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Synchrotron Infrared Spectroscopy of Microporous Materials

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Cover Page Footnote

The author's work with synchrotron infrared spectroscopy was a collaborative project with Professor Paul Wright's group at the University of St. Andrews. Students and postdoctoral fellows involved include Dr. Alex Greenaway, Dr. A. Lorena Piccone, Eike Eschenroeder, Alessandro Turrina, and David Price. The Diamond Light Source is acknowledged for providing beam time on BM22, and the work would not be possible without the support of the beam line staff of Dr. Gianfelice Cinque and Dr. Mark Frogley.

Synchrotron Infrared Spectroscopy of Microporous Materials

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Abstract

This review describes the ways in which synchrotron infrared radiation can be used to perform infrared spectroscopy on catalyst materials. The enhanced brightness of the synchrotron source over a conventional laboratory source allows for microspectroscopy to be performed on single crystals of microporous materials down to 10 microns in size. A second application was performed in the far-infrared region, which is generally difficult using laboratory instruments. The review presents typical results from both areas and discusses future prospects.

Abstrak

Spektroskopi Inframerah berbasis Sinkrotron untuk Material Mikropori. Review ini menjelaskan bagaimana radiasi inframerah sinkrotron dapat digunakan untuk melakukan spektroskopi inframerah pada bahan katalis. Peningkatan kekuatan cahaya (*enhanced brightness*) dari sumber sinkrotron terhadap sumber cahaya pada laboratorium konvensional memungkinkan mikro-spektroskopi dapat dilakukan pada kristal tunggal dari bahan mikropori sampai ke ukuran 10 mikron. Aplikasi kedua dilakukan di wilayah inframerah-jauh, yang umumnya sulit dilakukan menggunakan instrumen laboratorium. Review ini menampilkan hasil khas dari kedua bidang tersebut dan membahas prospek masa depan dari mikro-spektroskopi inframerah.

Keywords: catalysts, infrared microspectroscopy, microporous materials, synchrotron, terahertz spectroscopy

Introduction

Infrared spectroscopy is a familiar technique used for the characterisation of catalysts, the observation of adsorbed species, and more recently, in-situ operando studies of reaction pathways [1]. Spectra are typically recorded either by transmission through pressed disks of catalyst or by diffused reflectance from a bed of catalyst powder. In both modes of operation, reaction cells are available, which allow samples to be heated in vacuo or in flowing gas streams and spectra to be obtained at elevated temperatures under in-situ conditions.

Infrared microspectroscopy uses a microscope fitted with reflective objective and condenser lenses to focus the infrared beam from an FTIR spectrometer onto a sample and collect either the reflected or transmitted radiation. The actual area sampled is defined by a set of adjustable apertures. The smallest sample size that can

be measured is limited to about 5 microns due to diffraction effects. In practice, signal to noise considerations limit the spatial resolution achievable with a conventional laboratory FTIR spectrometer to about 20 microns, and several scans must be averaged to obtain a spectrum of reasonable quality.

Several groups have nevertheless used the method to measure spectra of single crystals of zeolites and related materials. One attraction of this experiment is the possibility of using polarised infrared radiation to observe the orientations of molecules adsorbed within the pores of a single crystal, by measuring spectra with different angles of polarisation relative to the crystal axes [2]. Such information cannot be gained from a conventional measurement on a polycrystalline sample. It is however a slow experiment with measurement time dictated by signal to noise.

A second type of infrared experiment that is very much limited by signal to noise with a conventional spectrometer is far infrared or terahertz spectroscopy (below 500 cm^{-1}). Conventional infrared sources and detectors have a low efficiency in the far infrared region, and there are only a few reports of successful far infrared measurements on zeolites or other heterogeneous catalysts [3].

IAs discussed further below, infrared radiation from a synchrotron source can be 2 or 3 orders of magnitude brighter than a conventional laboratory infrared source. This increased intensity means that infrared microspectroscopy can be done on smaller samples and much more quickly than was possible with laboratory infrared microscopes [4], and that far infrared spectroscopy also becomes much more user friendly.

This review presents examples of both types of experiments and illustrates the advantages of using synchrotron infrared spectroscopy for studies of microporous materials as catalysts or adsorbents.

