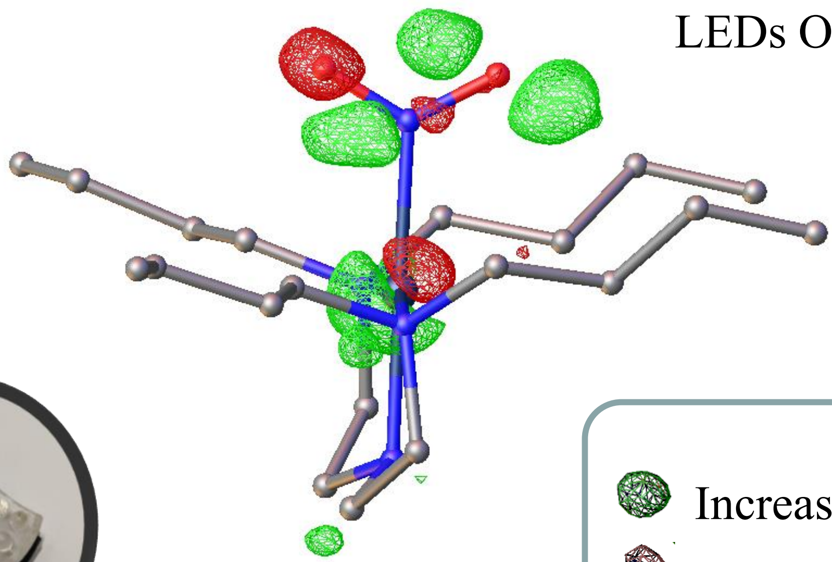
KEY

Increase in electron density

Decrease in electron density

Molecular Movie

Dataset 5
Excitation time
42s
LEDs OFF



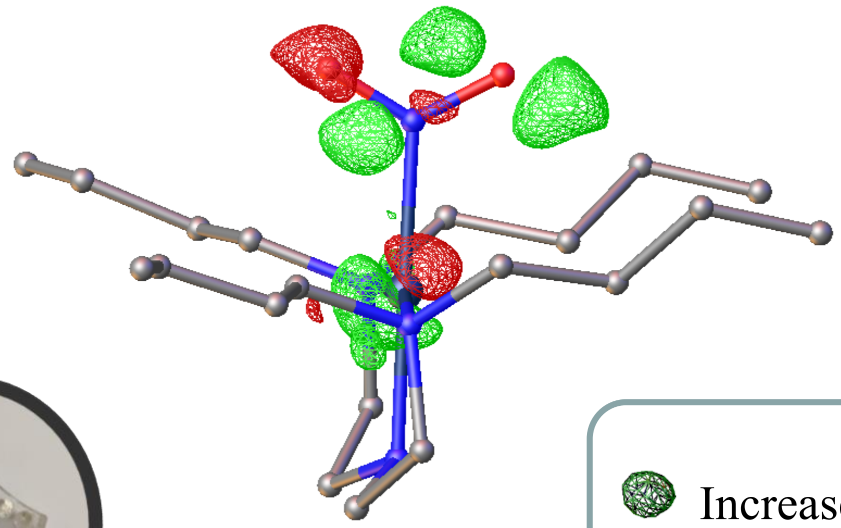
KEY

Increase in electron density

Decrease in electron density

Molecular Movie

Dataset 6
Decay time 4s
LEDs OFF



KEY

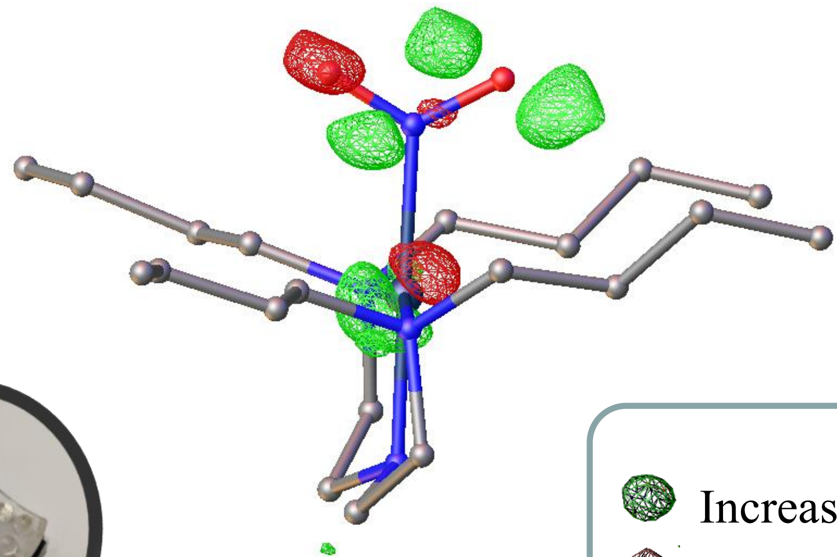
Increase in electron density

Decrease in electron density

diamond

Molecular Movie

Dataset 7
Decay time 13s
LEDs OFF



KEY

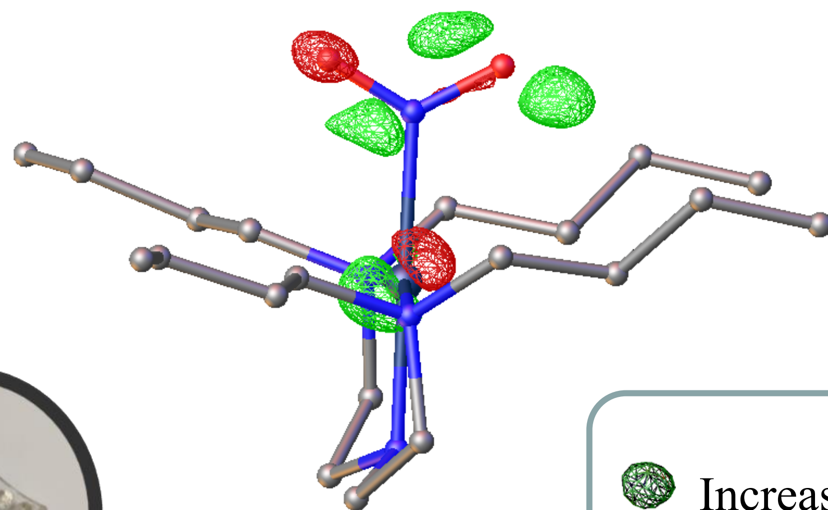
Increase in electron density

Decrease in electron density

diamond

Molecular Movie

Dataset 8
Decay time 23s
LEDs OFF



KEY

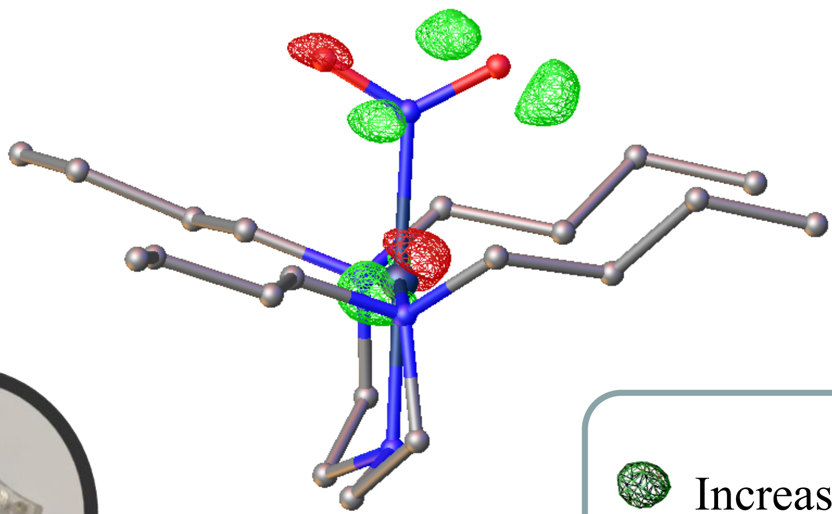
Increase in electron density

Decrease in electron density

Molecular Movie

Dataset 9
Decay time 33s
LEDs OFF

Current level: 0.7

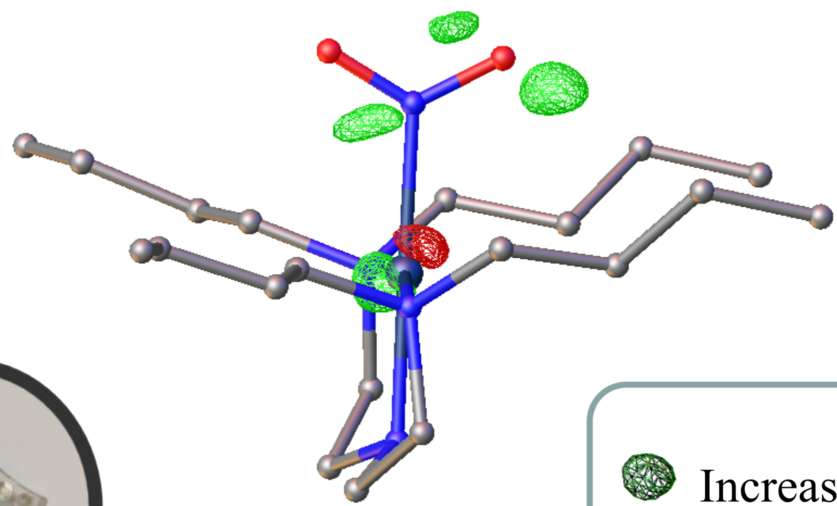


