

Vibrational Spectroscopy with Neutrons: Inelastic Neutron Scattering (INS)



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Stewart F. Parker
OSNS 10th September 2024

Why vibrational spectroscopy?

Applicable to all three states of matter: gas, liquid, solid.

Long range order is not a prerequisite.

Provides information on the dynamics of a system: probes chemical changes



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What are we measuring?

A gas phase atom has 3 degrees of freedom: x , y , z

A molecule in the gas phase consisting of n atoms therefore has $3n$ degrees of freedom.

It has 3 degrees of translational freedom and 3 degrees of rotational freedom, the remaining $(3n - 6)$ degrees of freedom are the vibrational modes.

(Note: a linear molecule has $(3n - 5)$ modes).

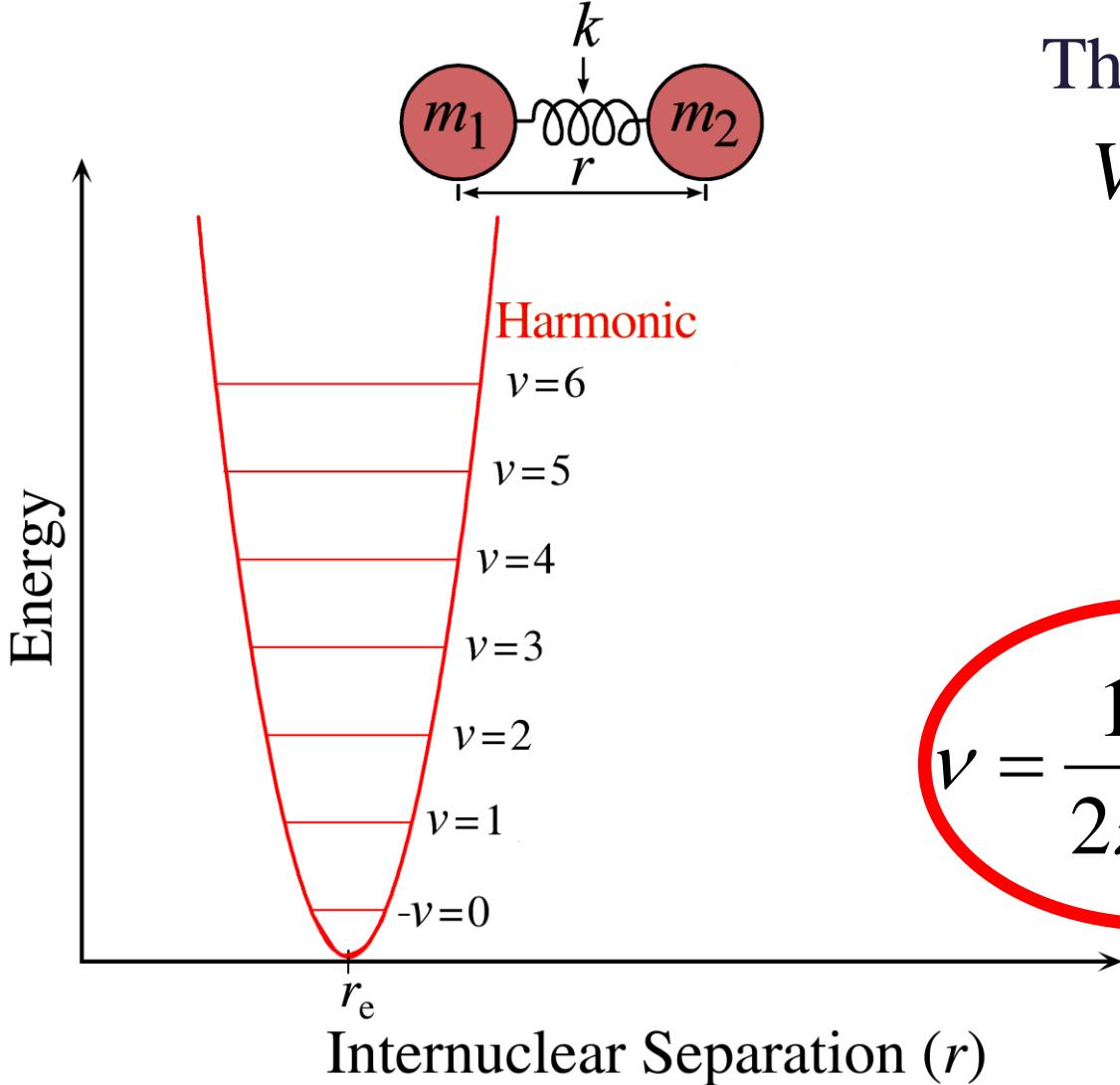


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What are we measuring?

A vibrational spectrum measures the energy difference between the quantised vibrational levels.



The harmonic oscillator

$$V(r) = \frac{1}{2} k(r - r_e)$$

$$E(n) = h\nu\left(n + \frac{1}{2}\right)$$

$$\Delta E(n) = \pm 1$$

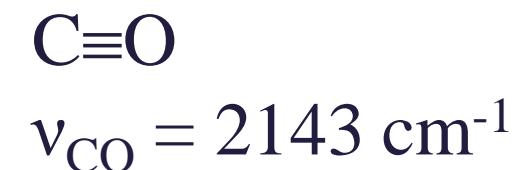
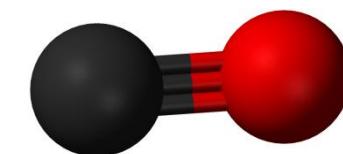
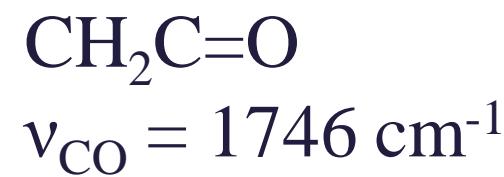
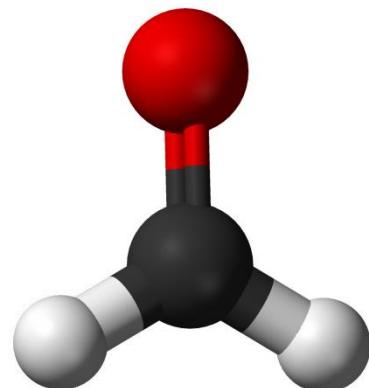
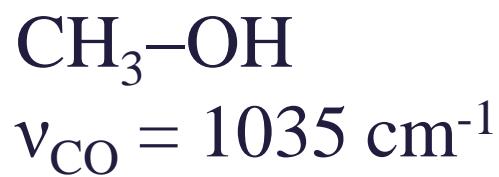
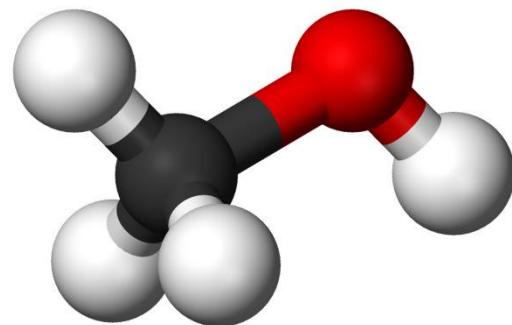
$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

k = force constant

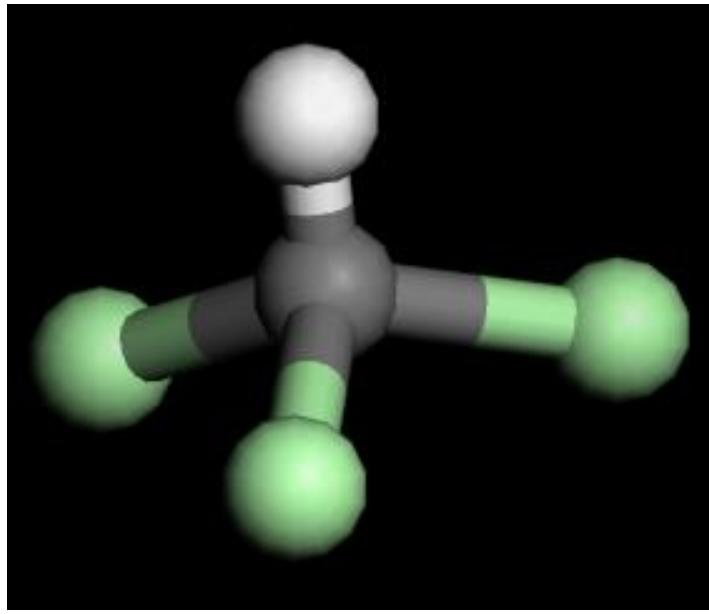
$$\mu = \frac{m_1 m_2}{m_1 + m_2}$$

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Effect of changing k



$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$



$$\text{Cl}_3\text{C}-\text{H} \nu_{\text{CH}} = 3024 \text{ cm}^{-1}$$

$$\text{Cl}_3\text{C}-\text{D} \nu_{\text{CD}} = 2256 \text{ cm}^{-1}$$

Effect of changing μ : CCl_3H vs CCl_3D
Predict:

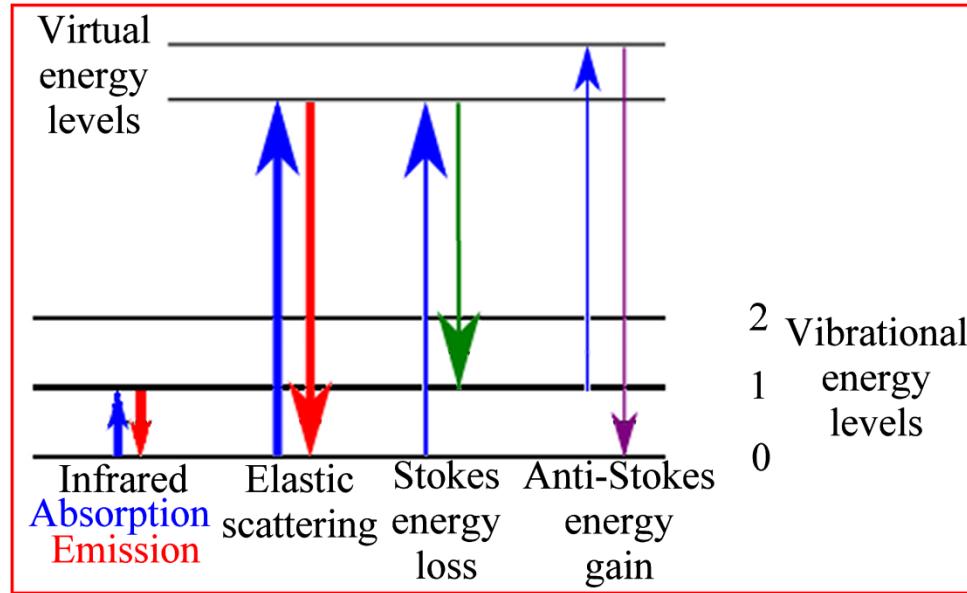
$$\frac{\nu_{\text{H}}}{\nu_{\text{D}}} = \sqrt{\frac{k}{\mu_{\text{H}}}} / \sqrt{\frac{k}{\mu_{\text{D}}}} = \sqrt{\frac{\mu_{\text{D}}}{\mu_{\text{H}}}}$$

$$= \sqrt{\frac{\frac{m_1 m_{\text{D}}}{m_1 + m_{\text{D}}}}{\frac{m_1 m_{\text{H}}}{m_1 + m_{\text{H}}}}} \approx \sqrt{\frac{m_{\text{D}}}{m_{\text{H}}}} \approx \sqrt{2} = 1.41$$

$$\frac{\nu_{\text{H}}}{\nu_{\text{D}}} = 1.34$$

The difference is the result of *anharmonicity*. Large for H (up to 10%), small for everything else.

How do we measure a vibrational spectrum?



Directly: Infrared absorption or emission

Indirectly: By inelastic scattering of particles

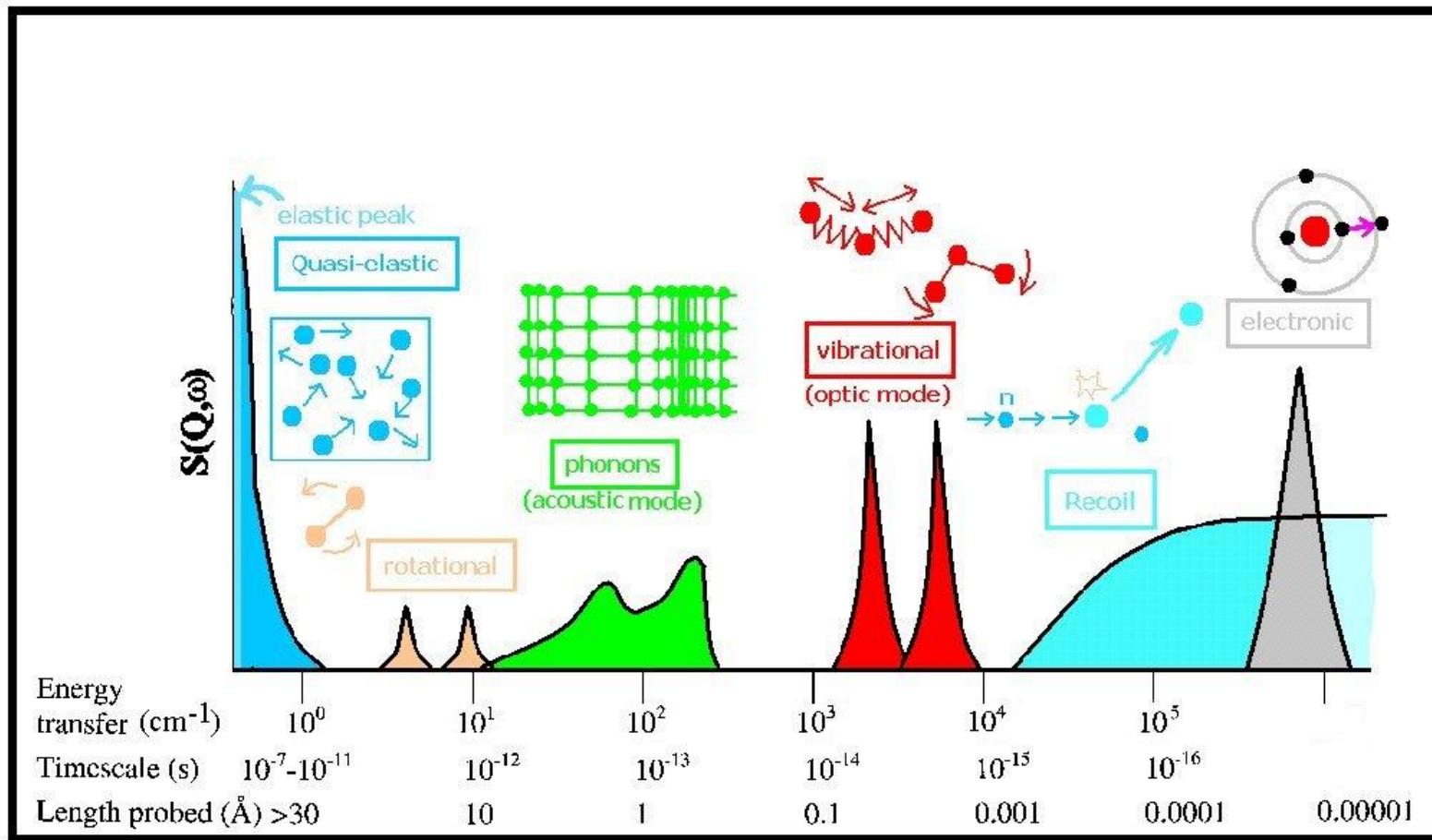
photons (Raman)

neutrons (INS)

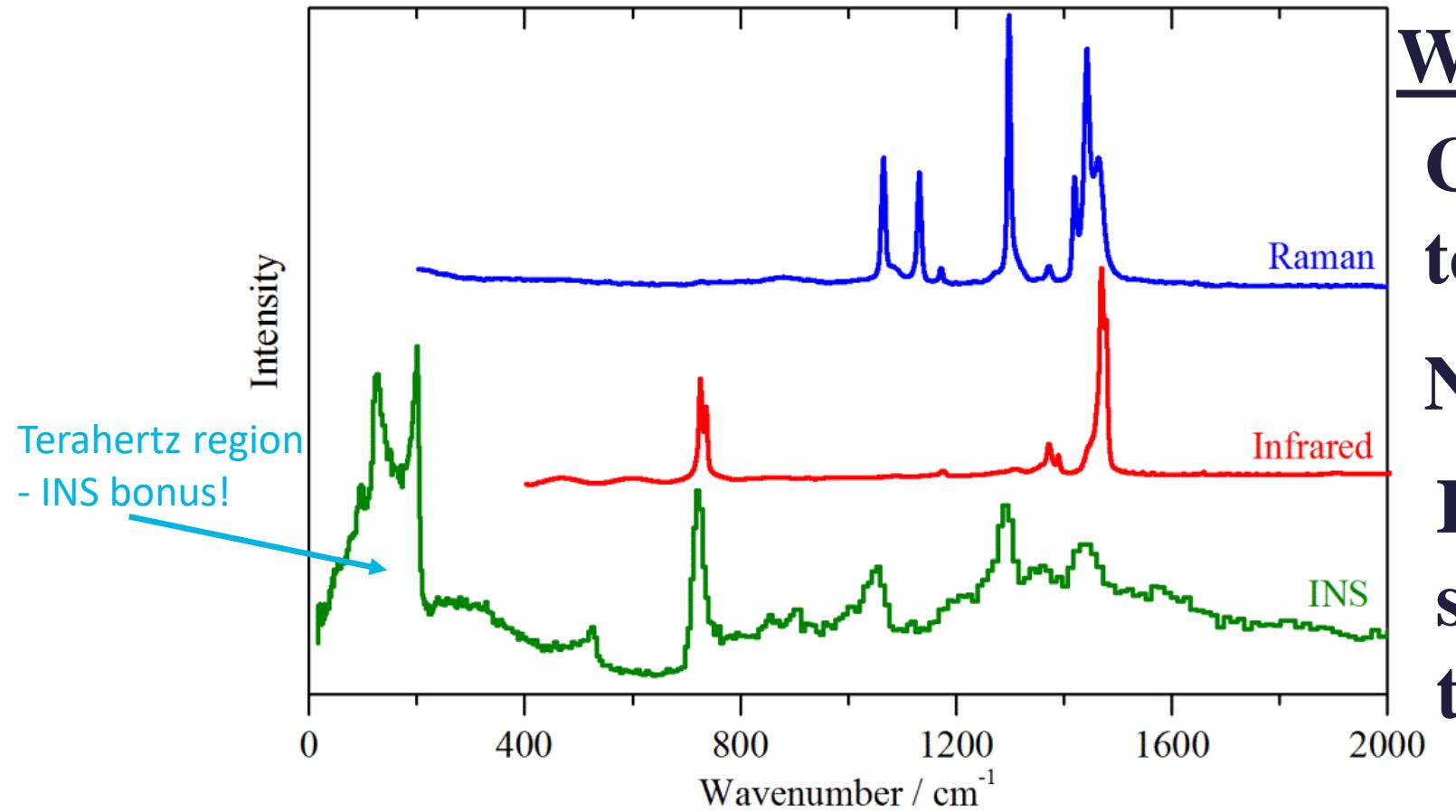
electrons (IETS, HREELS)

He atoms (HAS)

What is inelastic neutron scattering?