Synchrotron infrared radiation. Synchrotron radiation is produced when relativistic electrons (or positrons) are accelerated radially. This radiation comprises all components of the electromagnetic spectrum (Figure 1). More than 40 synchrotron light sources have now been developed around the world. Historically, the X-ray region was first exploited in the 1970s, and X-ray beam lines for diffraction, scattering, and imaging still dominate most synchrotrons. The first demonstration of infrared spectroscopy using a synchrotron as the infrared source was at the BESSY synchrotron in Germany in 1985. Since that time, many synchrotrons have been equipped with dedicated infrared beam lines. The synchrotron provides an almost point source of radiation in contrast to a conventional black body laboratory source. This results in a dramatic enhancement in brightness. In infrared microspectroscopy, the higher brightness gives

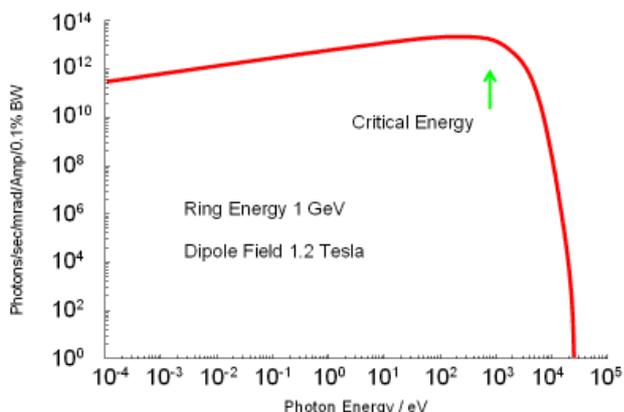


Figure 1. Typical Radiation Output Curve from a Synchrotron

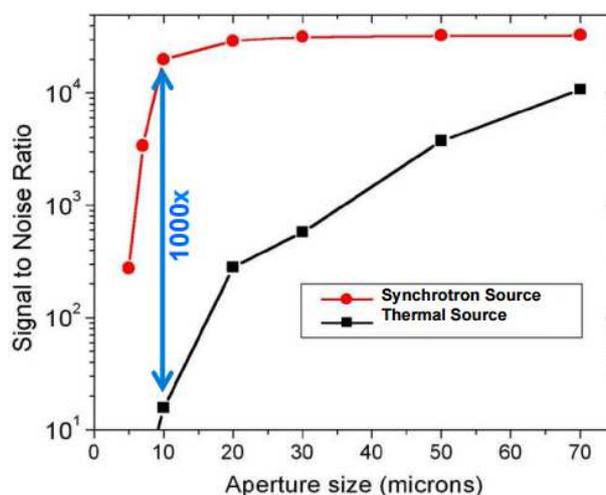


Figure 2. Comparison of Signal to Noise Ratios from a Conventional Laboratory Infrared Microscope and a Synchrotron Infrared Microscope in the Mid Infrared Region as a Function of Aperture Size (adapted from Reference)

a large improvement in signal to noise, particularly at smaller aperture sizes. Figure 2 illustrates this (taken from reference [5]). In the mid infrared region, the advantage of synchrotron radiation is much less at large apertures.

The author's research uses beam line B22 at the Diamond Synchrotron in the UK. The measured brightness advantage of this source over a theoretical black body source at 1500 K is ~ 100 in the mid infrared region but increases to ~ 1000 in the far infrared region (where a black body source loses intensity).

Actual performance improvements achieved in practice depend on the designs of the particular beam line and spectrophotometer used. Nevertheless, the expansion in the number of infrared beamlines worldwide shows that the benefits of using synchrotron radiation for infrared spectroscopy are widely recognised.

Infrared microspectroscopy of microporous materials.

The research focused on three applications of microspectroscopy using synchrotron radiation: the characterisation of single crystals of novel zeolites, investigation of CO_2 uptake in metallo-organic frameworks, and investigation of ZSM-5 zeolite single crystals as catalysts for the conversion of methanol to hydrocarbons. For the experiments, a commercial (Linkam) in-situ cell was used, which allowed samples to be heated in flowing helium or other gases up to $500\text{ }^\circ\text{C}$ while spectra were recorded.