KEY
Increase in electron density
Decrease in electron density

Molecular Movie

Current level: 0.7

Dataset 10
Decay time 42s
LEDs OFF



KEY

Increase in electron density

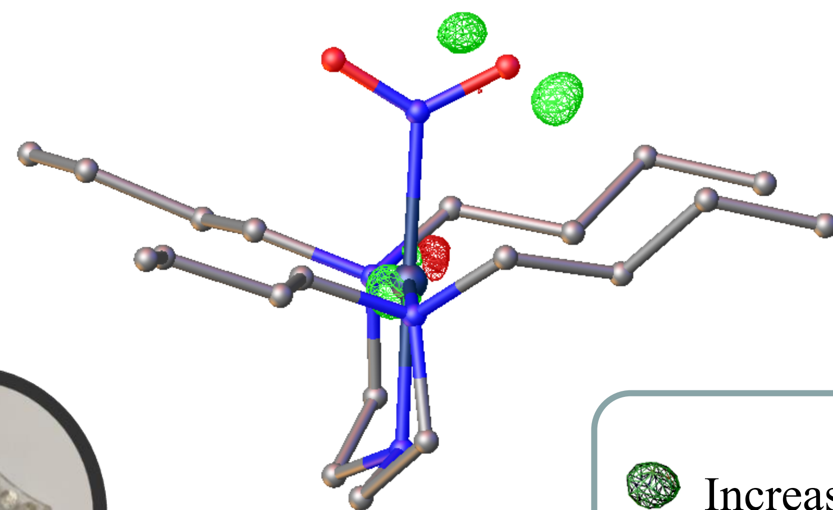
Decrease in electron density

diamond

Molecular Movie

Current level: 0.7

Dataset 11
Decay time 52s
LEDs OFF



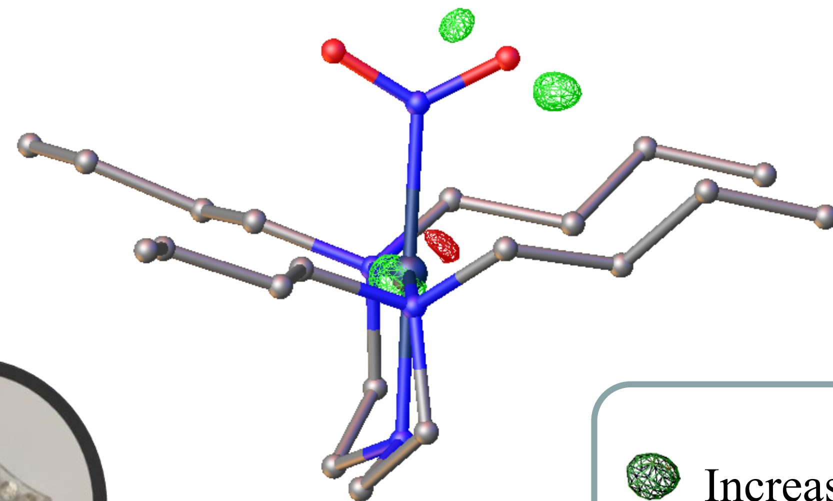
KEY

Increase in electron density

Decrease in electron density

Molecular Movie

Dataset 12
Decay time 61s
LEDs OFF



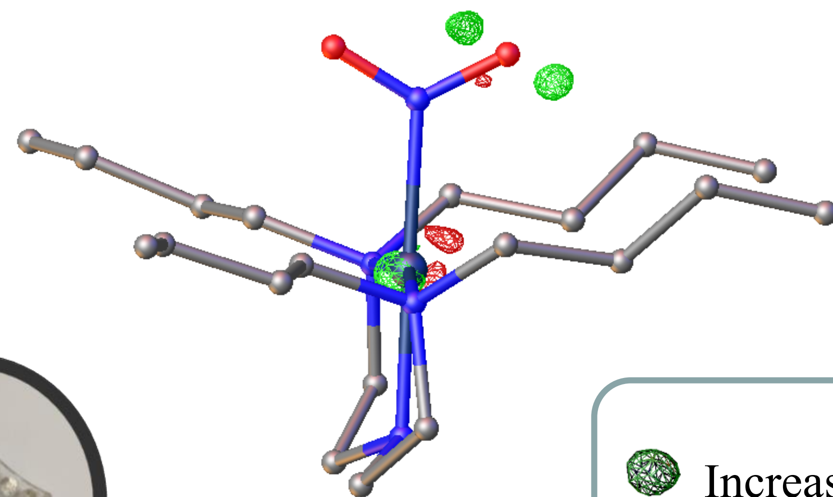
KEY

Increase in electron density

Decrease in electron density

Molecular Movie

Dataset 13
Decay time 71s
LEDs OFF



KEY

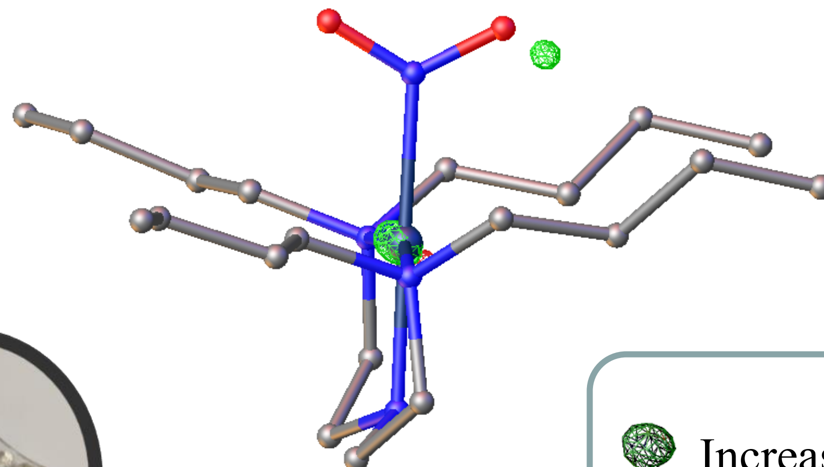
Increase in electron density

Decrease in electron density

Molecular Movie

Current level: 0.7

Dataset 14
Decay time 80s
LEDs OFF



KEY

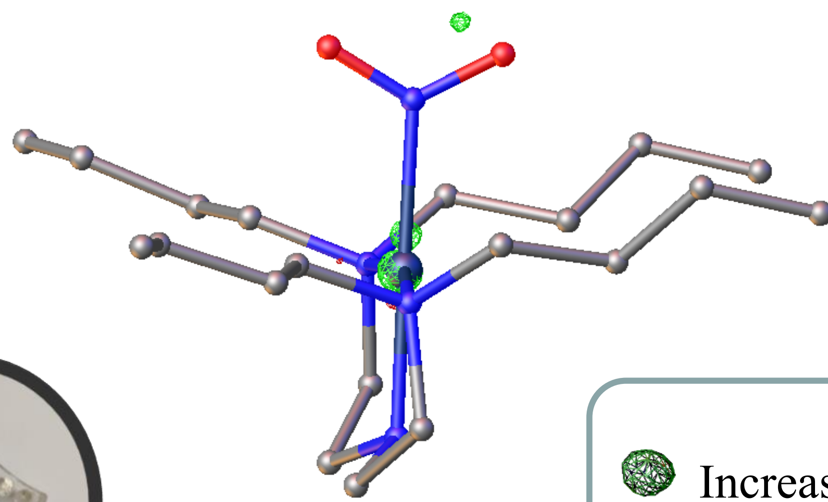