Polyethylene: world-wide production >60 Mtonnes year⁻¹
used for everything from packaging to insulation to
hip replacements.



Why use neutrons?

Complementary
to IR and Raman

No selection rules

Intensities
straightforward
to calculate



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$$S(Q, \omega) = \sigma Q^2 U_\omega^2 \exp(-Q^2 U_T^2)$$

Vibrations with INS - drawbacks

- Low sensitivity (Large samples: 0.1 – 1 g organic,
 >10 g inorganic, 10 – 50 g catalyst)
- Low resolution at high energy (*cf.* IR/Raman)
- Generally low temperature (20 K)
 - Minimise scattering from thermal motion (Debye-Waller factor)
- Expensive (but not to you!) and scarce
- Slow (1 - 12 hrs)



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Analysis of vibrational spectra

Group frequency tables

Wilson GF method

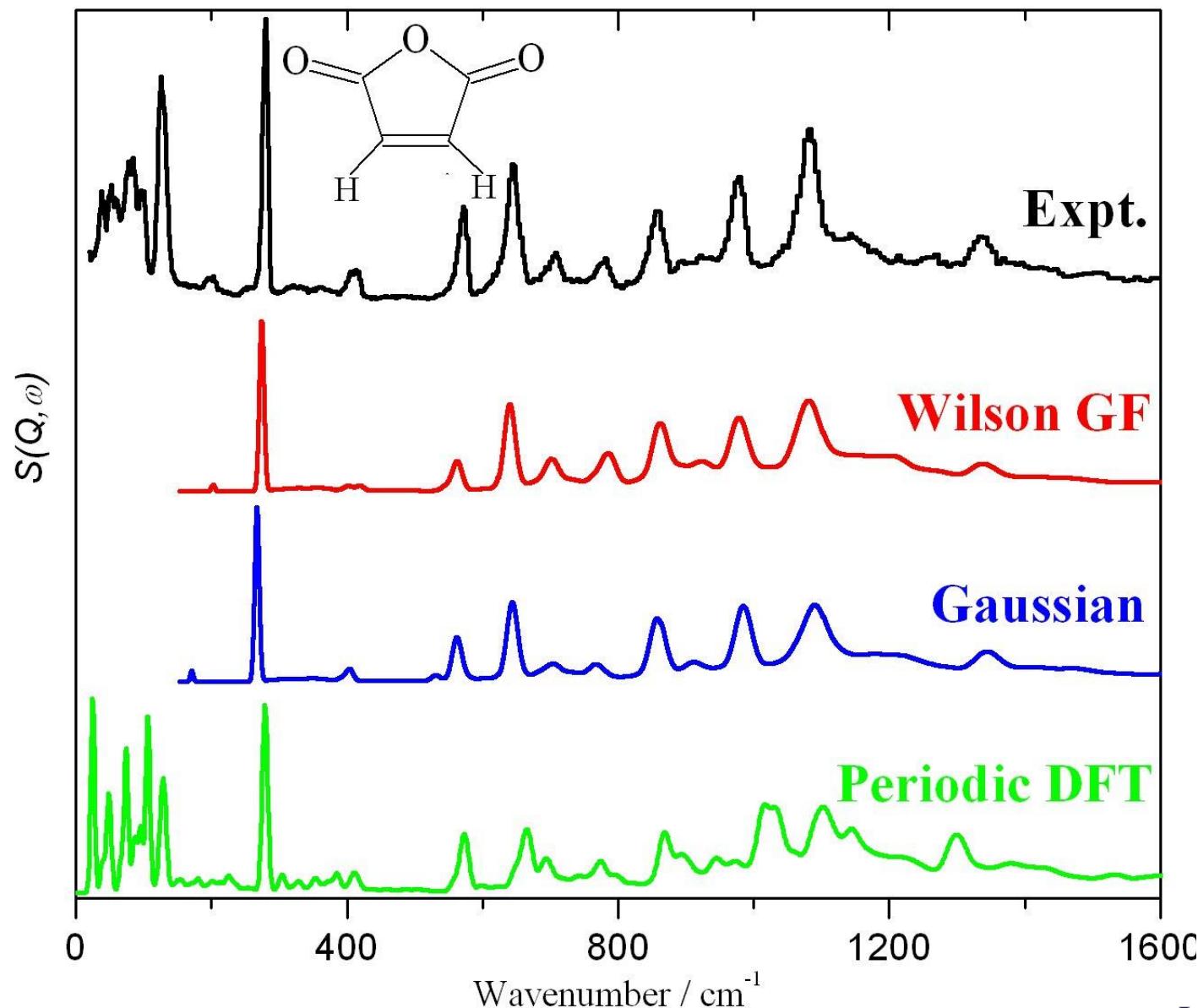
ab initio

$$\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi = \frac{i\hbar\partial}{\partial t} \Psi$$

Table 2-1.

Met		
C—		
Methyl terminal rocking		For $n < 10$
CCC deformation		975–835
Methylene twisting-rocking		895
Methylene rocking-twisting		535–0
$\text{CH}_3-\text{CH}_2, \text{CH}_2-\text{CH}_2$ torsion		1310–1175
		1060–719
		~220, 153–0

Comparison of analysis methods



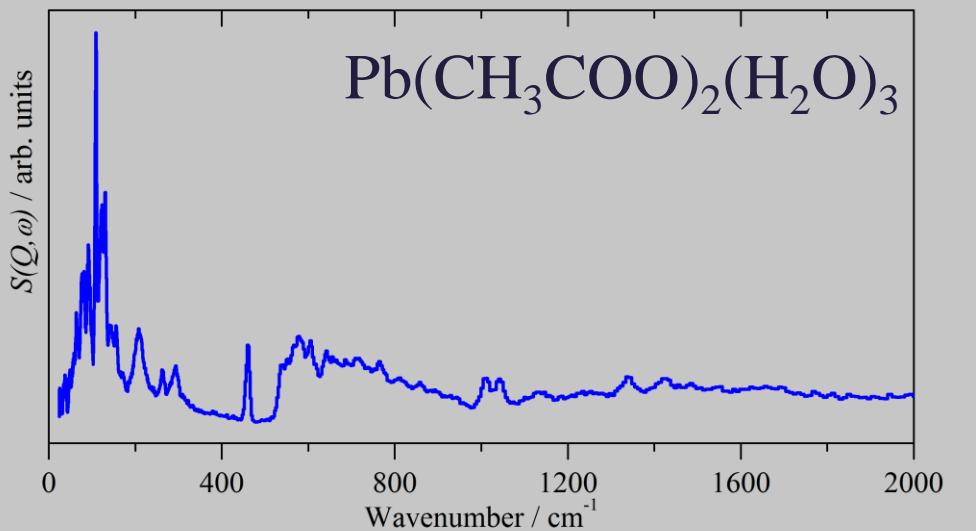
Hydrogen/Deuterium substitution

- Bands shift down by $\sim 1/\sqrt{2}$ on H→D
- Bands disappear/weaken – 7.6 vs 82.0 barn
- Needs to be well deuterated (99%)
 - other uses 90% deemed acceptable – INS will give approx. 50% signal due to H
- Can provide contrast or decrease unwanted signal from organic

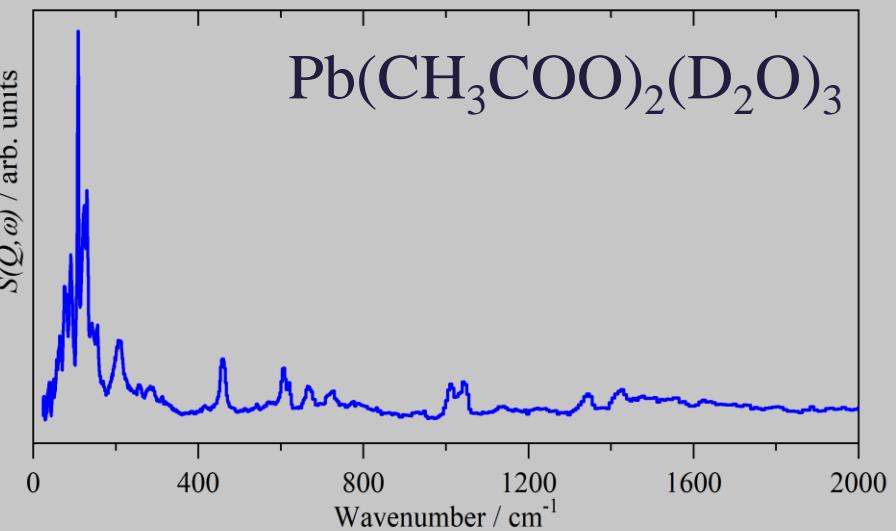
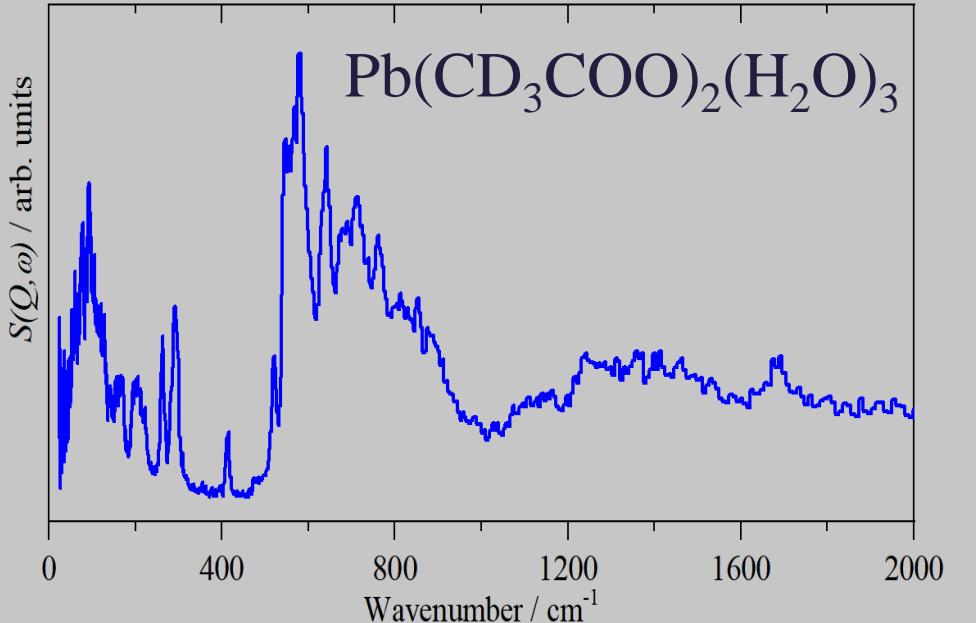


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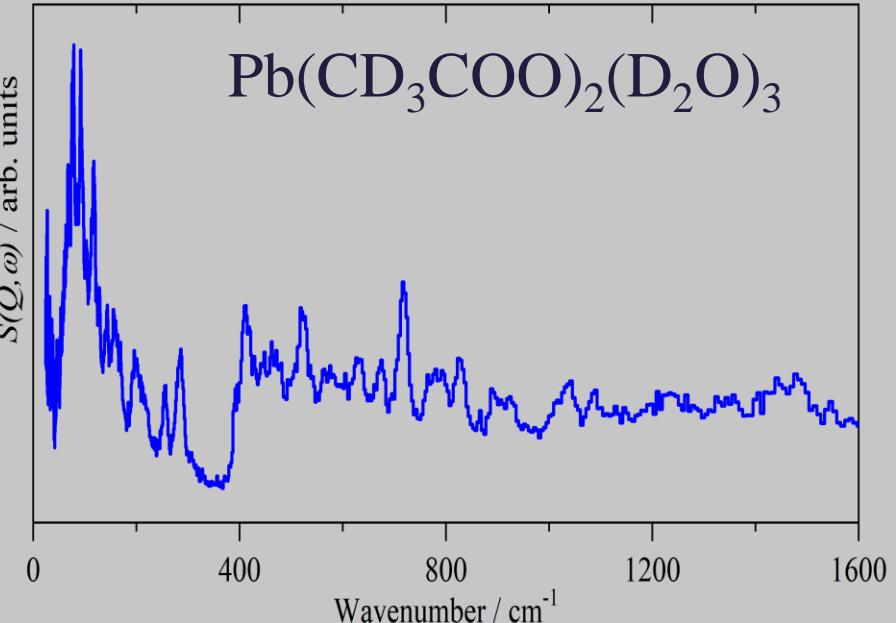




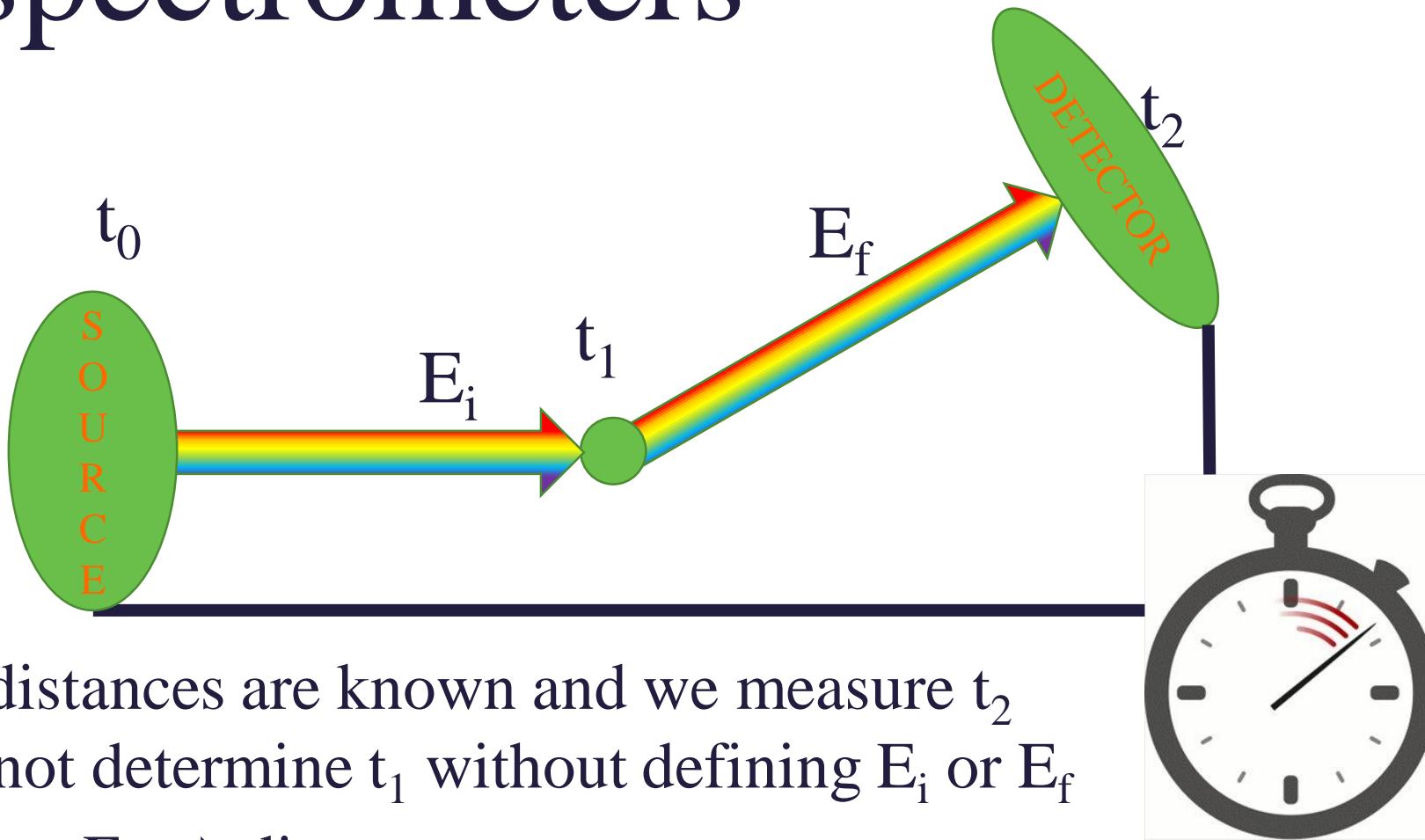
Lead acetate-D3 trihydrate
D. Visser, Loughborough University