Increase in electron density

Decrease in electron density

Molecular Movie

Current level: 0.7

Dataset 15
Decay time 90s
LEDs OFF



KEY

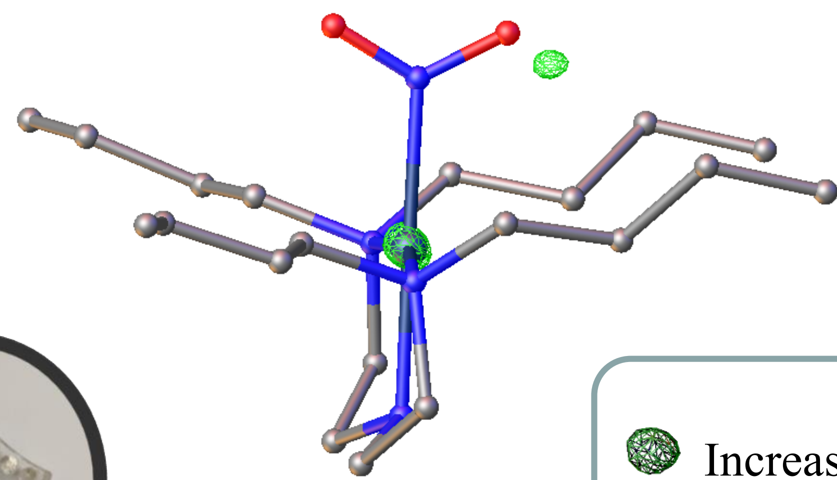
Increase in electron density

Decrease in electron density

Molecular Movie

Current level: 0.7

Dataset 16
Decay time 99s
LEDs OFF



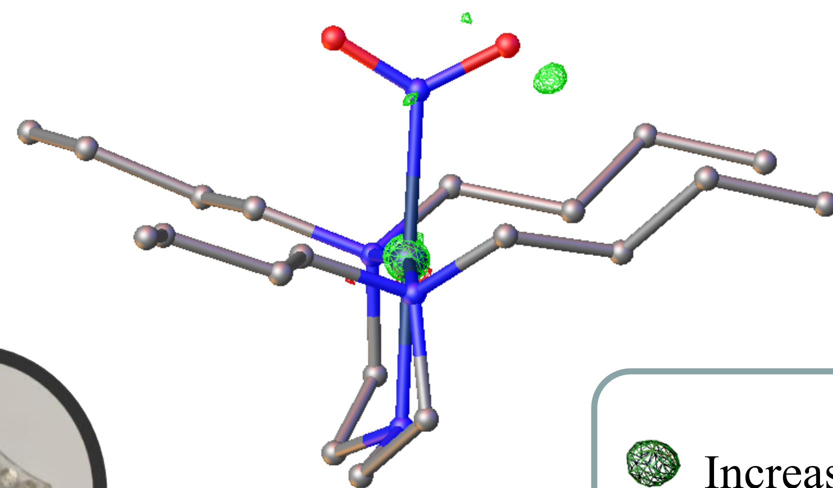
KEY

Increase in electron density

Decrease in electron density

Molecular Movie

Dataset 17
Decay time 109s
LEDs OFF



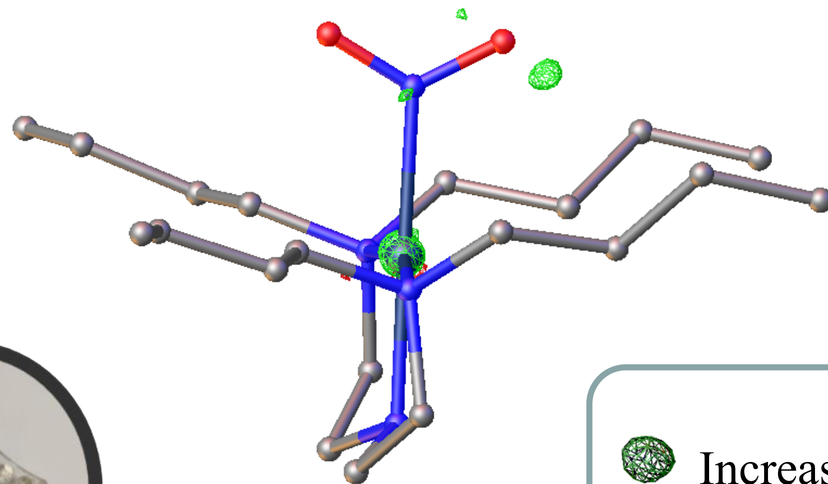
KEY

Increase in electron density

Decrease in electron density

Molecular Movie

Current level: 0.7



Dataset 0
Ground State
LEDs OFF

KEY

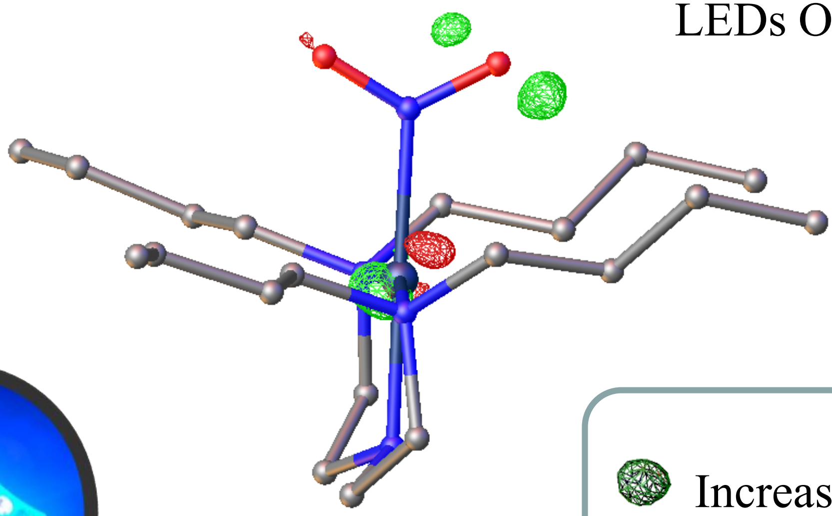
Increase in electron density

Decrease in electron density

Molecular Movie

Current Level: 0.7

Dataset 1
Excitation time
4s
LEDs ON



KEY

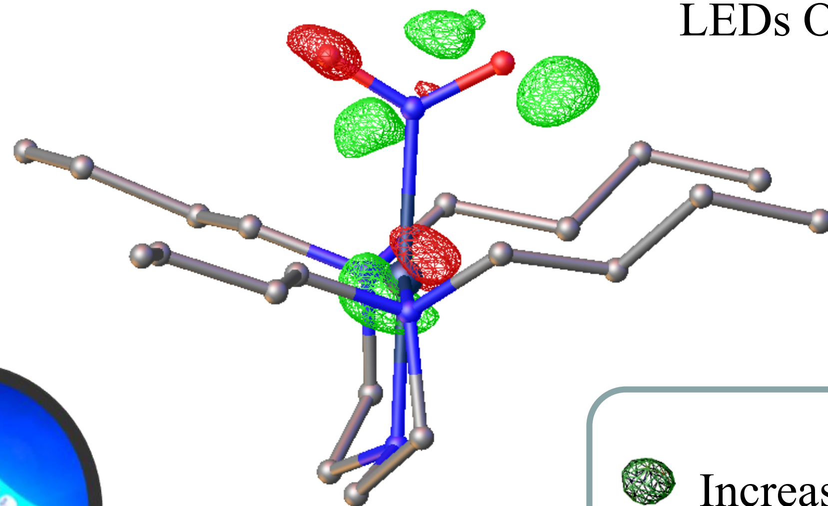
Increase in electron density

Decrease in electron density

diamond

Molecular Movie

Dataset 2
Excitation time
13s
LEDs ON



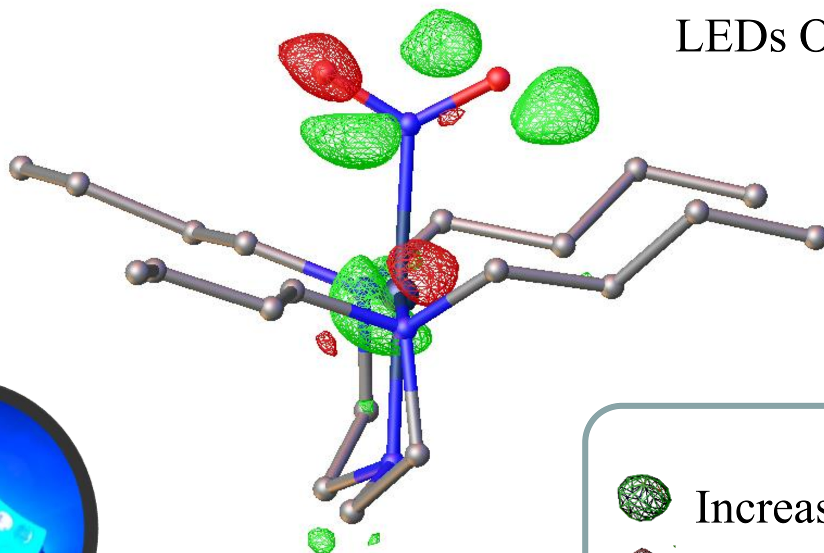
KEY

Increase in electron density

Decrease in electron density

Molecular Movie

Current Level: 0.7



Dataset 3
Excitation time
23s
LEDs ON

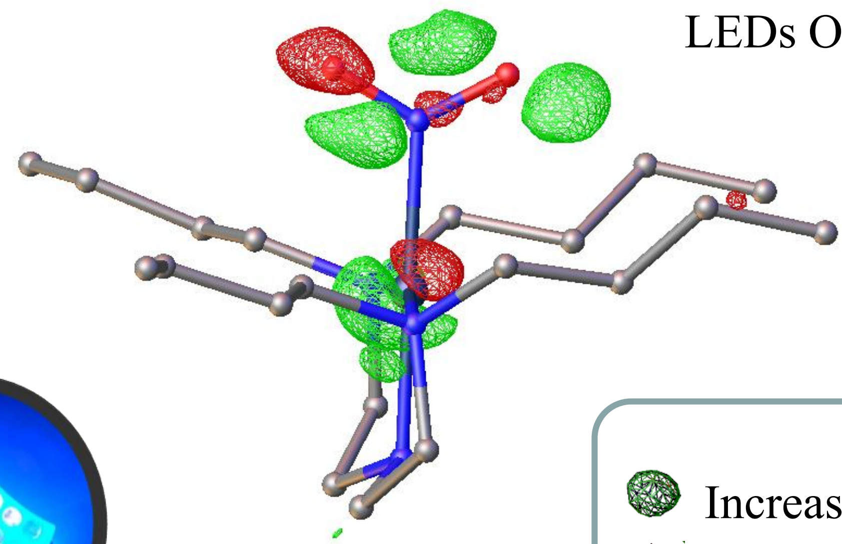
KEY

Increase in electron density

Decrease in electron density

Molecular Movie

Dataset 4
Excitation time
32s
LEDs ON



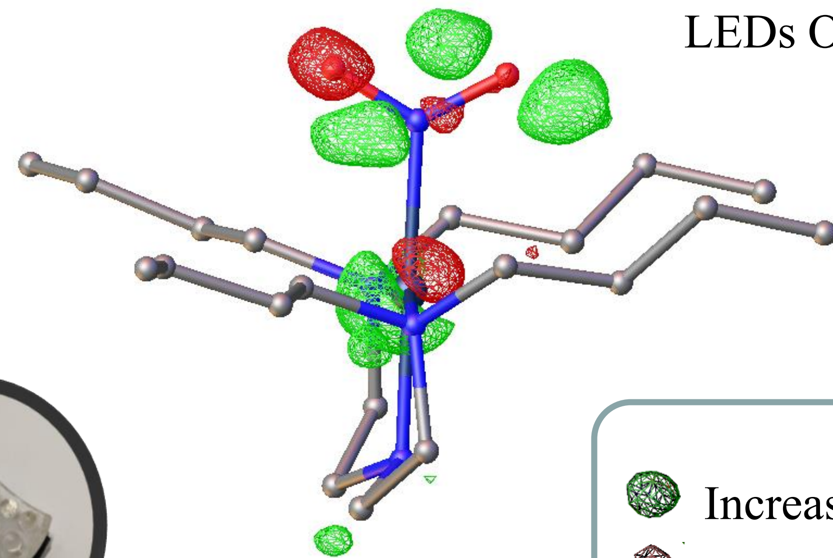
KEY

Increase in electron density

Decrease in electron density

diamond

Molecular Movie



Dataset 5
Excitation time
42s
LEDs OFF

KEY

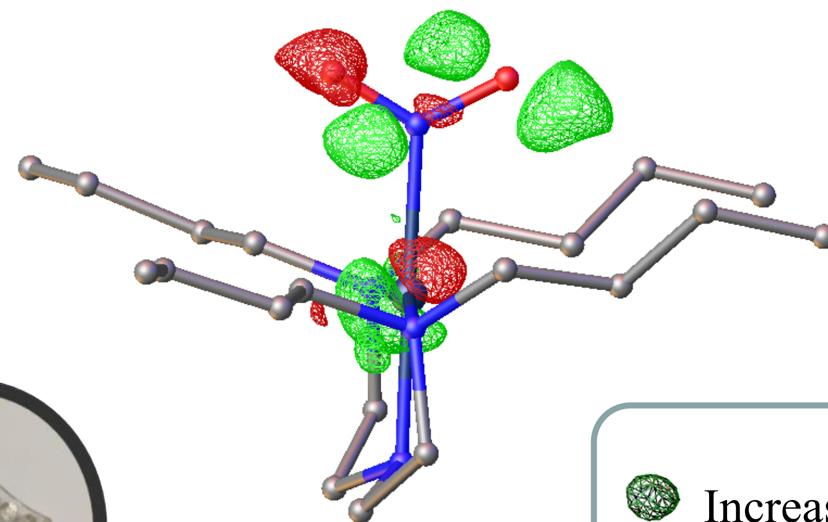
Increase in electron density

Decrease in electron density

Molecular Movie

Current level: 0.7

Dataset 6
Decay time 4s
LEDs OFF

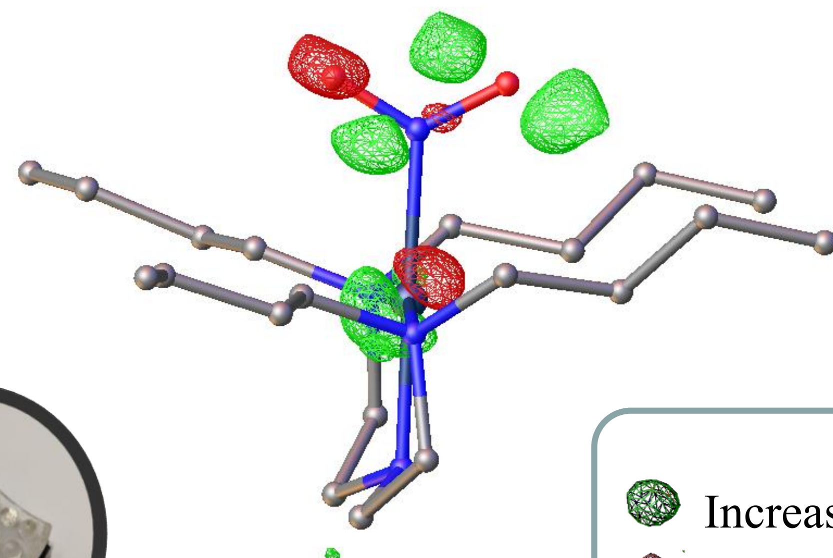


KEY