Lead acetate-D3 trideuterate
D. Visser, Loughborough University



INS spectrometers

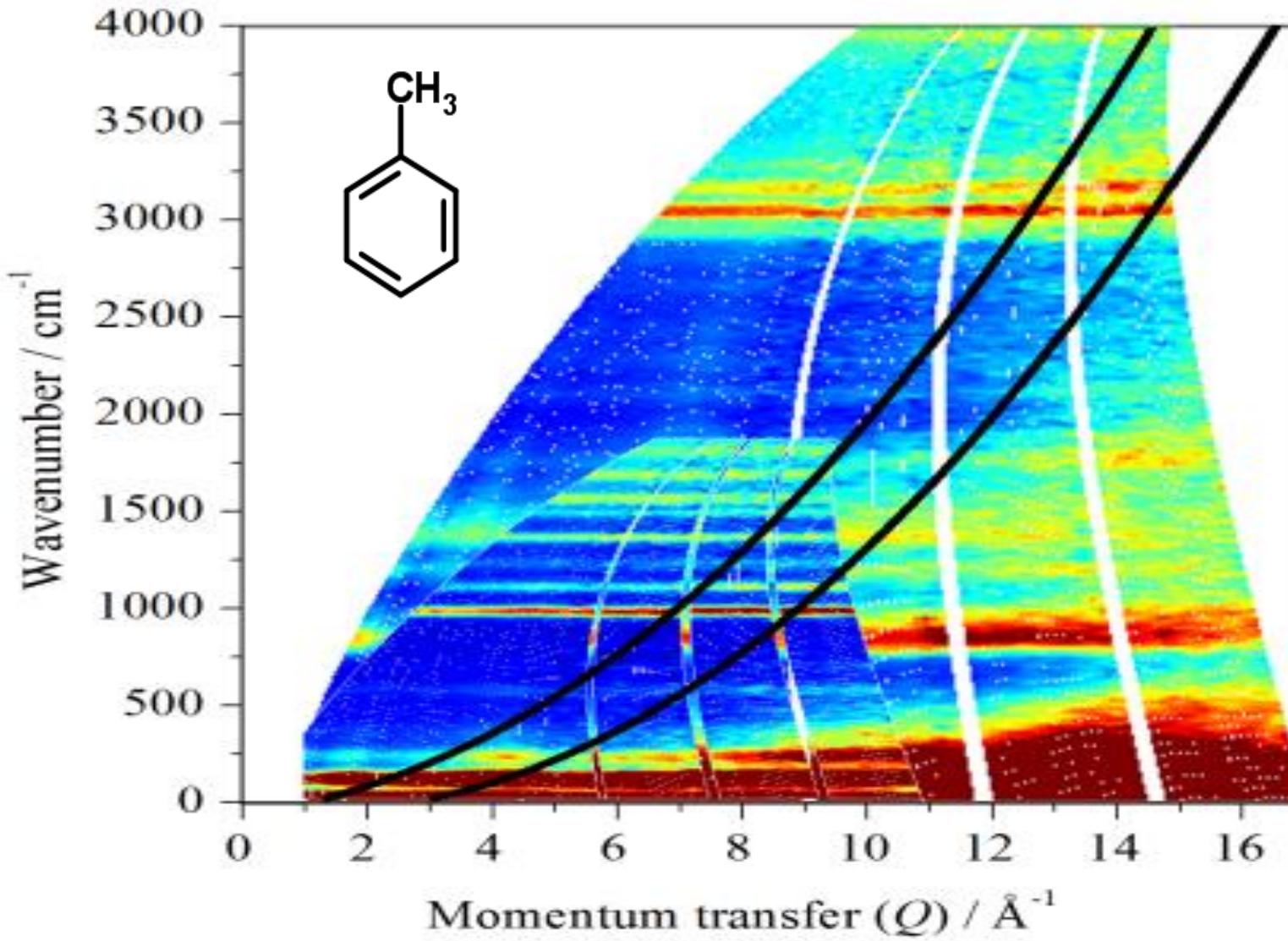


All distances are known and we measure t_2

Cannot determine t_1 without defining E_i or E_f

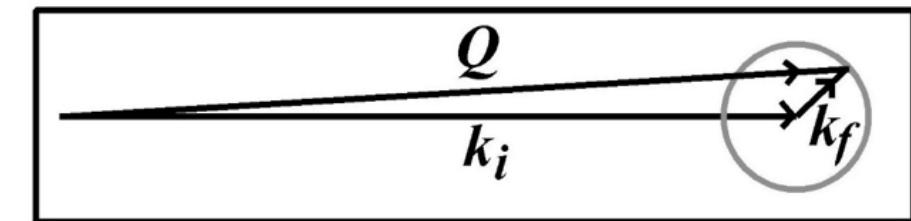
Select: $E_i \Rightarrow$ direct geometry

Select: $E_f \Rightarrow$ indirect geometry

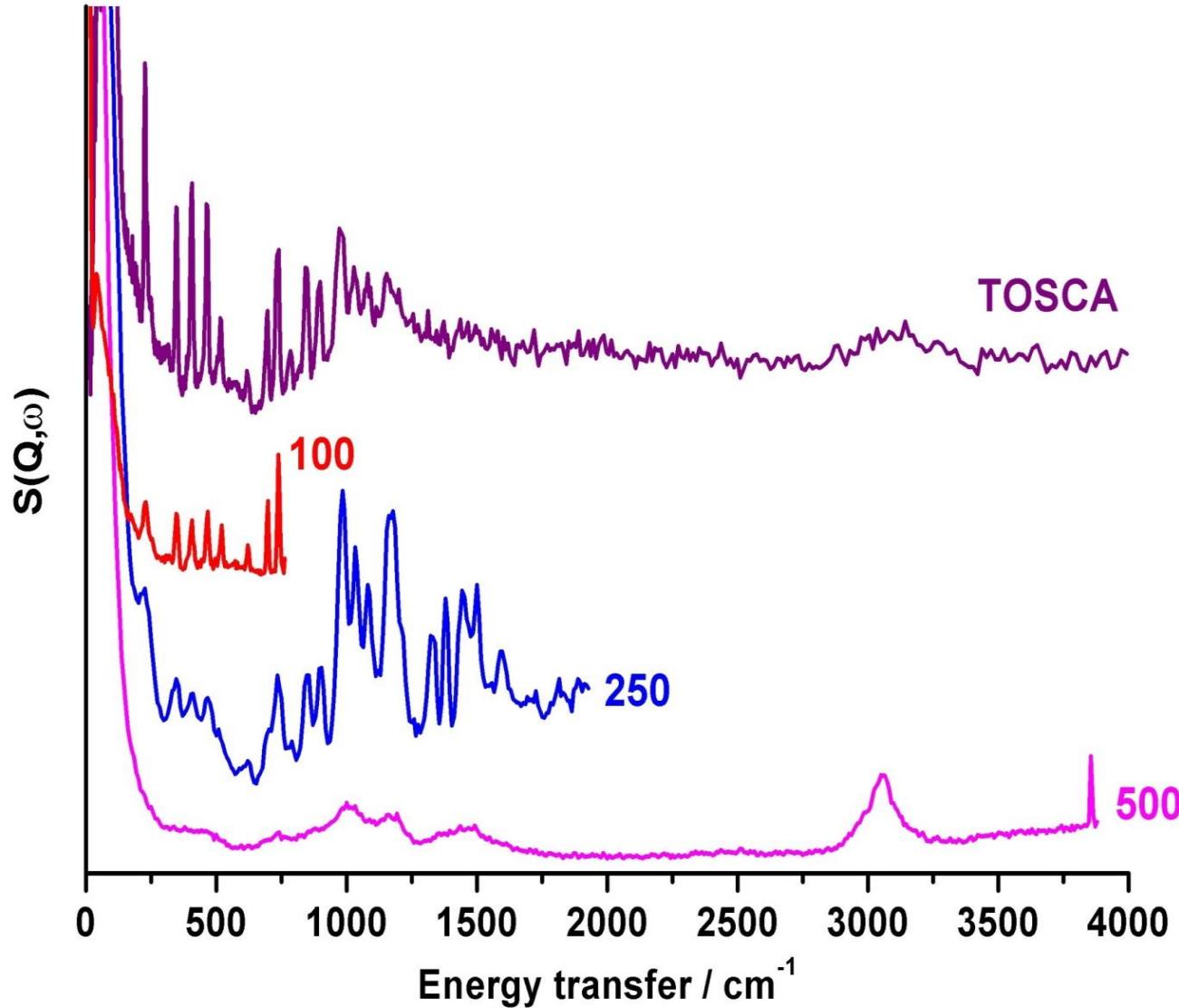


Indirect geometry

$$\vec{Q} = \vec{k}_i - \vec{k}_f$$



Toluene on indirect (TOSCA) and direct (MAPS) geometry spectrometers



Choose indirect

- Excellent resolution and sensitivity below ~2000 cm⁻¹
- Easy to use

Choose direct

- Higher energy features
- Q resolution required
- Trade resolution *vs* flux



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Sample loading

Multiple scattering events are less detrimental to indirect geometry

10-25 % scattered is optimum

Flat plate is preferred geometry

Aim for $> 6 \times 10^{21}$ H atoms in beam
(TOSCA)

Load in cryostat/CCR on centre stick

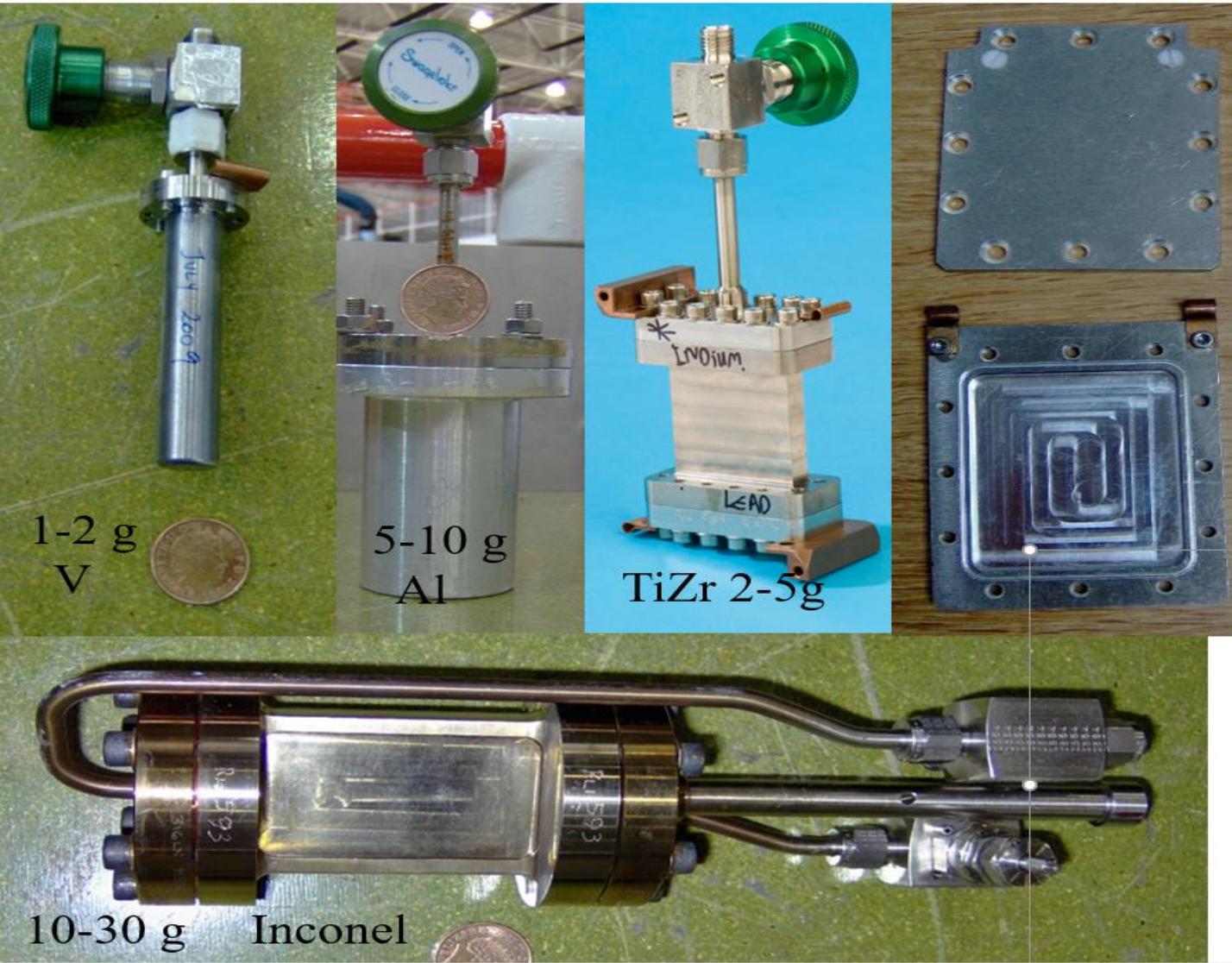
- 300 K difference between top and bottom
- Sharpens bands
- Decreases Debye-Waller factor



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Sample loading



Simple samples: let someone else do it!

- XPRESS measurements:
 - Available on all instruments
 - For TOSCA: solid and liquid samples
 - Simple sample handling (open lab)
 - Instrument scientist measures for you
 - 2 g organic (5 g preferred)
 - Inorganic samples – discuss before submission
 - After 2 years data from TOSCA becomes public domain
- INS database
 - <http://wwwisis2.isis.rl.ac.uk/INSdatabase/>
 - Currently 968 spectra and increasing!



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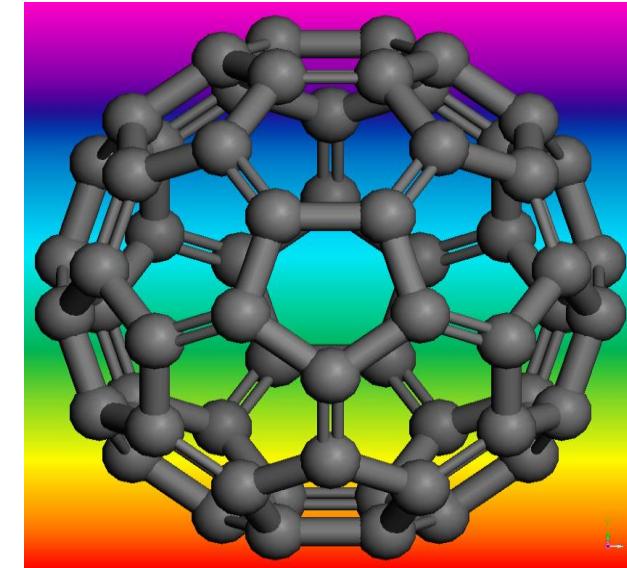
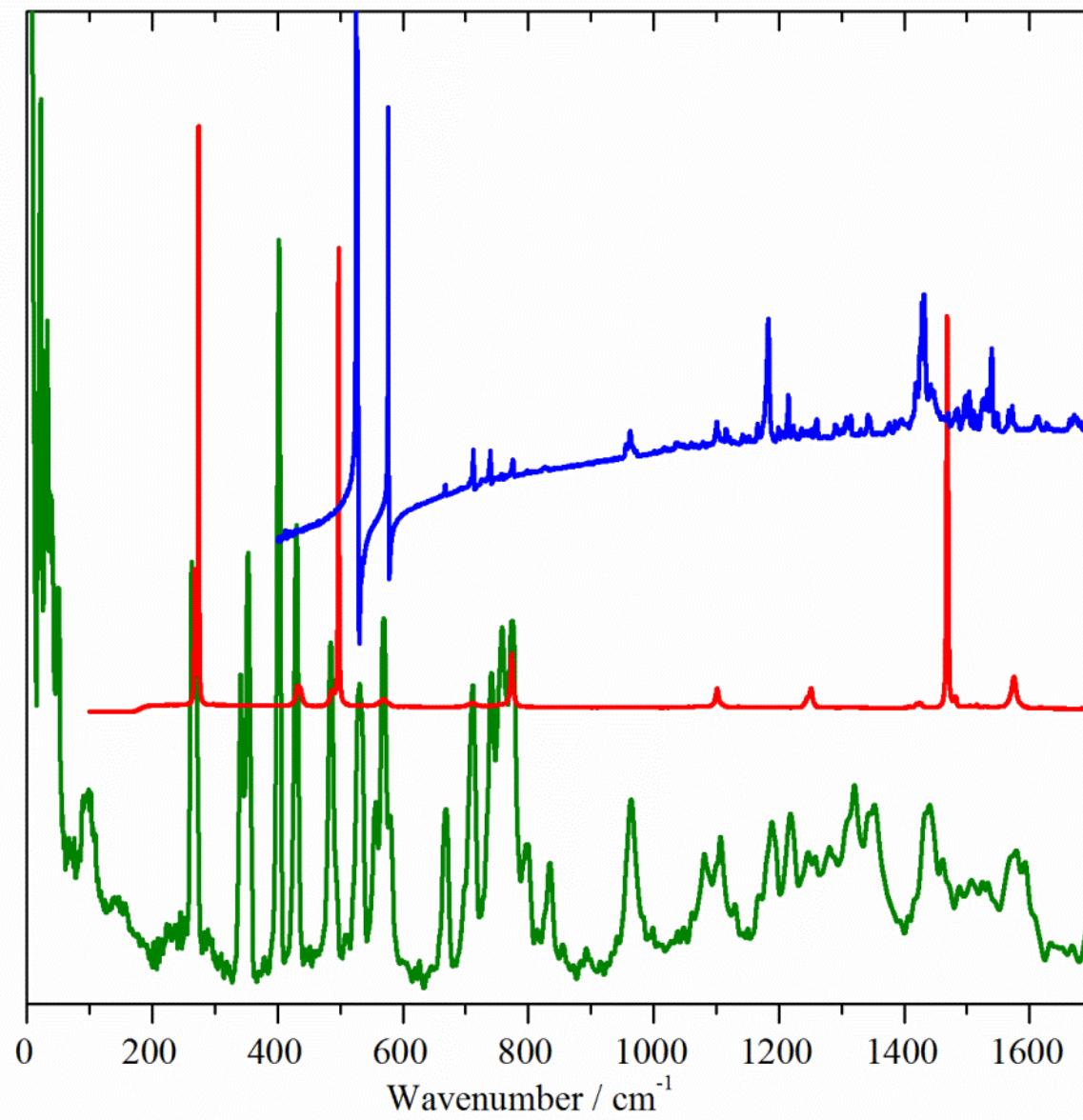
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EXAMPLES