Increase in electron density

Decrease in electron density

Molecular Movie



Dataset 7
Decay time 13s
LEDs OFF

KEY

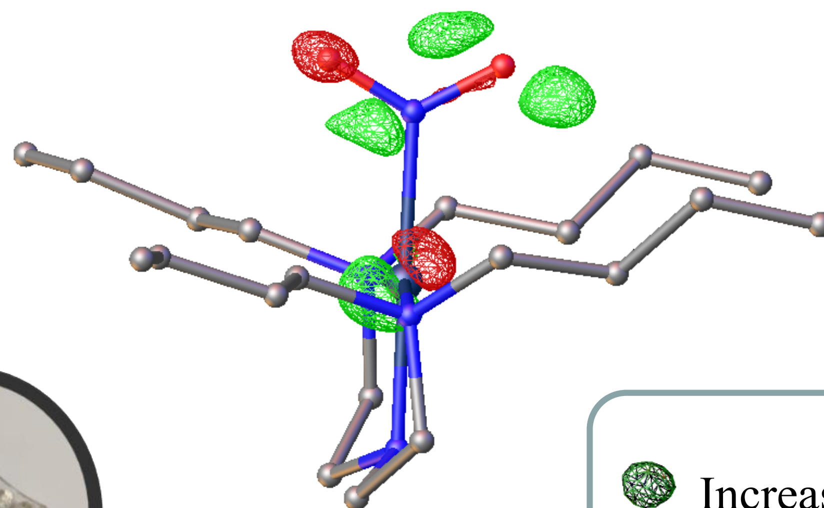
Increase in electron density

Decrease in electron density

diamond

Molecular Movie

Dataset 8
Decay time 23s
LEDs OFF



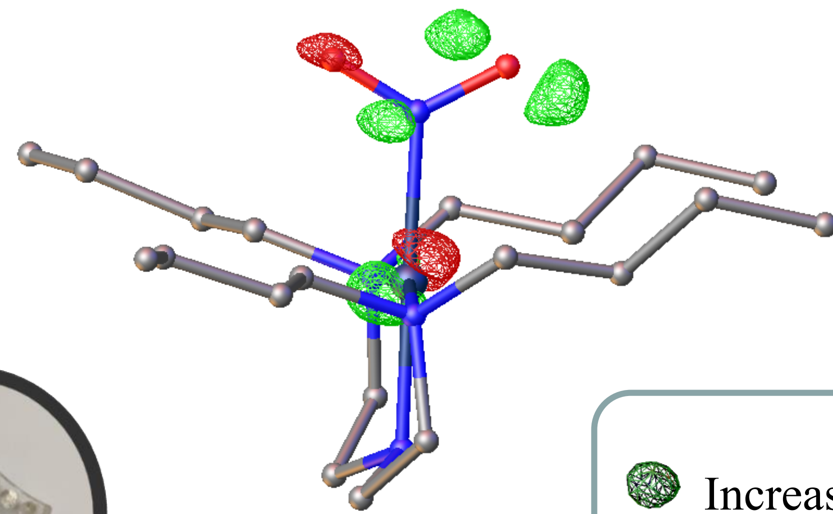
KEY

Increase in electron density

Decrease in electron density

Molecular Movie

Dataset 9
Decay time 33s
LEDs OFF



KEY

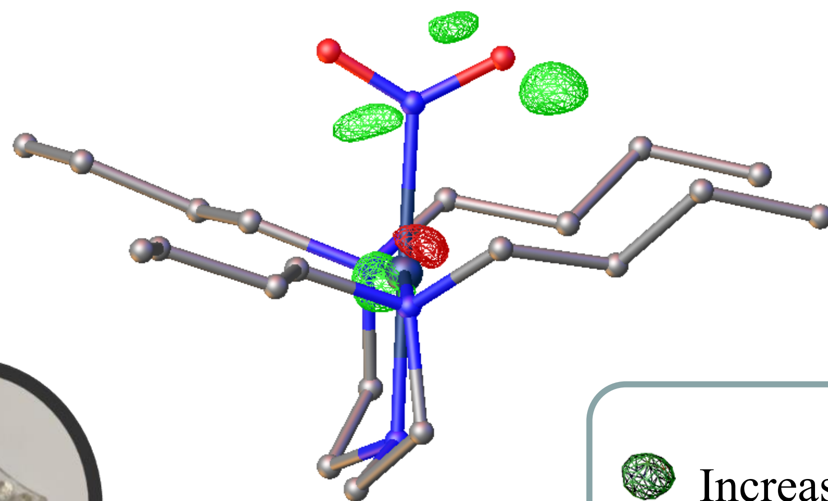
Increase in electron density

Decrease in electron density

Molecular Movie

Current level: 0.7

Dataset 10
Decay time 42s
LEDs OFF



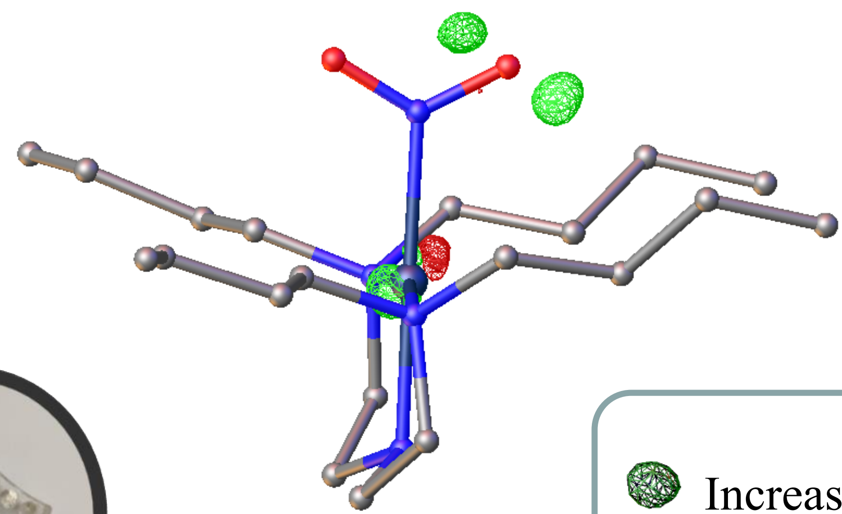
KEY

Increase in electron density

Decrease in electron density

Molecular Movie

Dataset 11
Decay time 52s
LEDs OFF



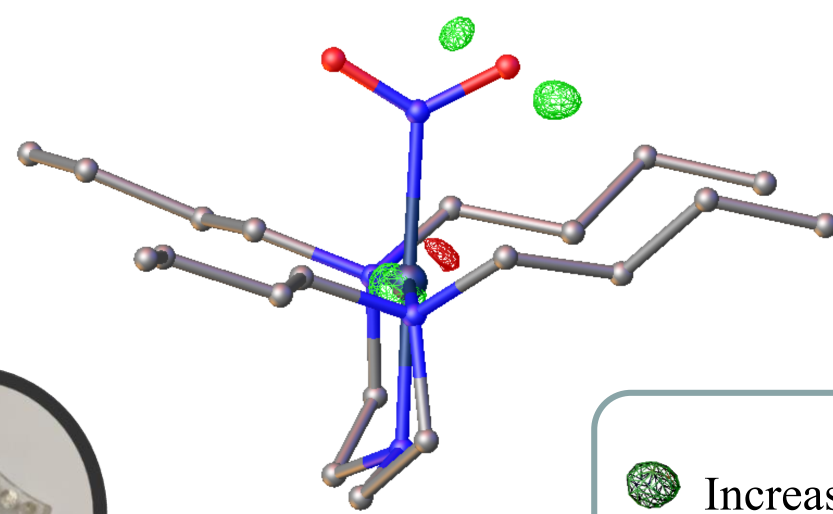
KEY
Increase in electron density
Decrease in electron density