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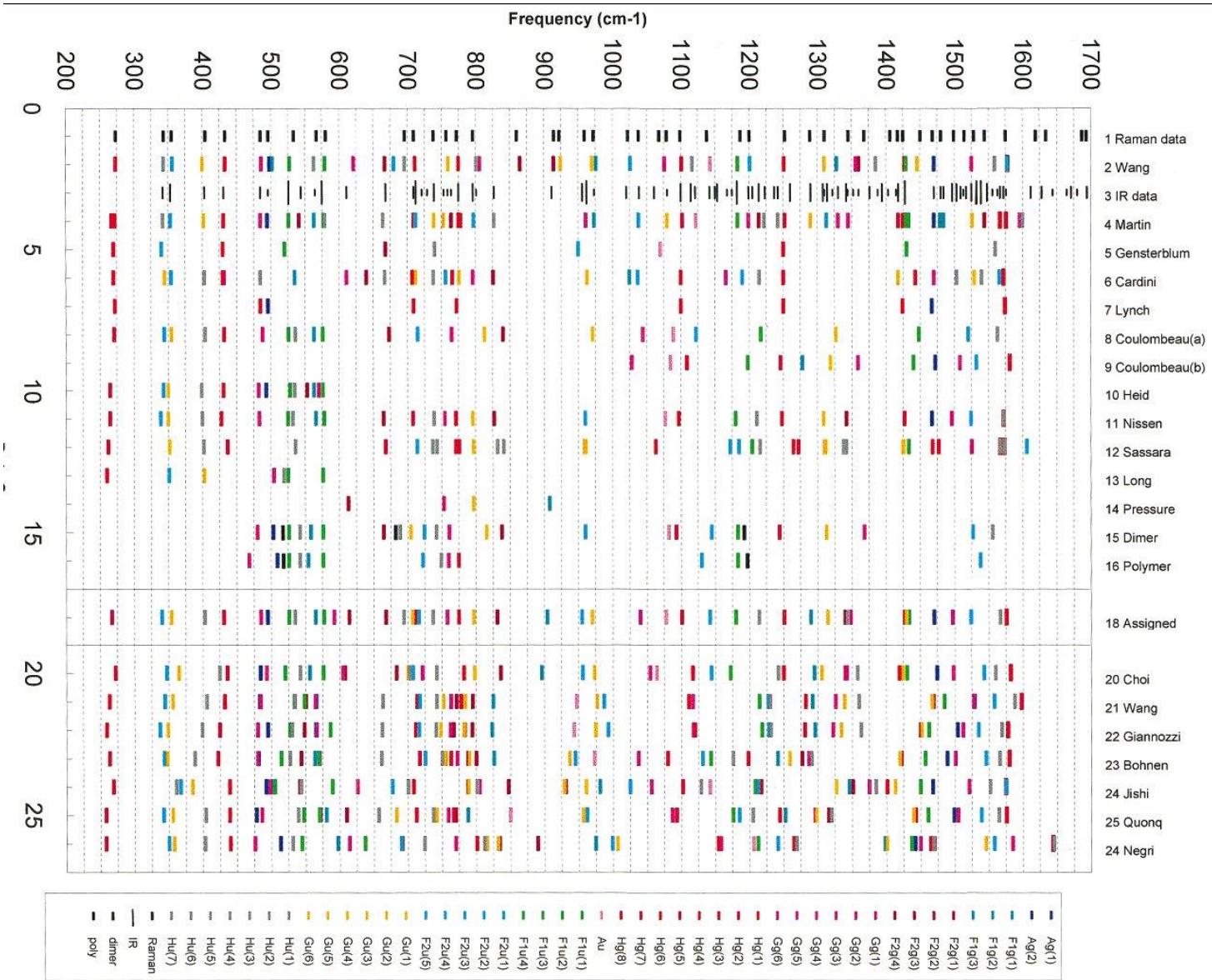
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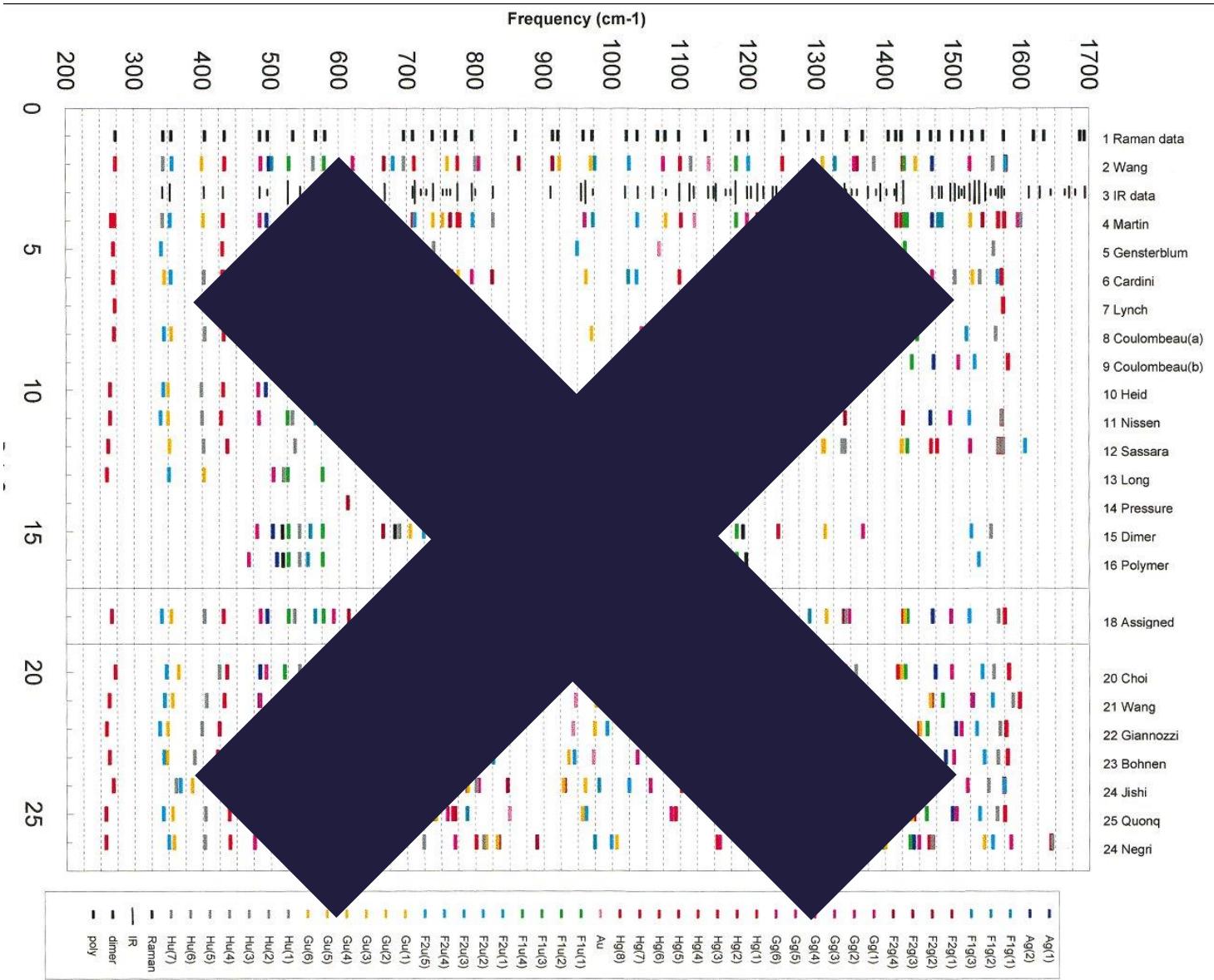
C₆₀

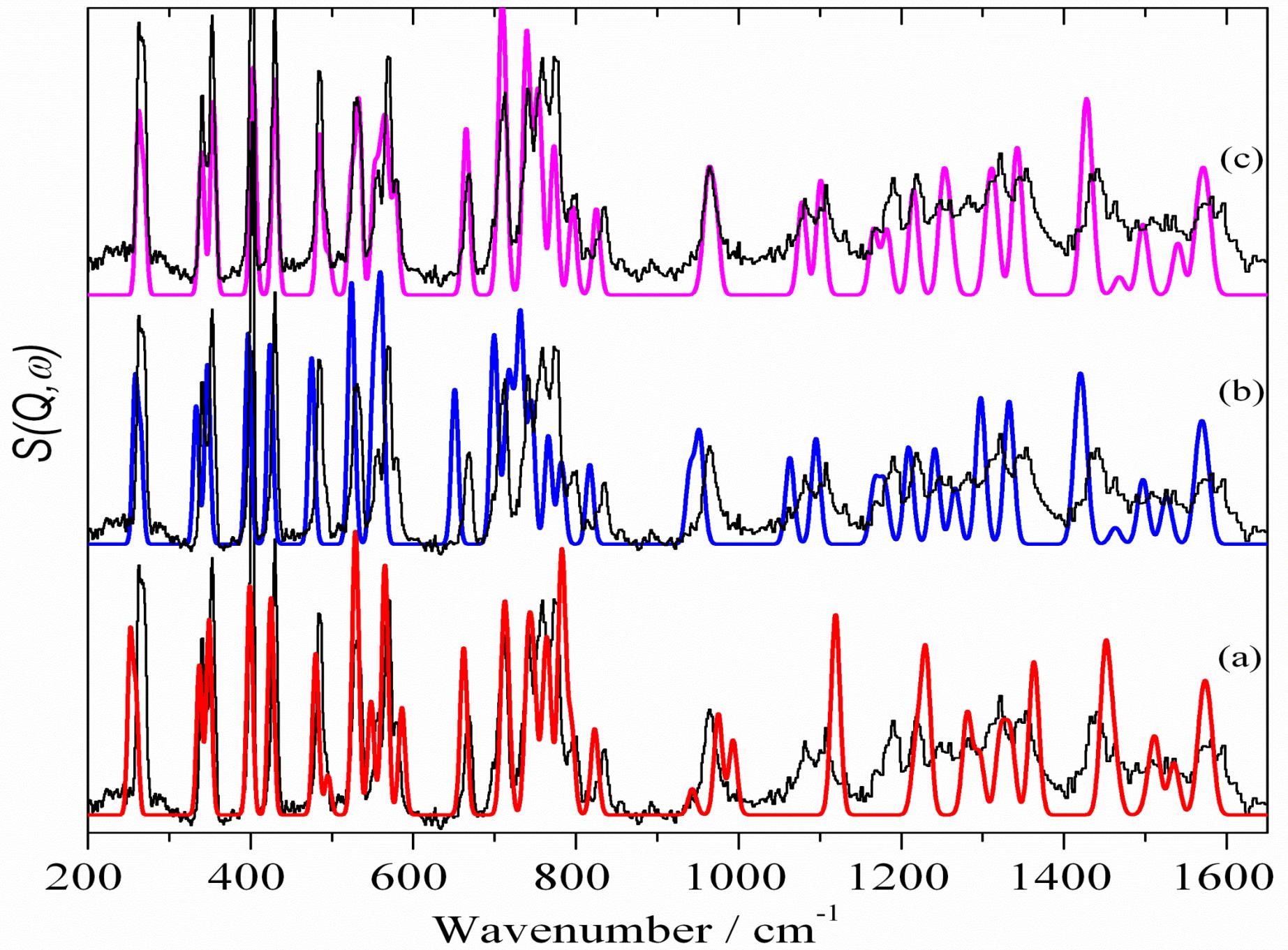
“The most
beautiful
molecule”

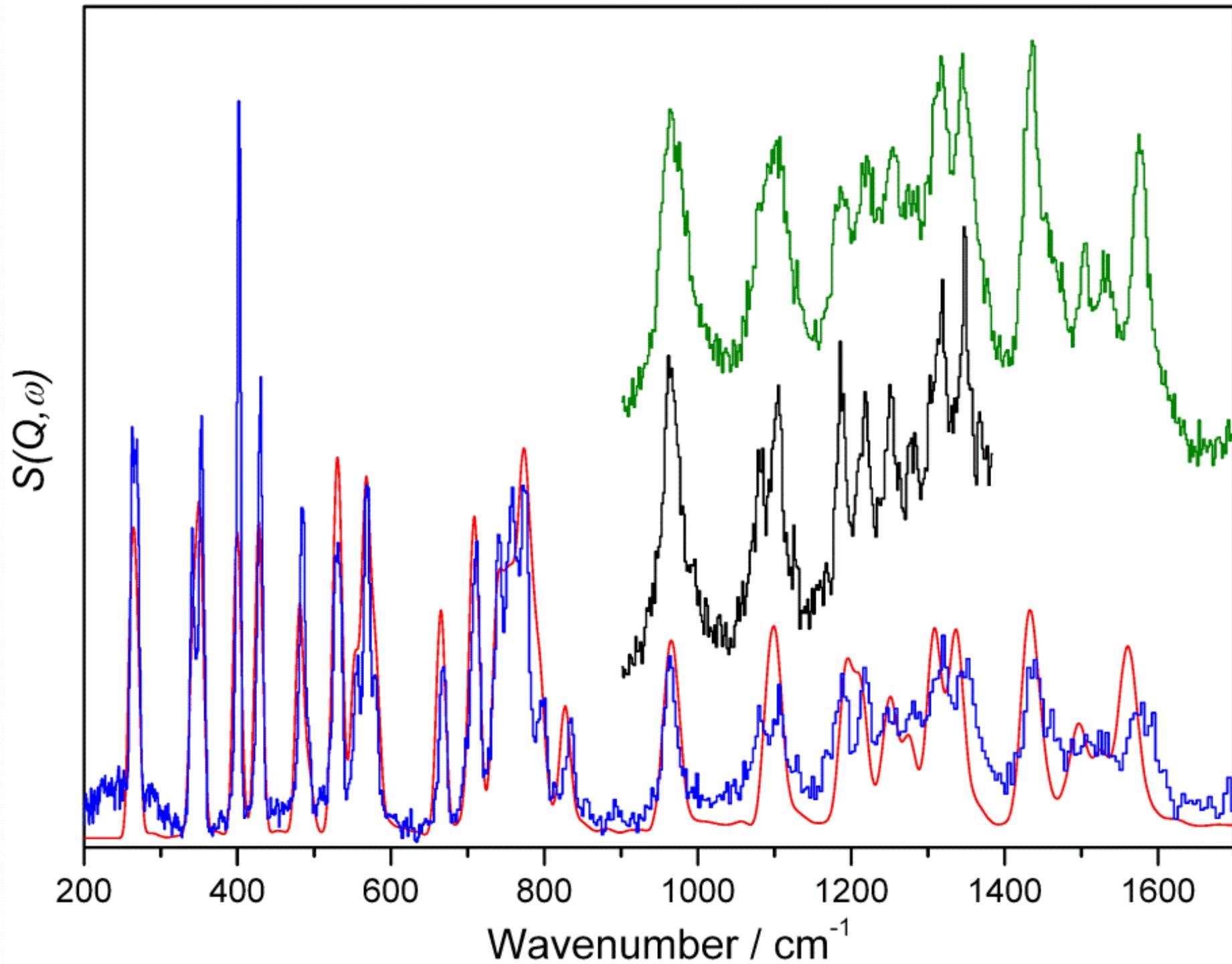
C₆₀



C₆₀







Why catalysis?

15-30% of GDP of advanced nations is directly or indirectly dependent on chemistry

>90% of chemical processes involve catalysis at some point

Hence both economic and environmental drivers to improve efficiency
(chemical industry responsible for 3.6% global CO₂ emissions)

Catalysis is inherently complex

Multi-scale: from Å to km

Materials are rarely crystalline; usually amorphous and/or nanoparticulate

Atomistic insight is essential in order to understand and then improve processes

Complexity means that model systems are needed

Density functional theory (DFT) calculates properties that are sufficiently accurate as to be useful, at an acceptable computational cost



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A model system: dodecanethiol on Pd nanoparticles

Nanoparticles are ubiquitous: in addition to their use in catalysis, they are present in products as diverse as sunscreens, car tyres, printing inks and tennis racquets.

Surface modification enables the properties to be tailored to the application. Crucially, it can prevent aggregation. But understanding what is on the surface is very difficult. For hydrogenous adsorbates, INS spectroscopy “sees” these very well.

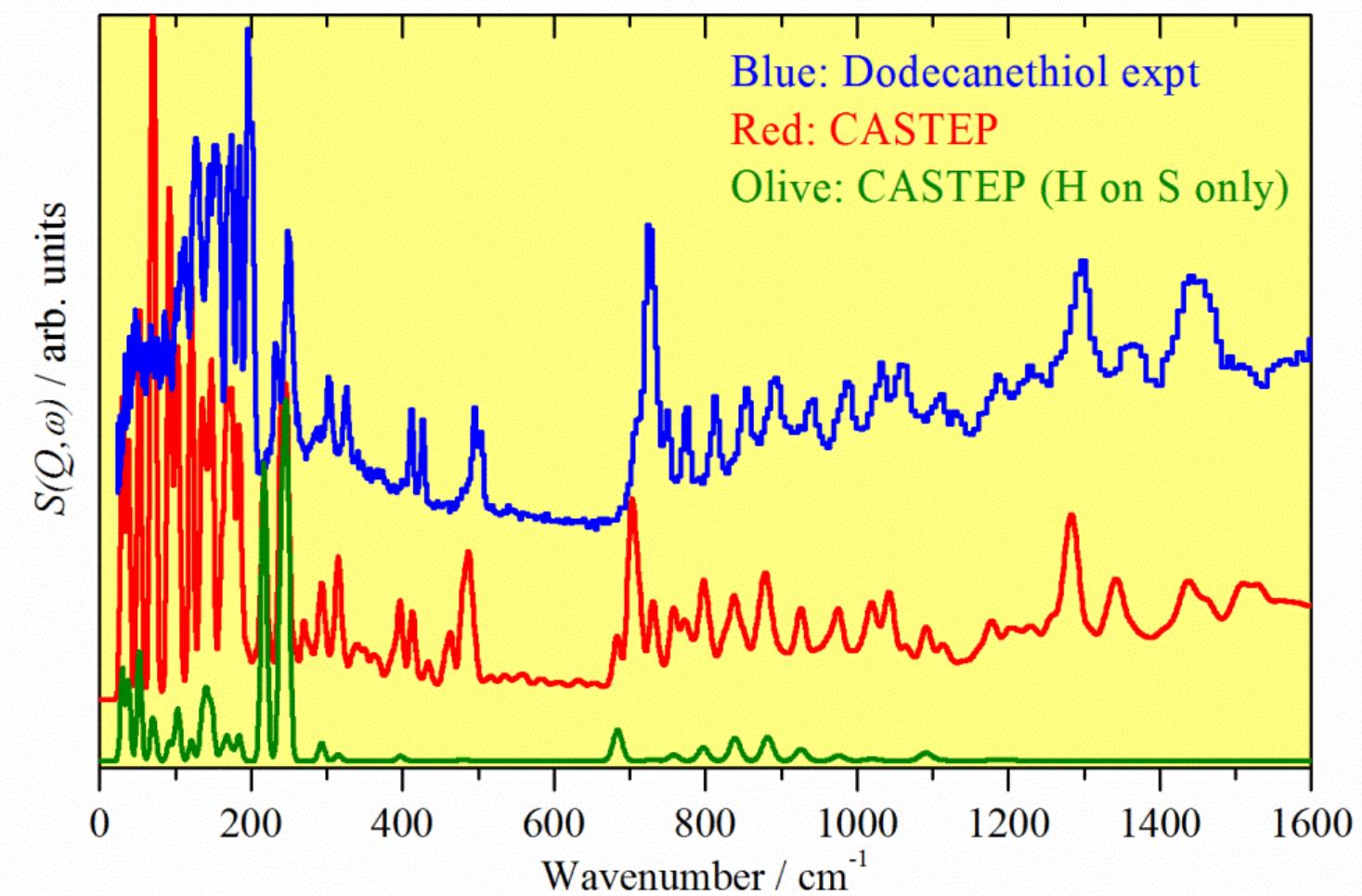
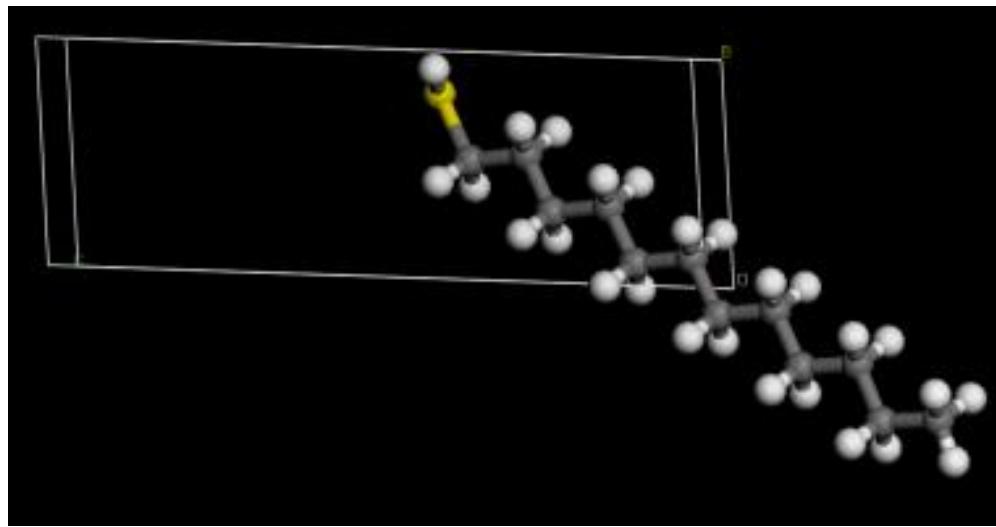