diamond

Molecular Movie

Current level: 0.7

Dataset 12
Decay time 61s
LEDs OFF



KEY

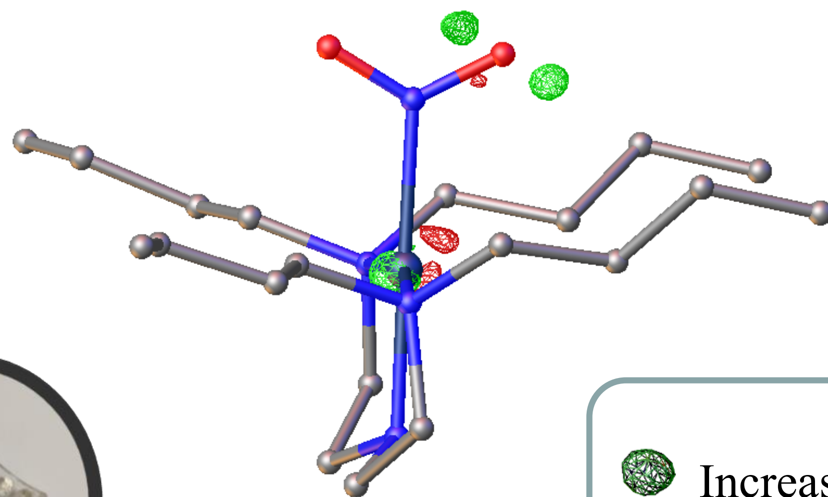
Increase in electron density

Decrease in electron density

Molecular Movie

Current level: 0.7

Dataset 13
Decay time 71s
LEDs OFF



KEY

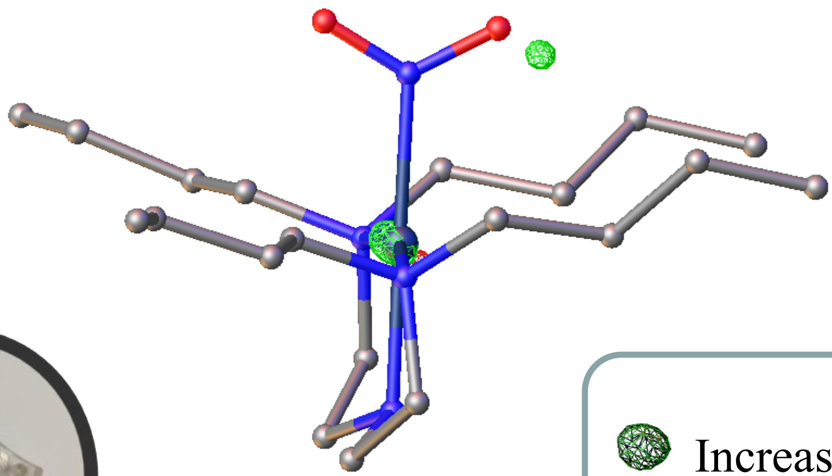
Increase in electron density

Decrease in electron density

Molecular Movie

Current level: 0.7

Dataset 14
Decay time 80s
LEDs OFF



KEY

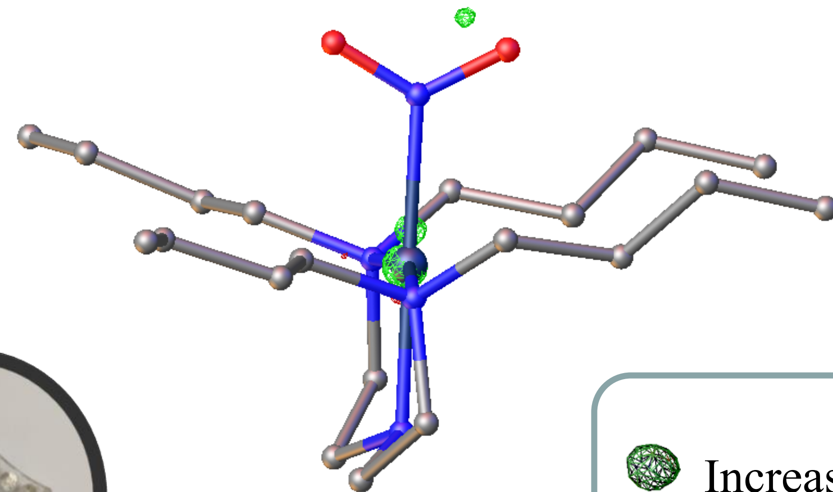
Increase in electron density

Decrease in electron density

Molecular Movie

Dataset 15
Decay time 90s
LEDs OFF

Current level: 0.7



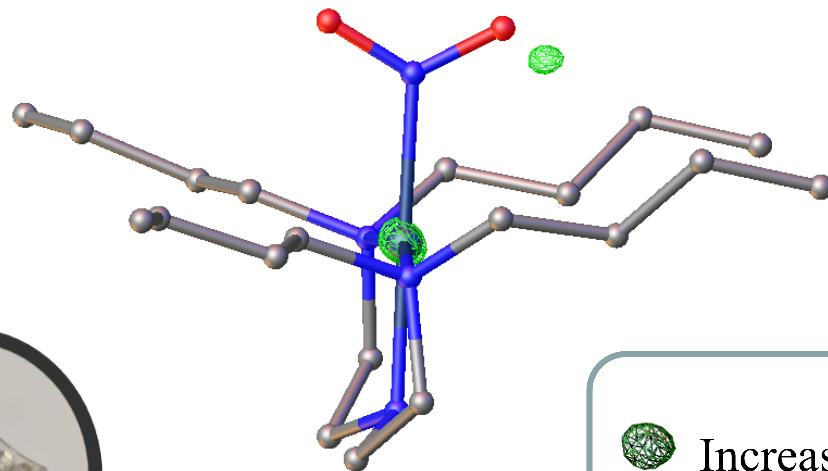
KEY

Increase in electron density

Decrease in electron density

Molecular Movie

Dataset 16
Decay time 99s
LEDs OFF



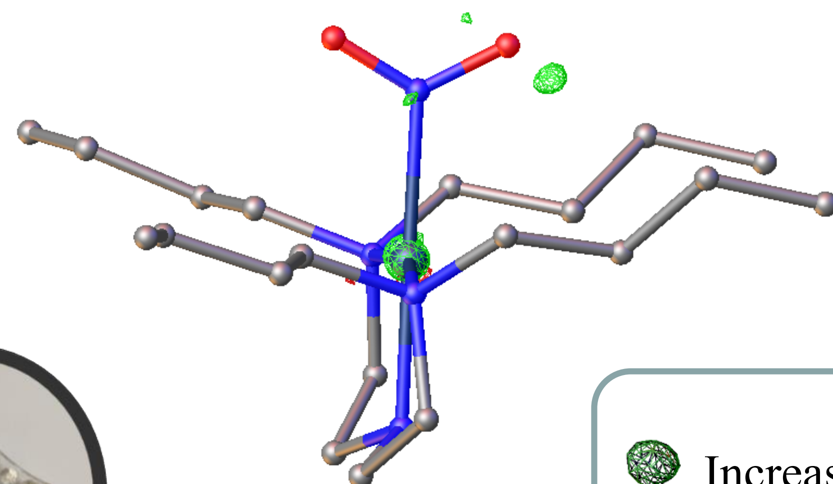
KEY

- Increase in electron density
- Decrease in electron density

Molecular Movie

Current Level: 0.7

Dataset 17
Decay time 109s
LEDs OFF



KEY

Increase in electron density

Decrease in electron density

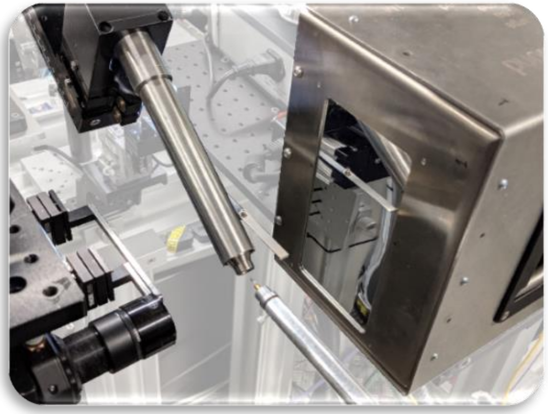
How fast can we go?

Pilatus 300K

- Using Pump-MultiProbe techniques, the Dectris Pilatus is limited by the image readout time with millisecond time-resolve at best.