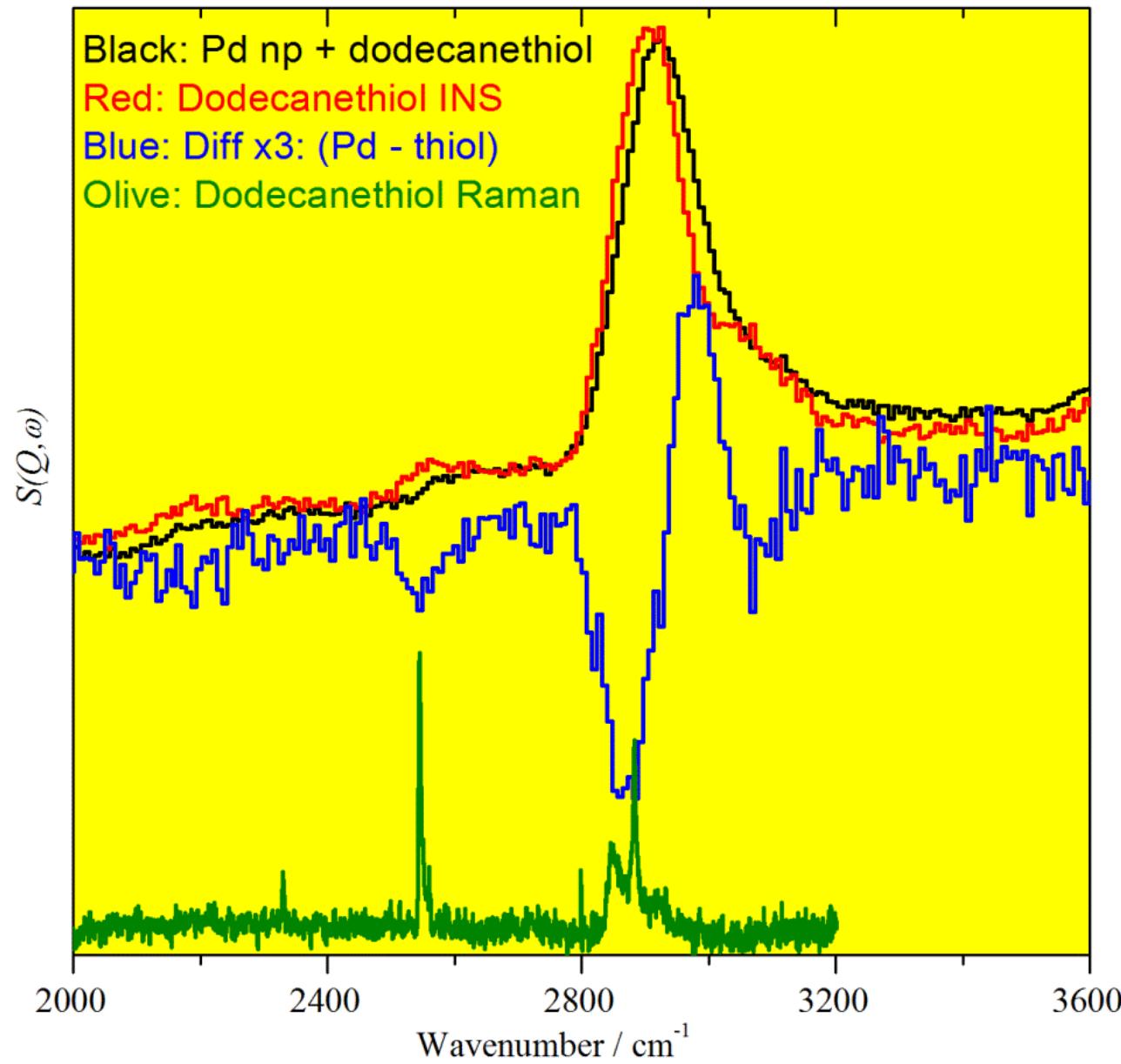
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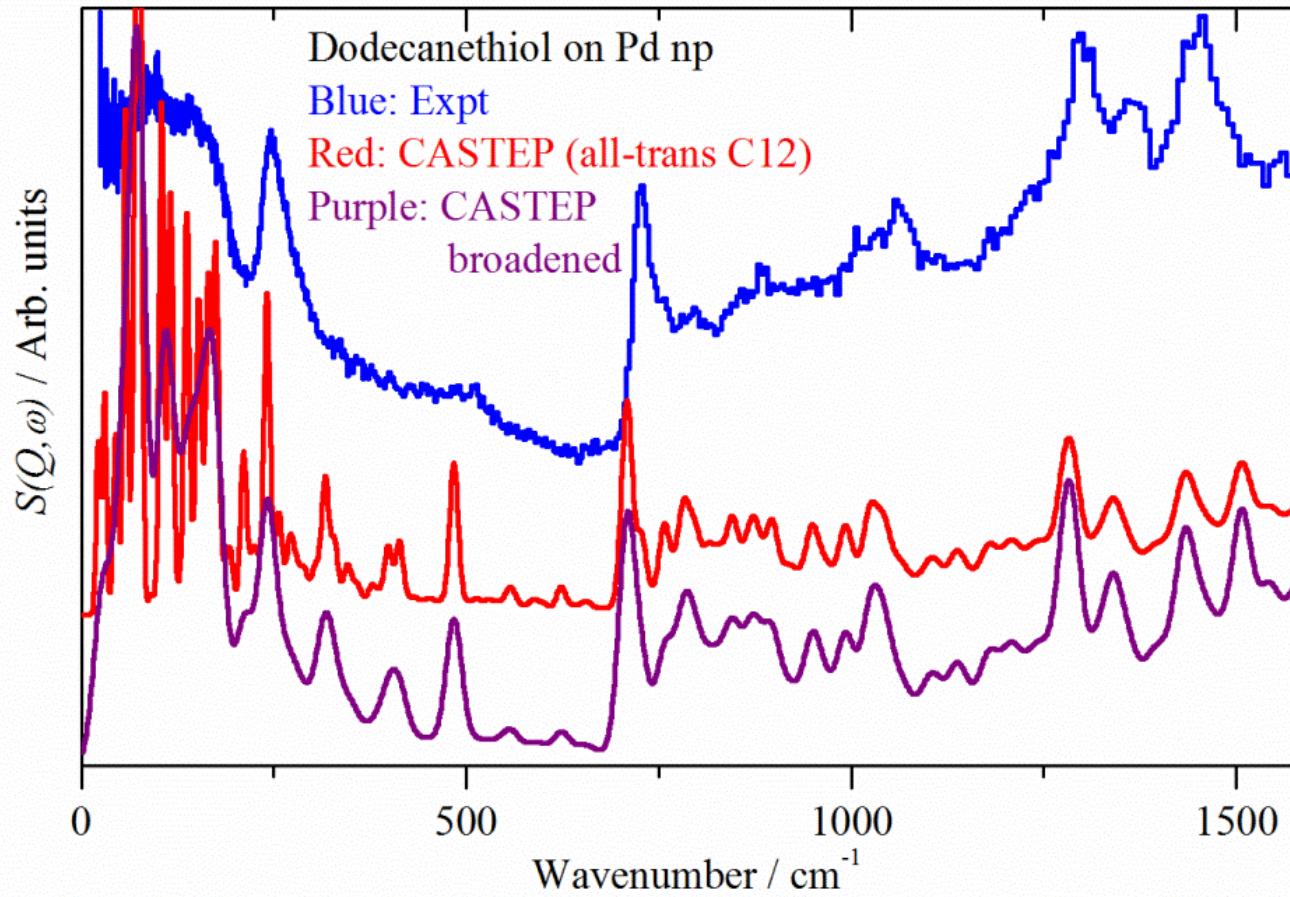
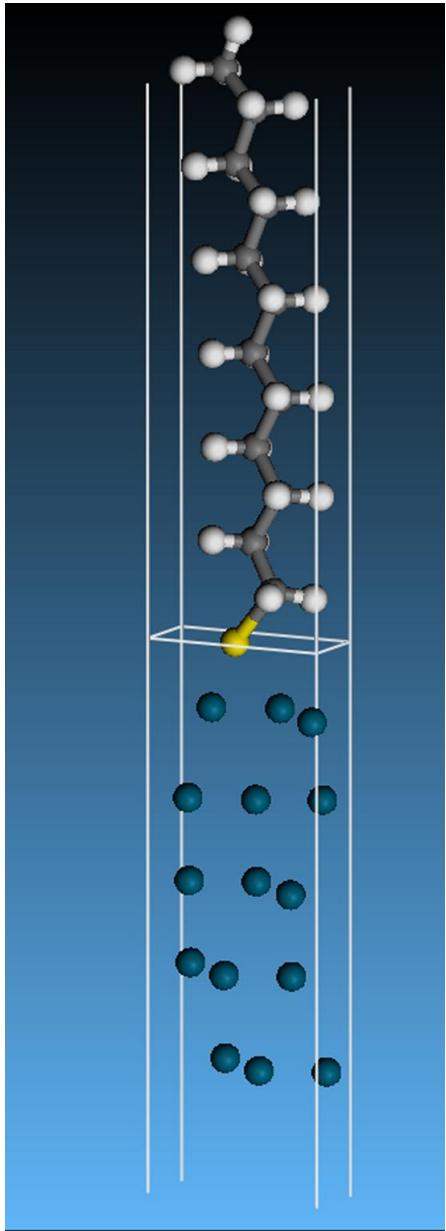
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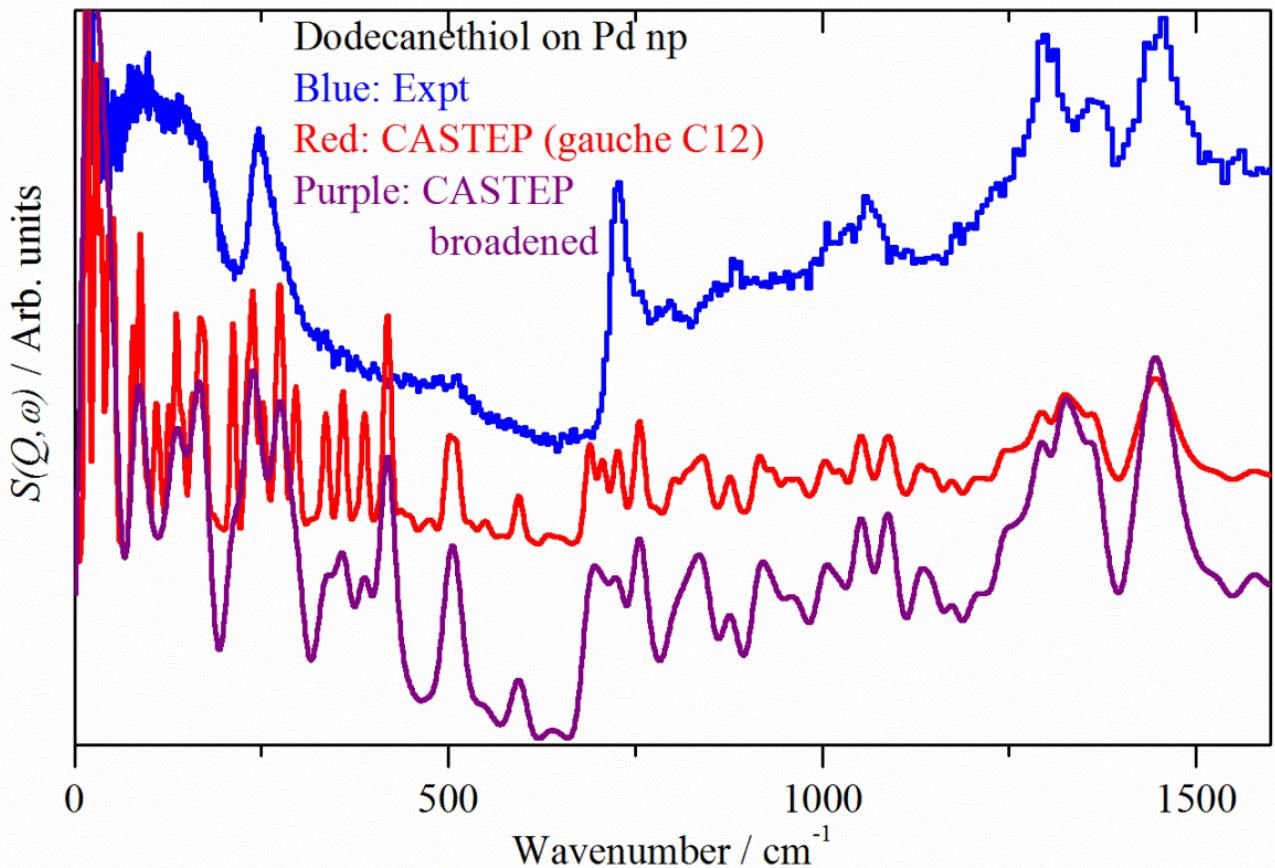
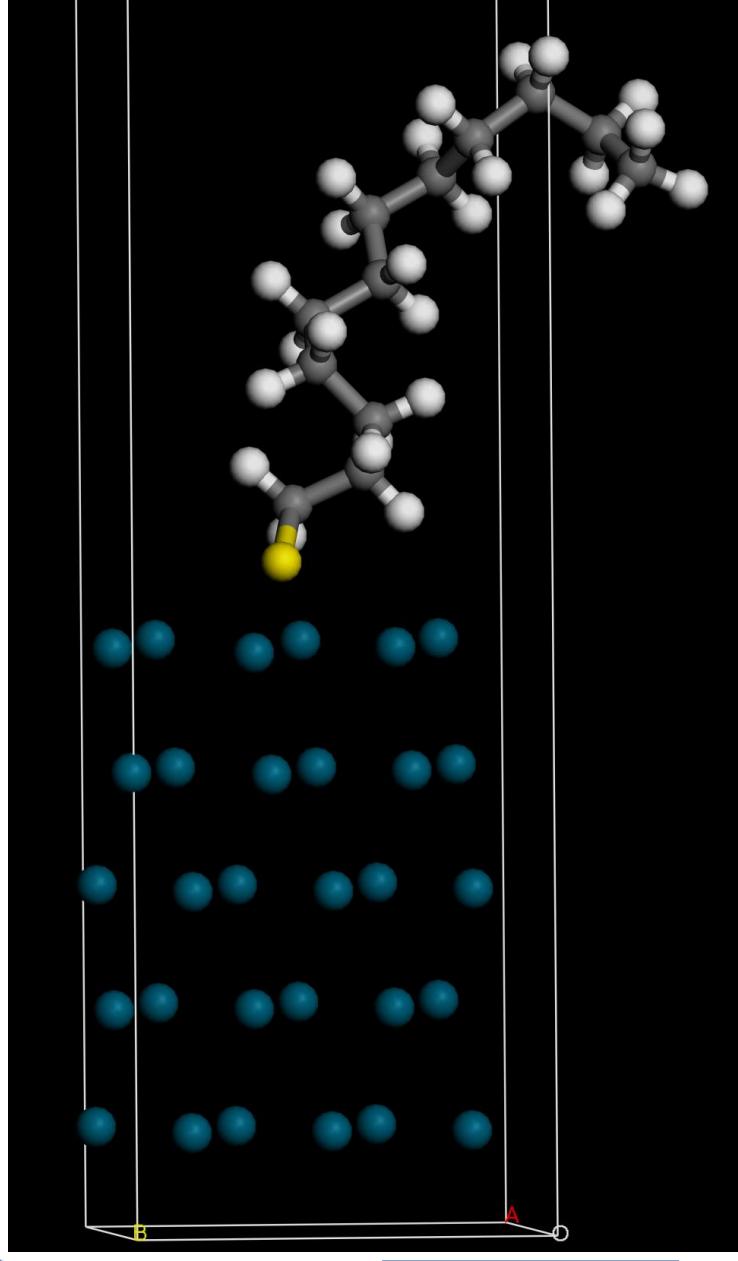
Rogers *et al*
Physical Chemistry Chemical Physics
18 (2016) 17265-17271
[doi: 10.1039/C6CP00957C]

A model system: dodecanethiol on Pd nanoparticles









Conclusions:
Dodecanethiol is chemisorbed via the S atom.
The alkyl chain is largely ordered.

Quantification by INS

$$S(Q, \omega) = \sigma Q^2 U_\omega^2 \exp(-Q^2 U_T^2)$$

In the harmonic approximation:

$$(U_\omega)^2 = \frac{\hbar}{2\mu\omega}$$

μ is reduced mass: C-H, O-H

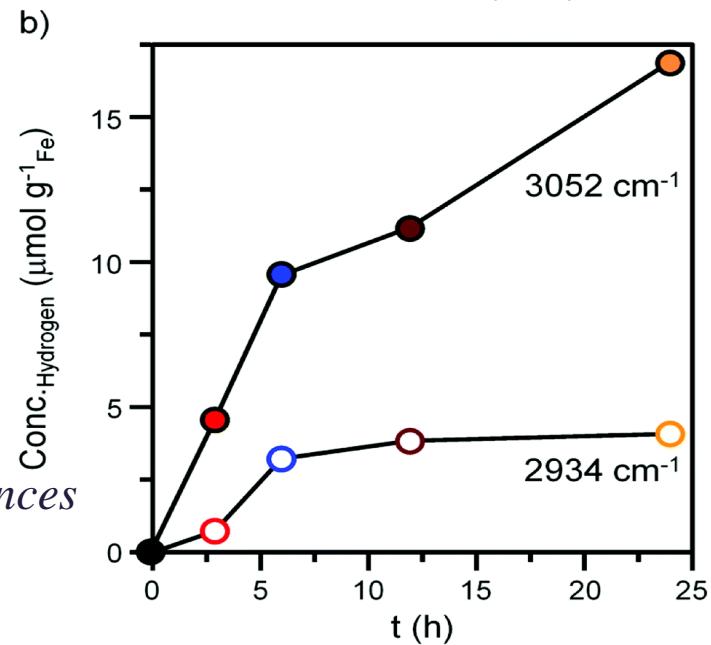
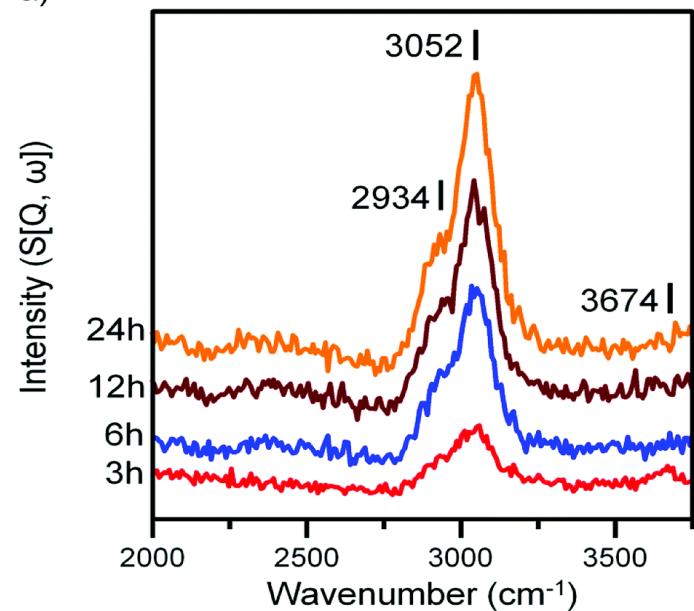
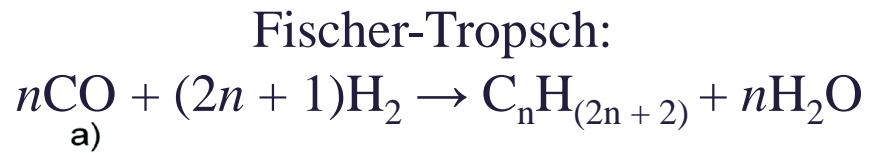
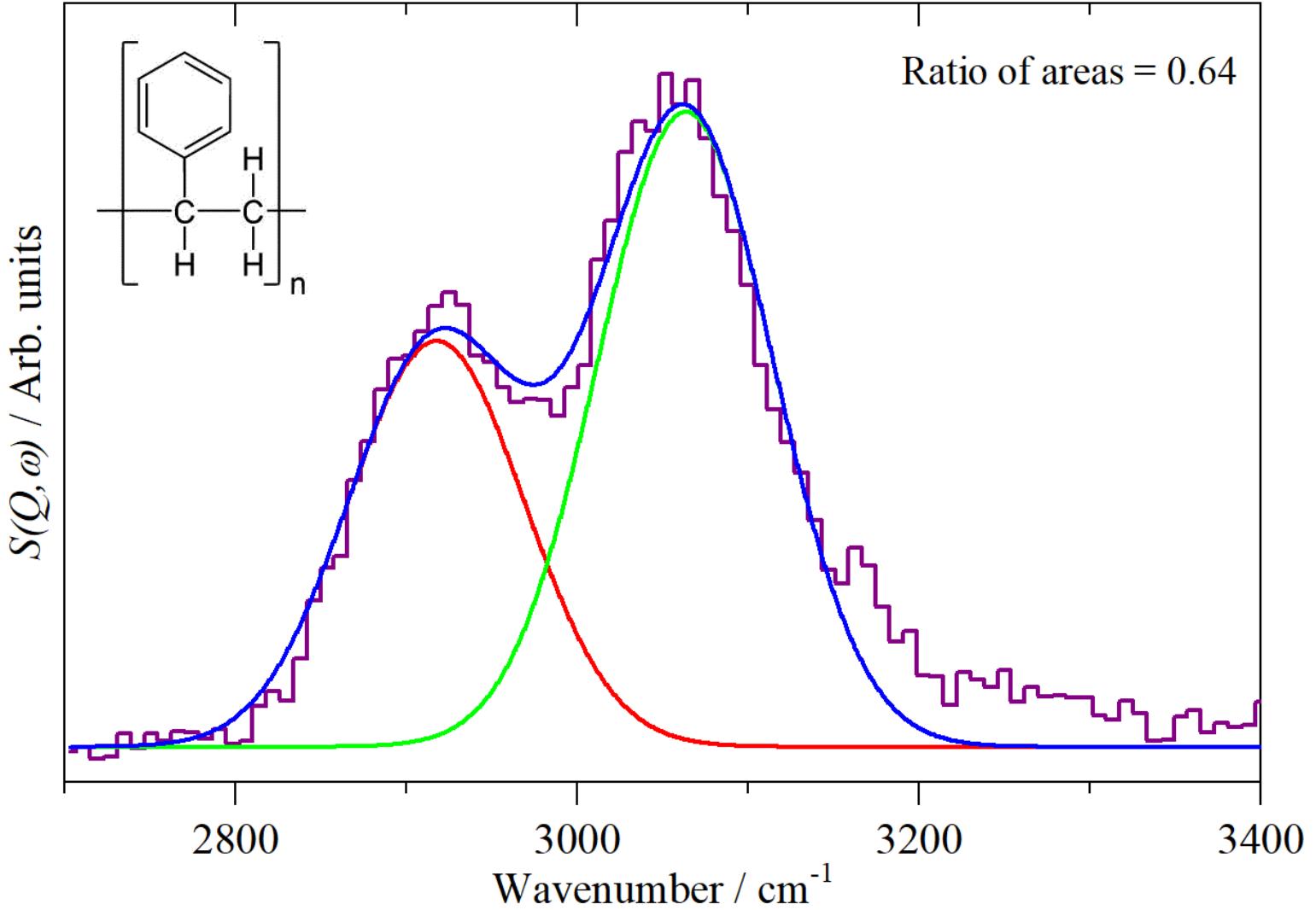
Hence U_ω is ~independent of nature of species.

We measure at small Q , to minimise effect of
Debye – Waller term.



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Warrington *et al.*, RSC Advances
9 (2019) 2608-2617
[doi: 10.1039/C8RA09731C]

INS studies of the methanol-to-hydrocarbon reaction

Stewart F. Parker; ISIS Neutron and Muon Source and University of Glasgow

Andrea Zachariou, Alexander Hawkins and David Lennon; University of Glasgow

Paul Collier; Johnson Matthey Technology Centre

Russell Howe; University of Aberdeen

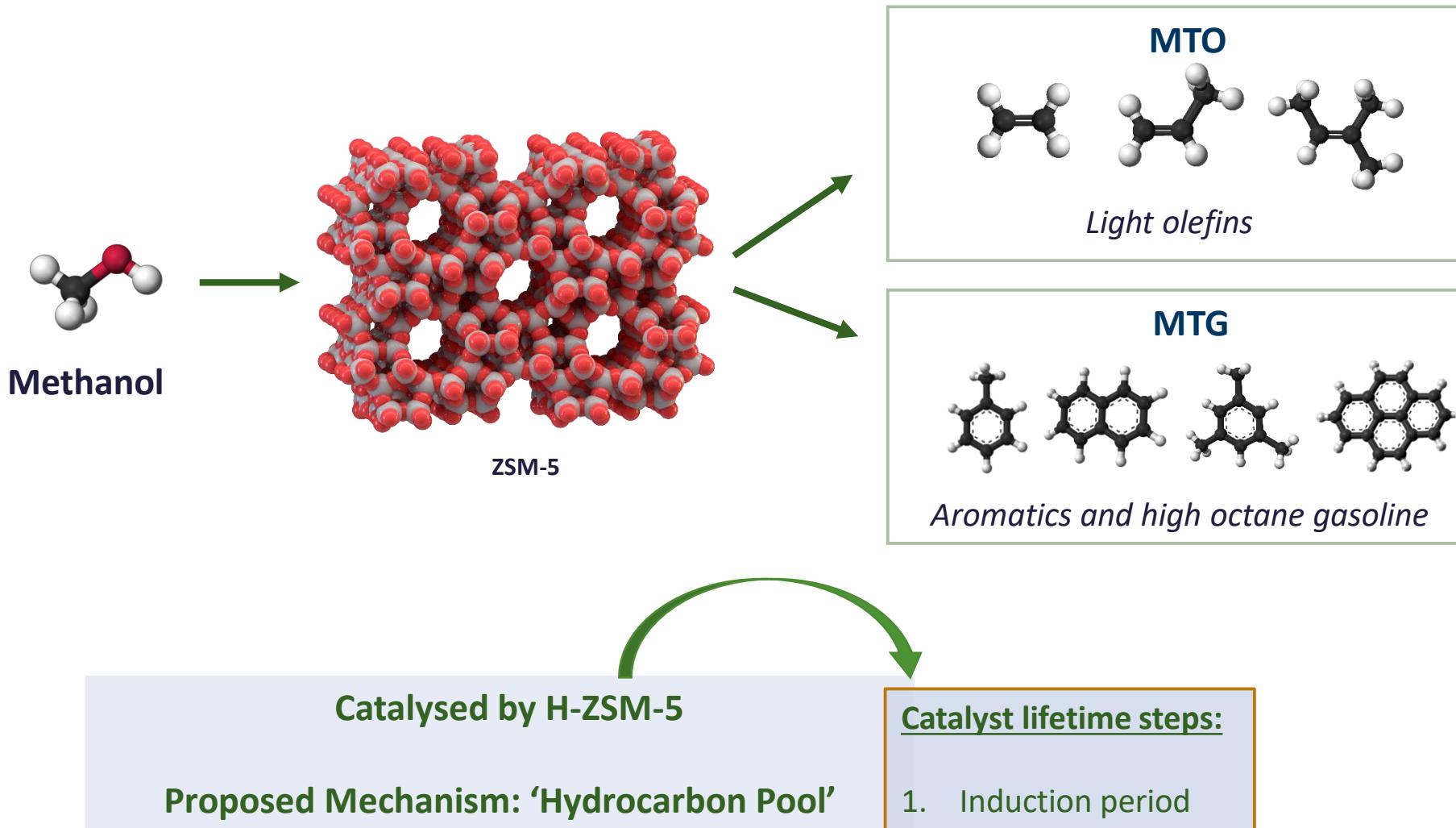
Suwardiyanto; Jember University, Indonesia



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Methanol-to-Hydrocarbons



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Li, Y.; Zhang, C.; Li, C.; Liu, Z.; Ge, W. *Chem. Eng. J.* **2017**, *320*, 458–467.

Howe, R. F.; McGregor, J.; Parker, S. F.; Collier, P.; Lennon, D. *Catal. Letters* **2016**, *146* (7), 1242–1248.

Howe, R. F.; Richard Catlow, C. A.; Gibson, E. K.; Hameed, A.; McGregor, J.; Collier, P.; Parker, S. F.; Lennon, D. *Faraday Discuss.* **2017**

Experimental

Sample	Temperature	MeOH	Total MeOH	He Flow	Duration	WHSV
	°C	g/g _{cat}	ml	ml/min	Hours	h ⁻¹
MTH-350-2h	350	1	30	150	2	0.99
MTH-350-4h	350	1	60.75	150	4	0.99
MTH-350-110h	350	1	1661.5	150	110	0.99
MTH-300-2h	300	1	30	150	2	0.99
MTH-300-60h	300	1	901.25	150	60	0.99
MTH-400-2h	400	1	32	150	2	1.45
MTH-400-44h	400	1	658	200	44	0.99

Online Analysis:

- Mass Spectrometer: *Hiden Analytical, HPR-20*
- Gas chromatography: *Agilent GC*
- (Coming: *UV-vis and Raman*)

Offline Analysis:

- Catchpot GC-MS: Agilent

Catalyst Analysis

- INS Spectroscopy: TOSCA and MAPS
- TGA: TA Q50
- DRIFTS: Agilent Carry 660
- BET: Quantachrome Quadrasorb EVO/SI

The ISIS/ Glasgow Catalysis Rig



ZSM-5 zeolite used was a commercial catalyst grade supplied in powder form by Johnson Matthey.

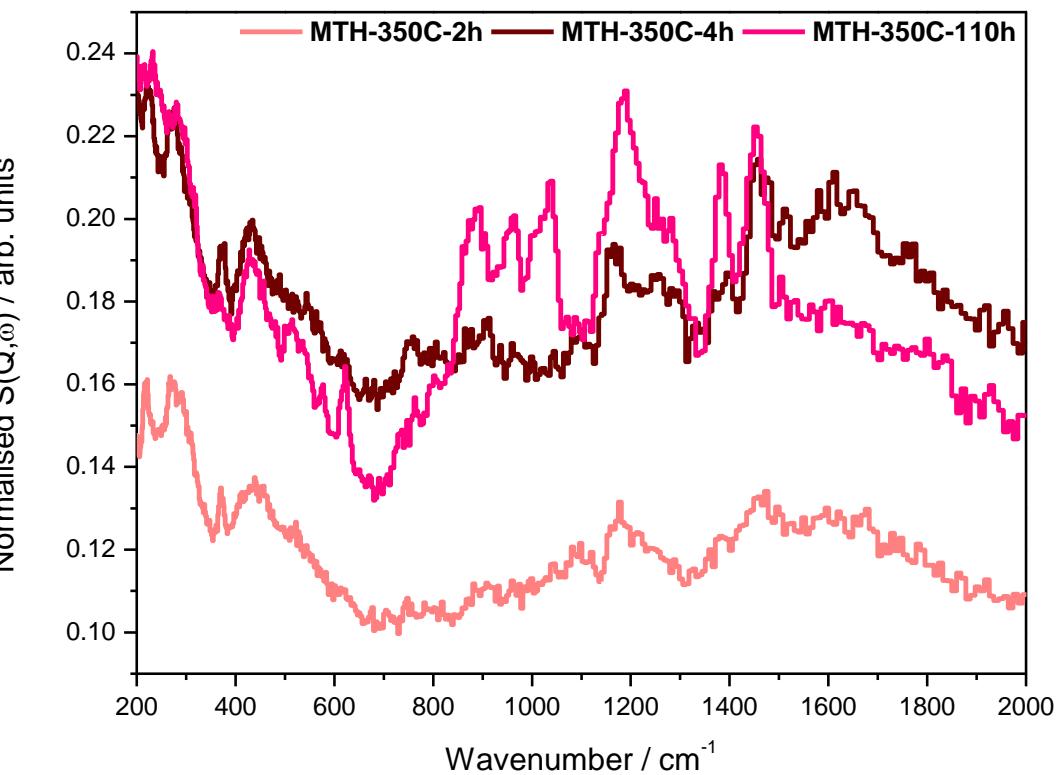


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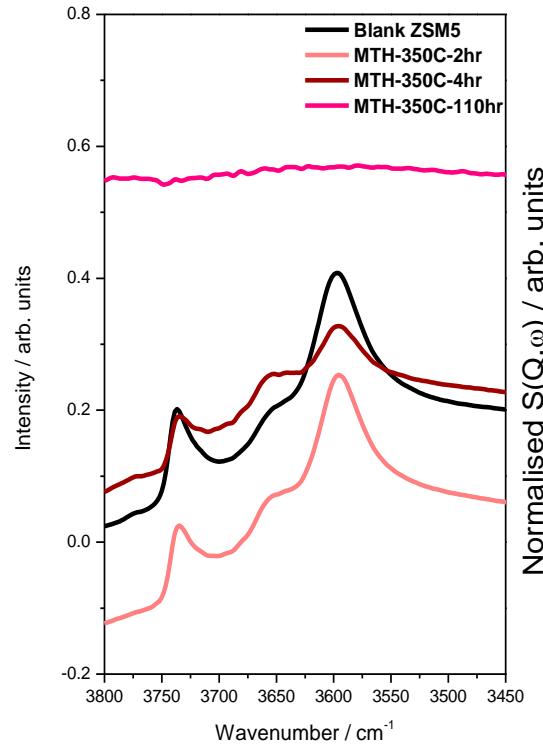
INS Spectra: TOSCA

*INS of catalyst reacted at 350°C for different periods of time.
Graph shows the evolution of the hydrocarbon pool with
increasing time-on-stream.*

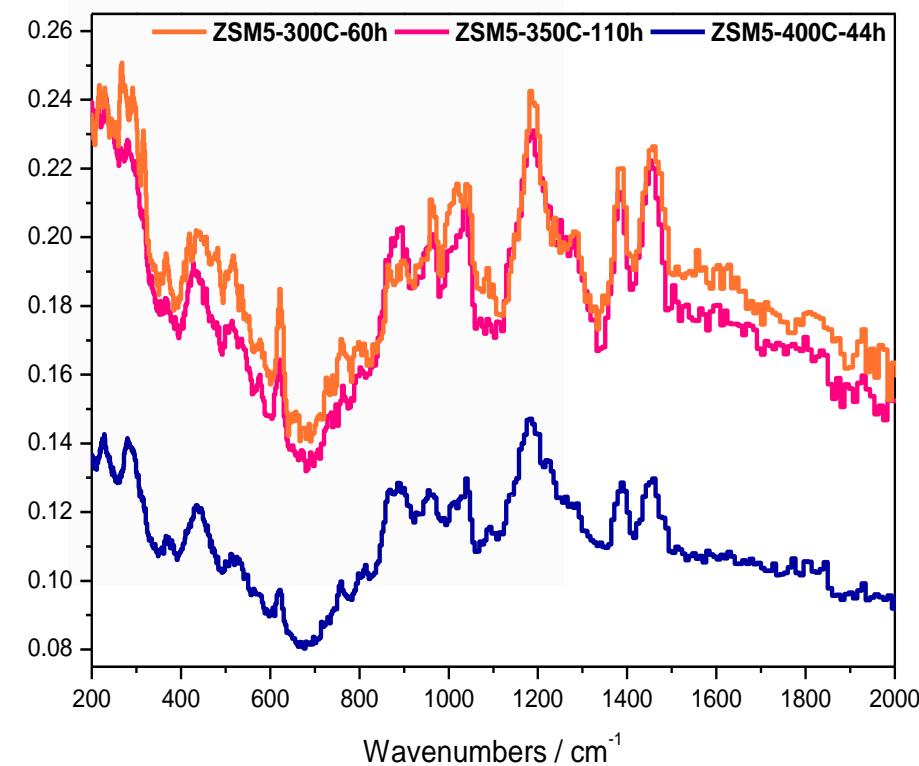


DRIFTS

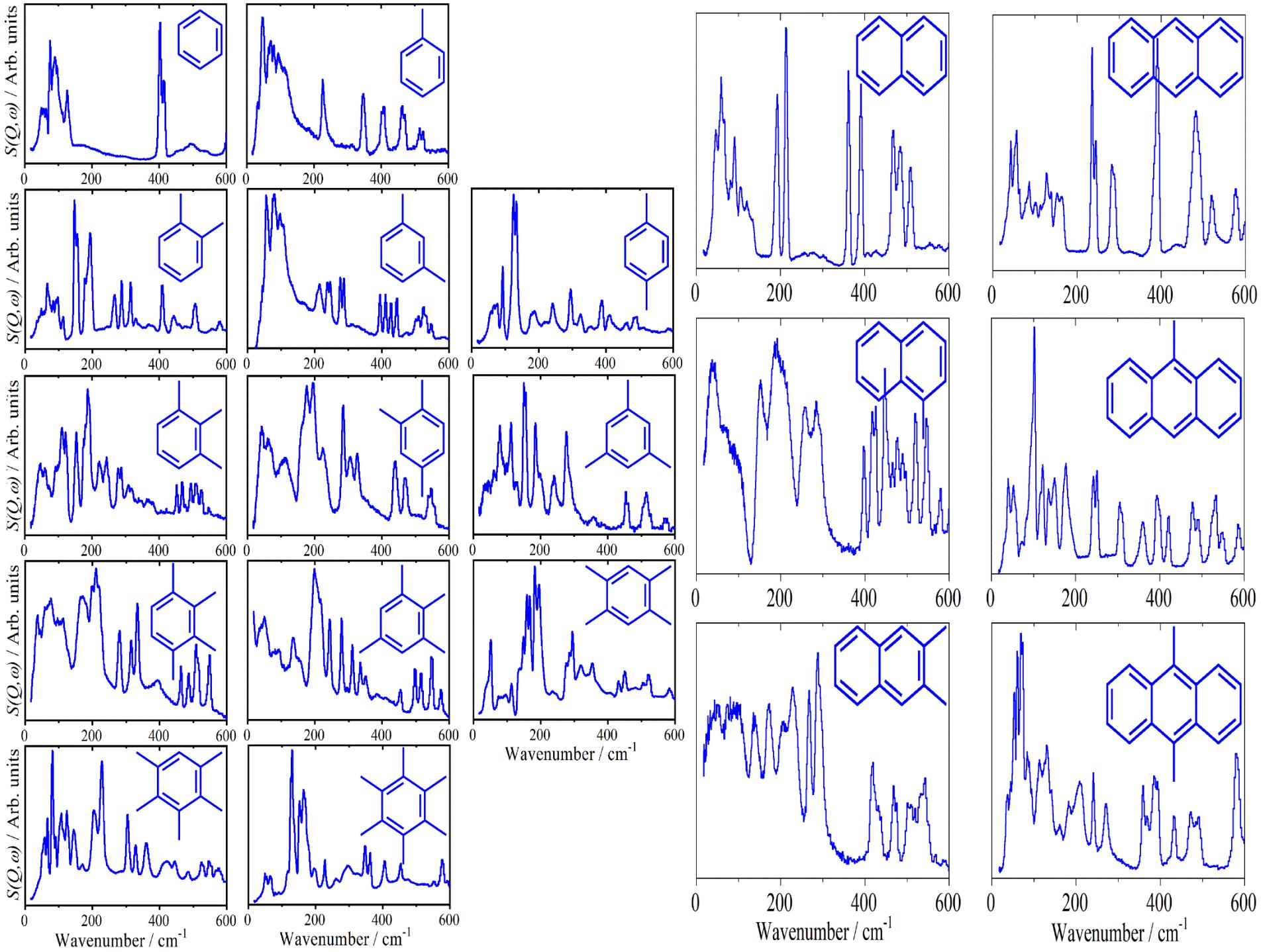
*Complete loss of active sites
with deactivation.*