- For a single time-delay the Pilatus can be electronically gated at 200 ns. To accumulate enough intensity may take numerous hours and would be unrealistic for multiple snapshots along a reaction pathway.

- Timepix detector is a continuous readout detector with 25 ns time-resolution.
- Rather than images, the detector records time and position of each photon as well as the laser trigger (or pump source) into the data stream.
- The time-resolution or data binning can be selected in processing.

Tristen/Timepix

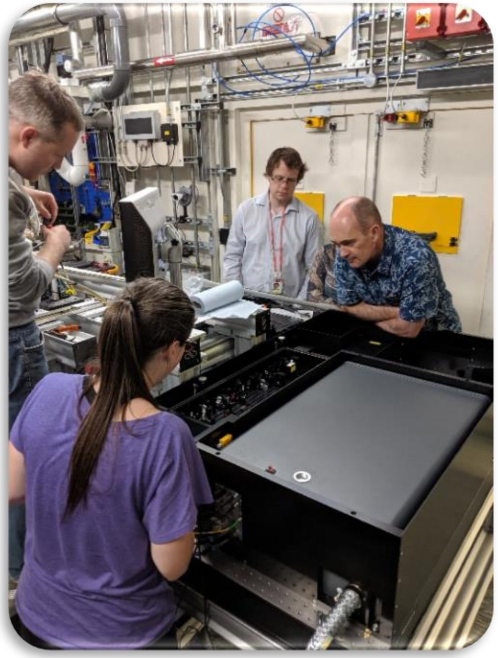


Can we go even faster?

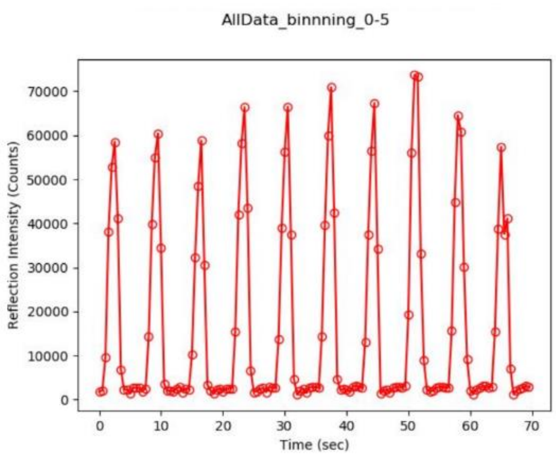
Faster speed required the activation light (pump) to be delivered in a short time period. Pulsed laser are ideally suited for these experiments.

PORTO laser **Andy Dent and Ann Fitzpatrix**

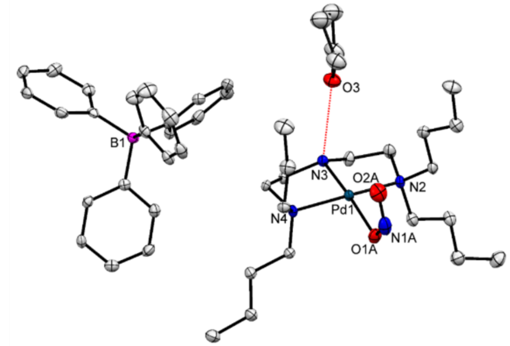
- The PORTO laser provides a tuneable high-repetition rate pulsed laser for Diamond beamlines. It is portable and can be installed in a suitably equipped experiments hutch within a few days.
- A wavelength range of 210 nm to 2600 nm can be achieve using the OPA.
- The laser pulse width is 290 fs.
- The variable repetition rate of the laser can be adjusted from a single pulse up to 600 KHz, which is greater than the orbit frequency of Diamond.