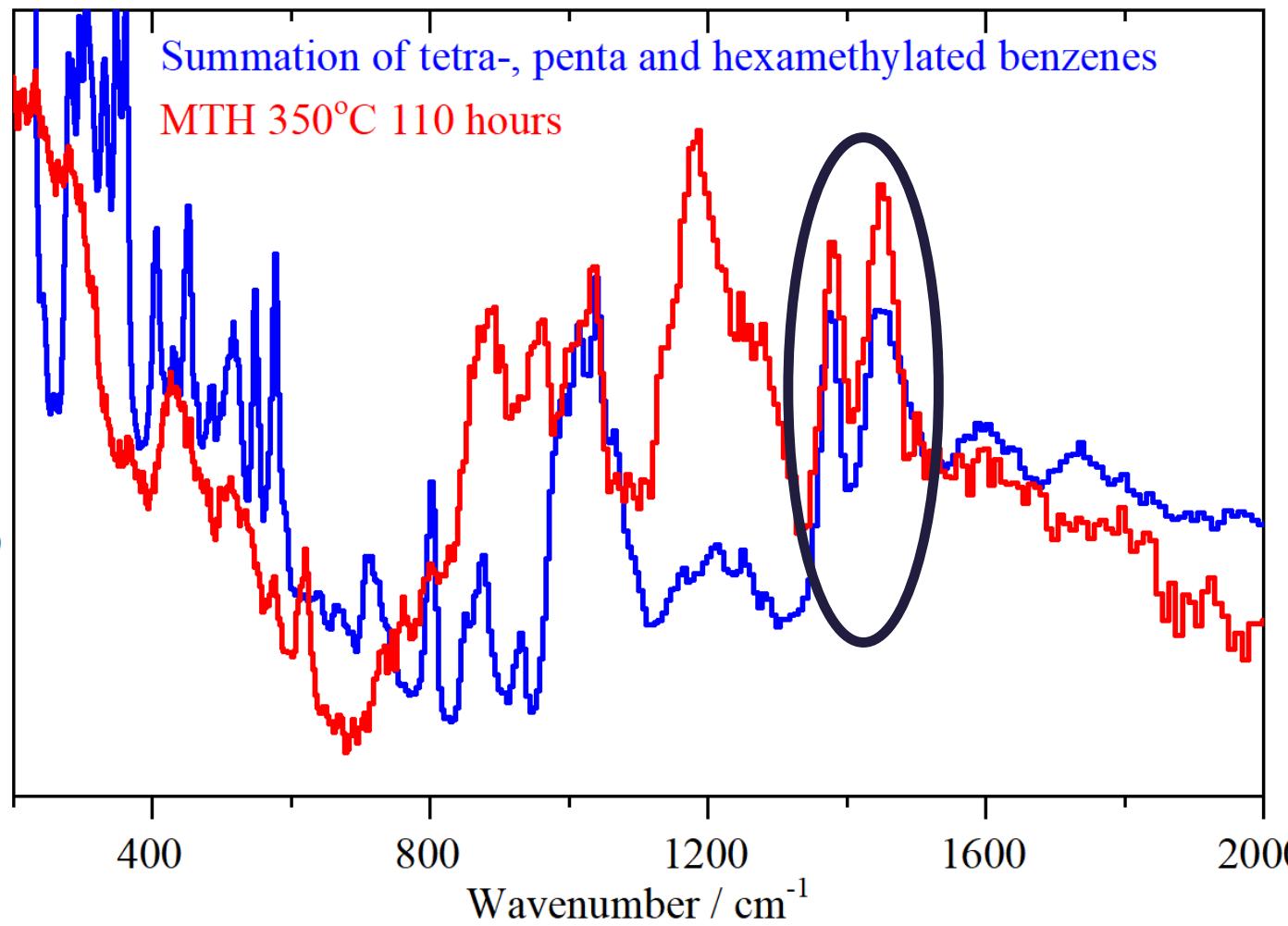
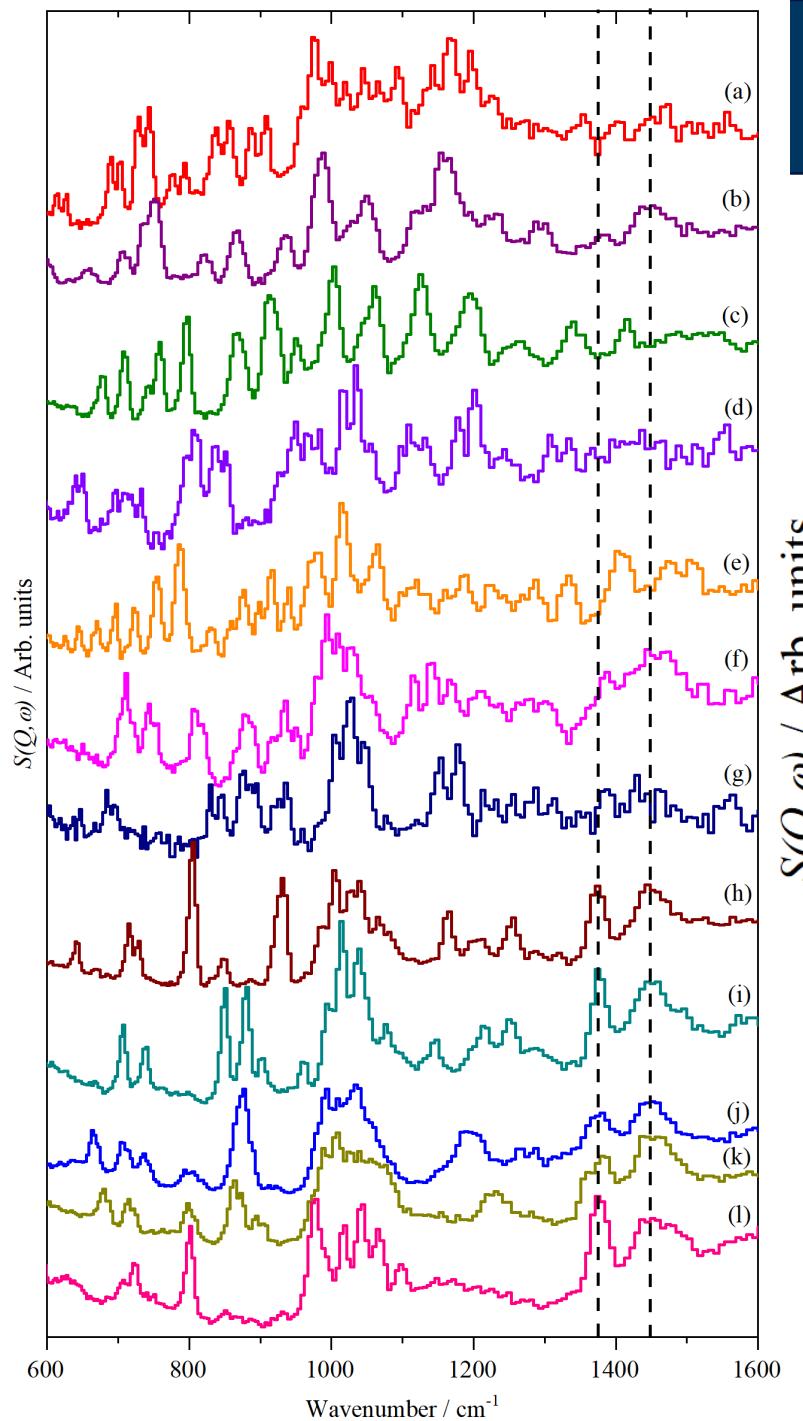
INS Spectra: TOSCA



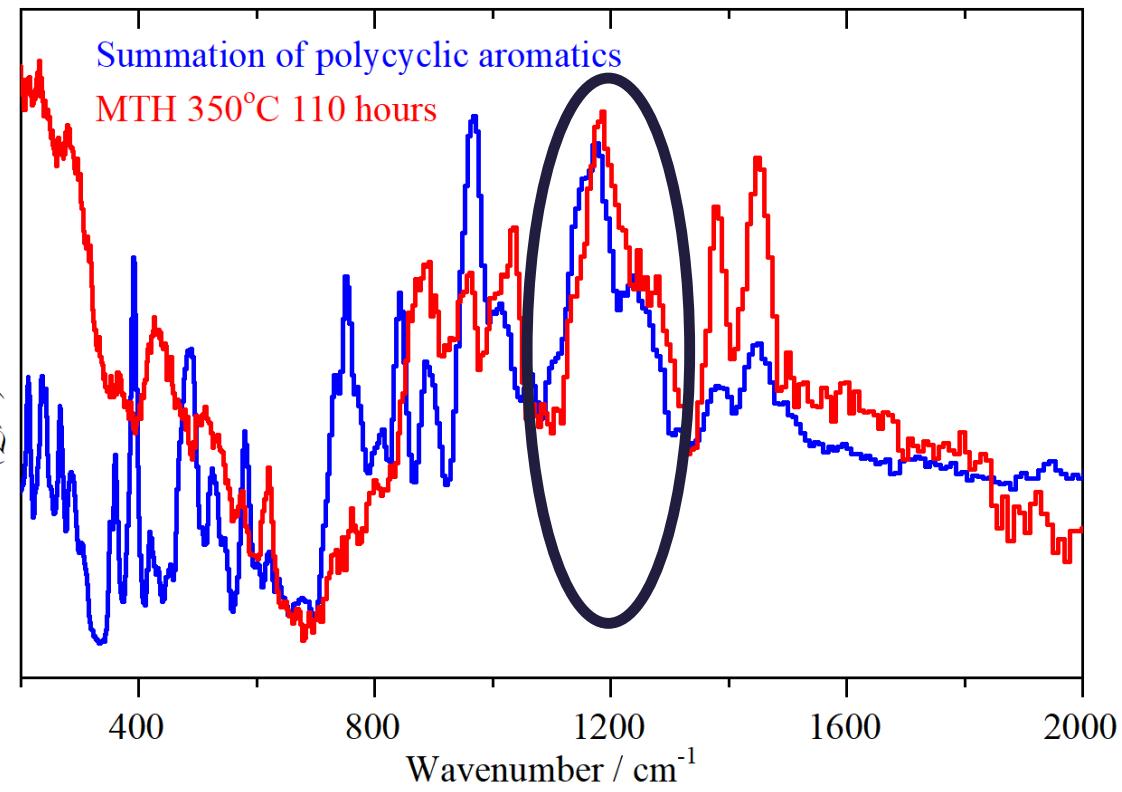
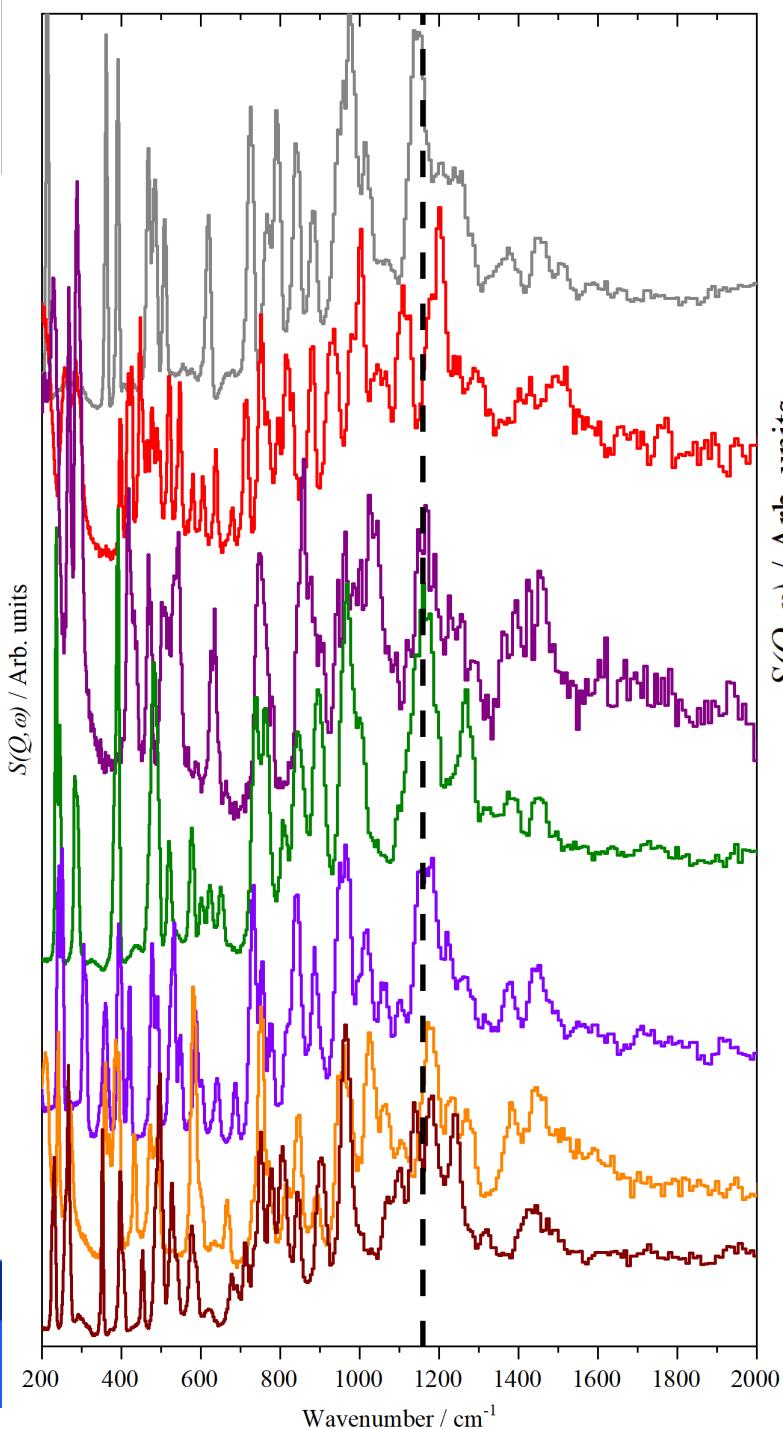
**This is the “fingerprint”
of the hydrocarbon pool**

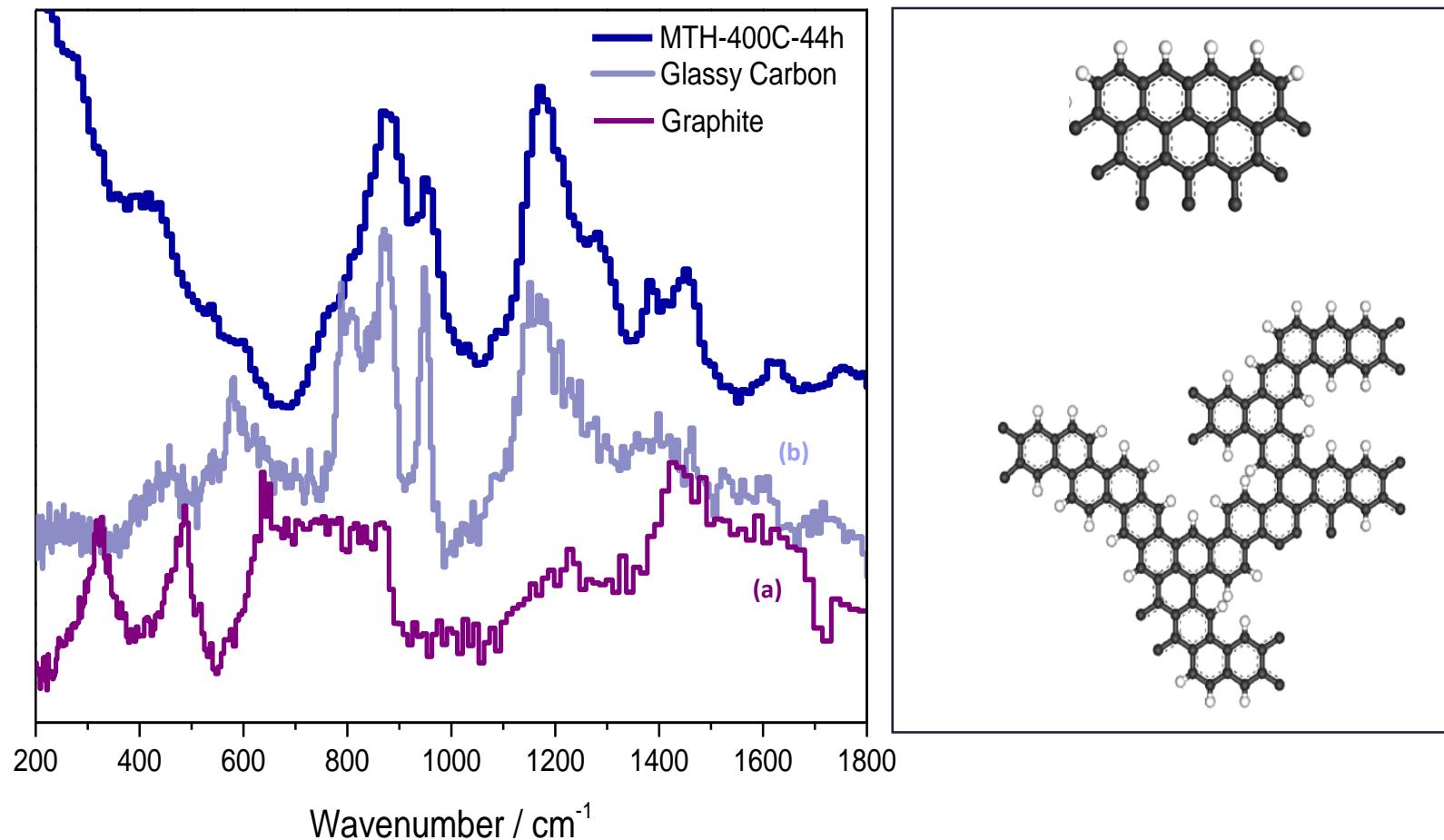


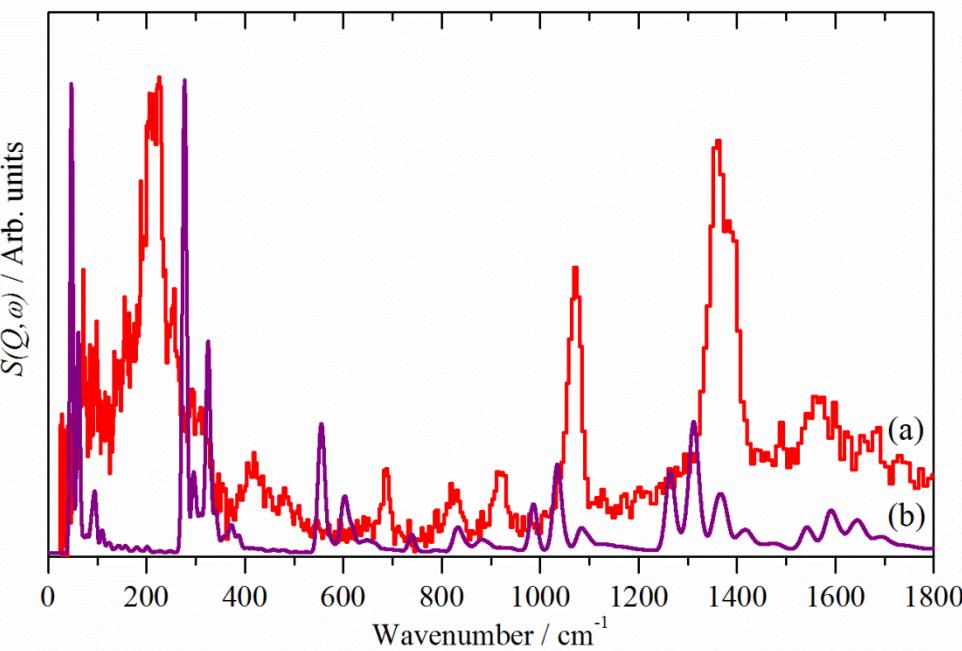
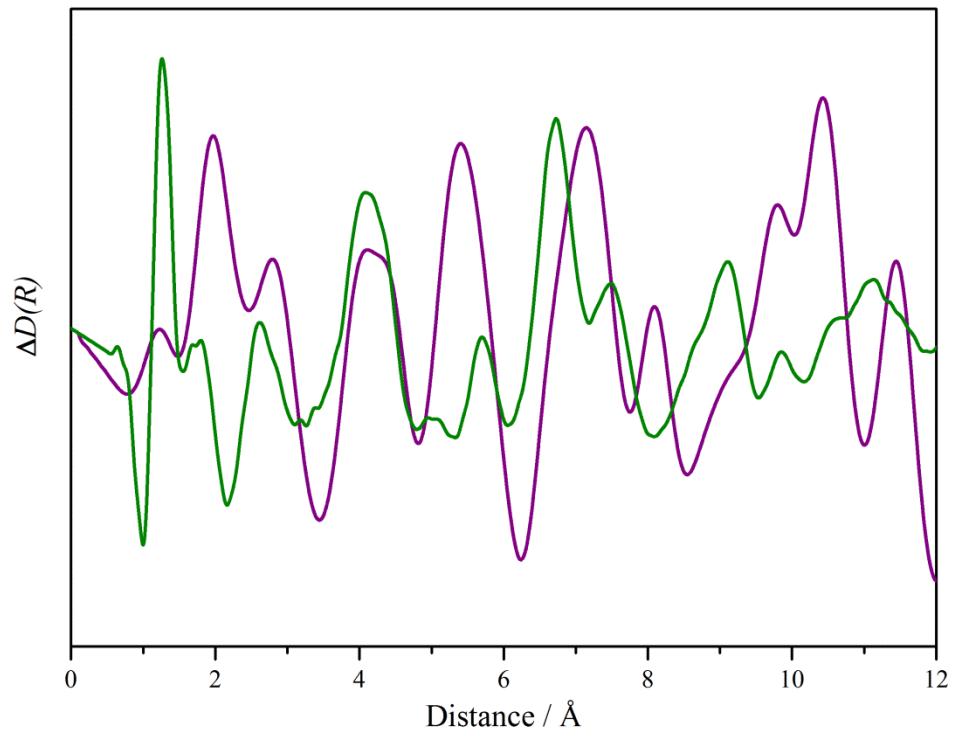
Assignments 1



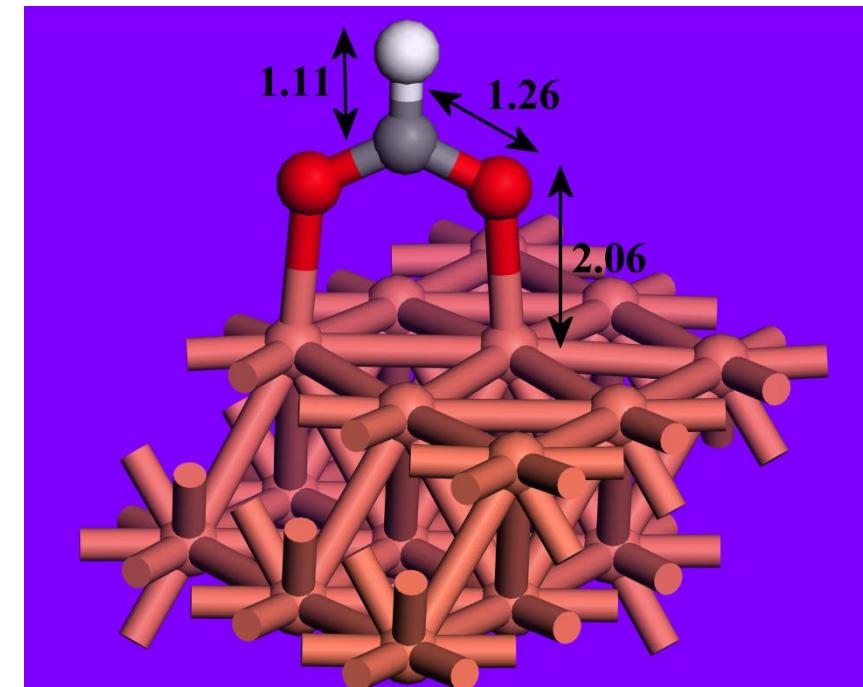
Assignments 2



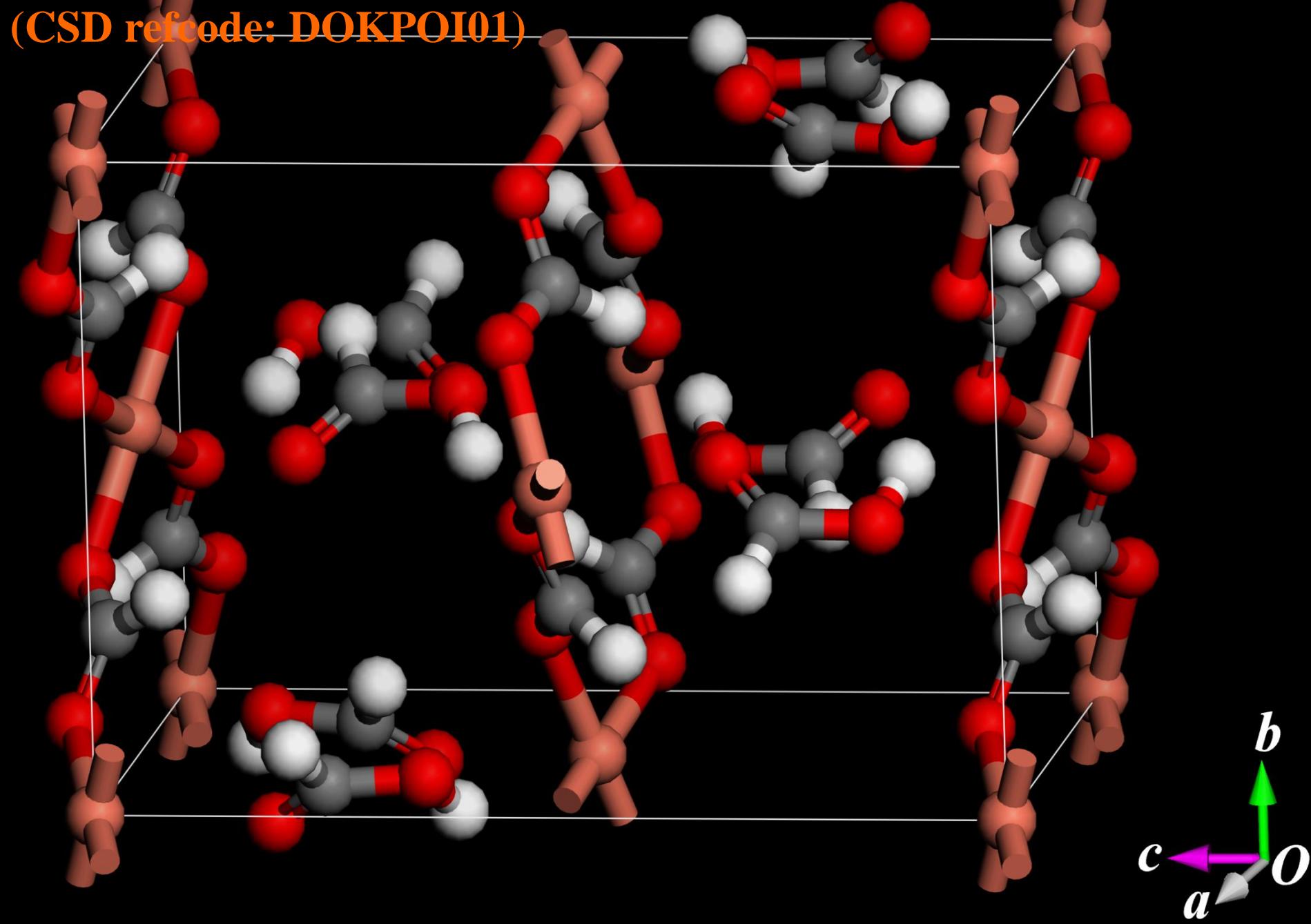


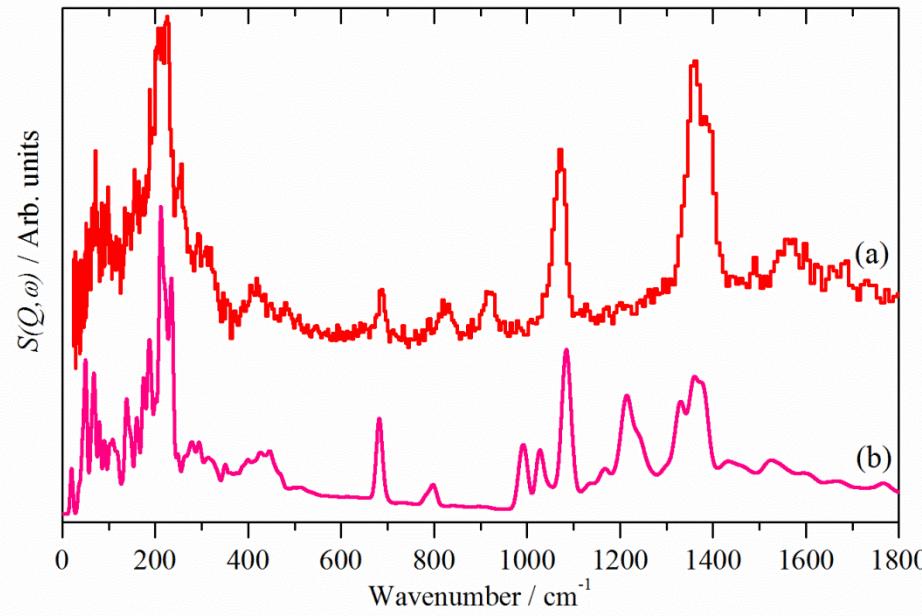
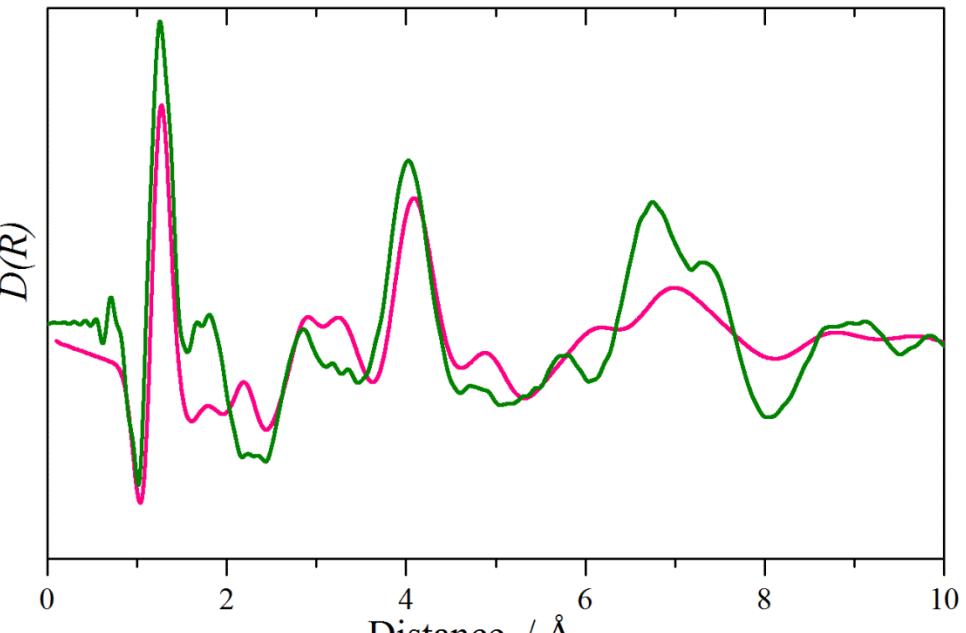
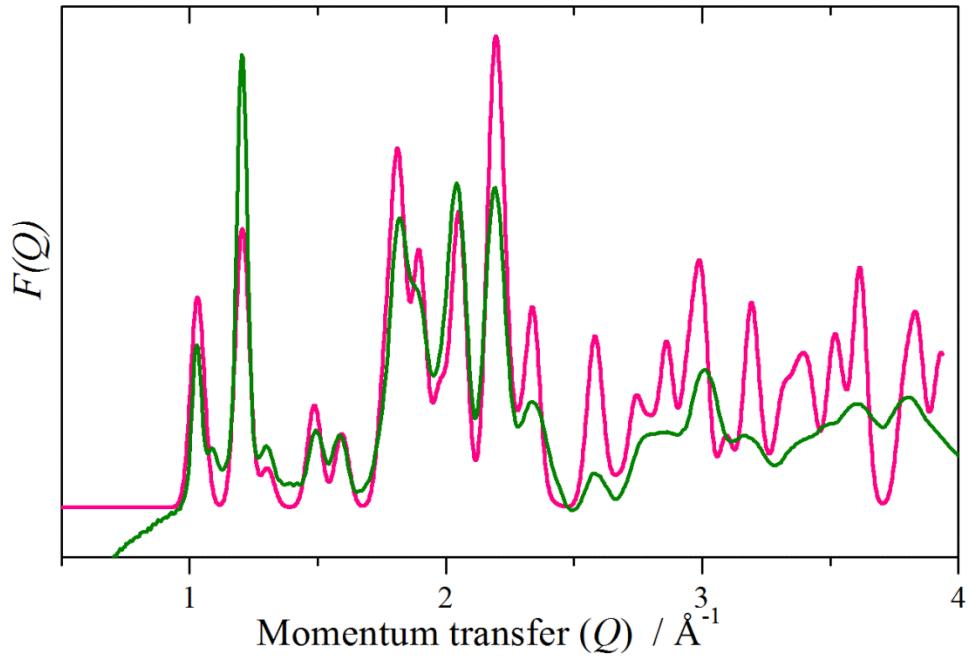


Formate on copper:
a cautionary tale!
Callear et al,
Proc. Royal Soc. A,
472 (2016) 20160126



Catena-(μ^2 -formato-O,O')-bis(formic acid-O)-copper(II)
(CSD refcode: DOKPOI01)





$4n \text{ HCOOH} + n\text{Cu} \rightarrow$
 $[\text{Cu}(\text{HCOO})(\text{HCOOH})]_n + n\text{H}_2$
 A rare example of formic acid
 acting as an oxidant rather than,
 as more commonly found, as a
 reductant.
 The direct reaction between
 copper and formic acid at room
 temperature to yield DOKPOI01
 is unprecedented.

Summary

- Vibrational spectroscopy with neutrons provides access to hydrogen-related properties of materials. Non-hydrogenous require more sample and more patience!
- Hydrogenous surface species on nanoparticles are readily observable.
- Access to the complete “mid-infrared” $0 – 4000 \text{ cm}^{-1}$ is a major advantage.
- Neutron scattering in combination with *ab initio* methods enables an in-depth understanding of materials. Systems with long-range order are (usually) tractable, the challenge is to be able to treat disordered and/or nanoparticulate systems with the same rigour.

Thank you



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