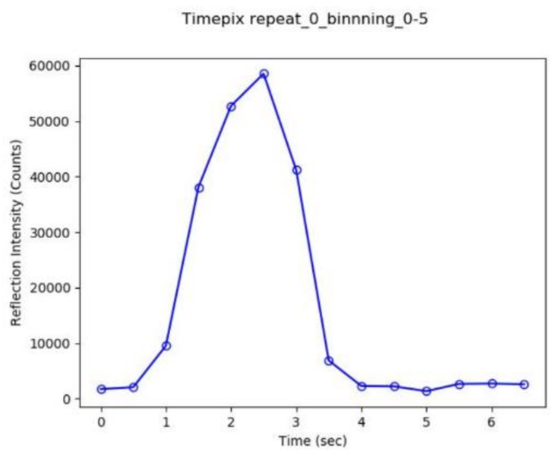
How fast can we go?

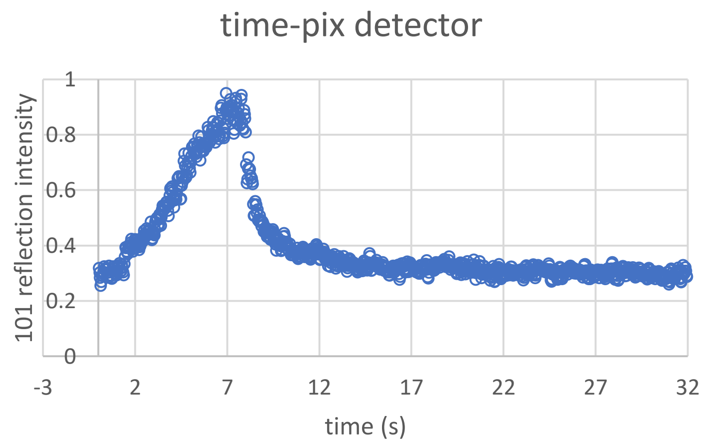


[Pd(Bu$_4$dien)(NO$_2$)]BPh$_4$



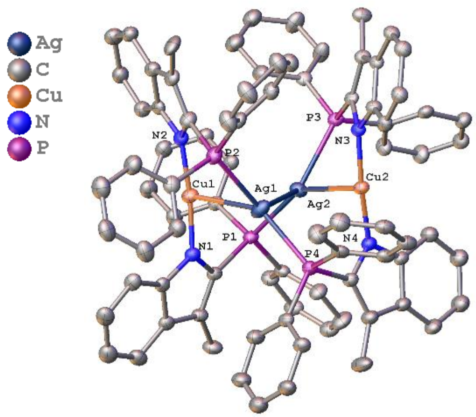
- Experimental condition can be optimized by monitoring a single reflections (LED power, temperature, crystal size etc) before collecting an entire dataset

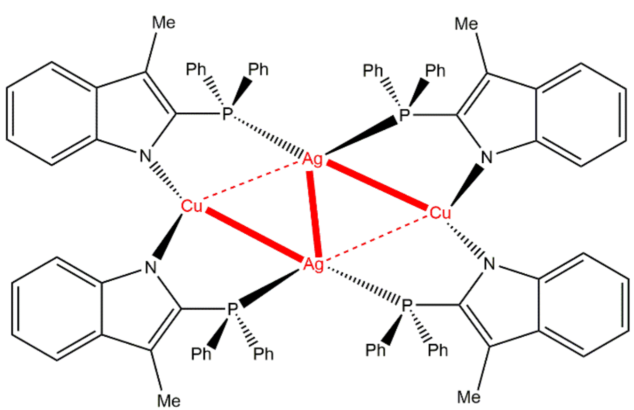




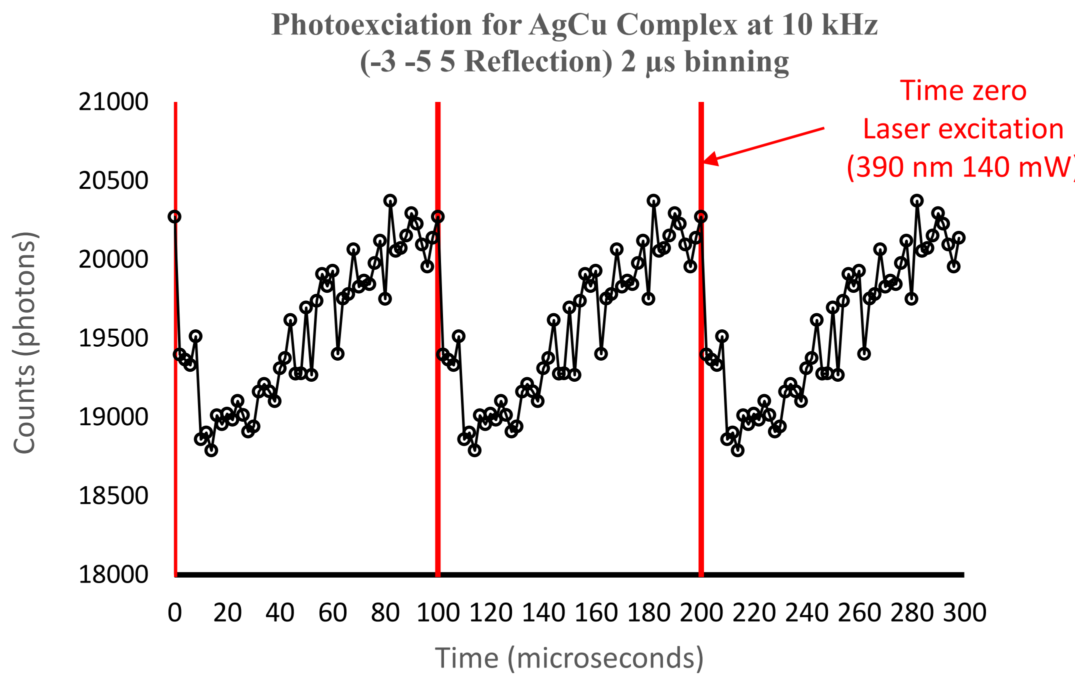
Can we go even faster?

Ag2Cu2L4
(L = 2-diphenylphosphino-3-methylindole ligand)





In collaboration with Radosław Kamiński



Each point is composed of the accumulated number of counts from 1000 seconds

Jarzembska K. N.; *et. al.*, Inorg Chem. 2014, 53(19), 10594–10601.

diamond

Acknowledgments

I19 team	Dave Allen, Sarah Barnett, Lucy Saunders, Adrian Wilcox Andy Dent, Ann Fitzpatrick Giulio Crevatin, Nicola Tartoni, David Omar
Data processing, Controls and Software	Ben Williams, Noemi Frisina, Graeme Winter, Markus Gerstel and Richard Gildea, Paul Hathaway and Andrew Foster and William Nichols
Collaborators	Paul Raithby, Lauren Hatcher, Jonathon Skelton, Anuradha Pallipurath, Clare Stubbs, Radosław Kamiński

Thank you for listening

diamond