Figure 3 shows polarised spectra measured during the in-situ calcination of a copper containing silico-

aluminophosphate zeolite, STA-7 [6]. This material was synthesised in the presence of two template molecules: tetraethyl ammonium and a copper cyclam complex [7]. Infrared microspectroscopy on single crystals ~ 20 microns in size allowed us to follow the process of template removal in flowing air as a function of temperature. This calcination process is necessary to generate an active catalyst for NO_x reduction [7]. By using polarised radiation, the orientation of molecules within the zeolite pores can also be examined.

The spectrum measured at 100 °C showed a broad band ~ 3600 cm⁻¹ due to adsorbed water, an N-H stretching band at 3240 cm⁻¹ due to the cyclam ligand, and C-H stretching bands ~ 3000 -2800 cm⁻¹ due to both the cyclam and the tetraethyl ammonium cations. The N-H band was strongly polarised; it showed a maximum intensity when the radiation was polarised parallel to the c-axis of the crystal (solid trace) and almost zero intensity when the radiation was polarised perpendicular to the c-axis (dotted trace). This indicates that the N-H bonds are oriented close to parallel to the c-axis. There were no obvious polarisation effects in the C-H bands, which is consistent with a random orientation of the tetraethyl ammonium template. As the crystal was heated to higher temperatures, the bands of adsorbed water were lost, and the N-H band broadened and became less polarised, while the C-H bands were unchanged. At up to 250 °C, these changes were completely reversible; cooling to room temperature in air restored the original spectrum. The spectral changes are completely consistent with molecular modelling

calculations, which show that loss of water molecules coordinated to the copper cyclam complex causes a relaxation of the planar structure of the complex.

Heating above 250 °C causes the gradual and irreversible decomposition of both templates, and the N-H and C-H bands of the cyclam and the tetraethyl ammonium cation were progressively lost. The decomposition produced Cu²⁺ cations and protons to balance the negative charge of the zeolite framework, and a strong O-H stretching band (actually a closely spaced doublet) appeared. Thus, there were no polarisation effects, indicating that the OH groups were randomly oriented throughout the crystal.

These in-situ infrared microspectroscopic measurements have given new insights into the structure of the as-synthesised catalyst and the processes that occurs when the catalyst is active by high temperature calcination. Due to the short data collection times (~ 1 minute per spectrum), information is gathered in a much shorter time than is possible with other techniques.

A second example is the use of infrared microspectroscopy to measure carbon dioxide adsorption in single crystals of a microporous metallo-organic framework (MOF) material. Physical adsorption of carbon dioxide into microporous solids is being widely explored as an attractive method for sequestering carbon dioxide from exhaust gas streams or from fuel gas prior to combustion [8]. The usual method of evaluating the

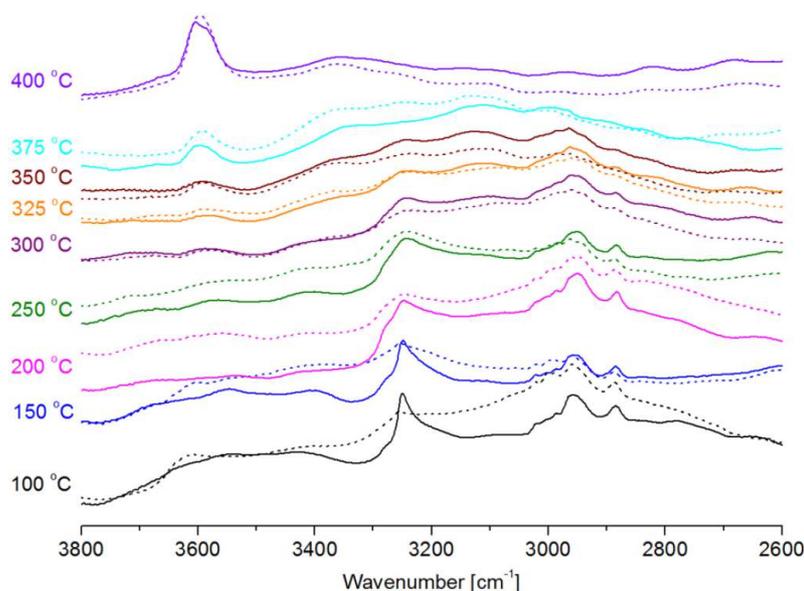


Figure 3. Sequence of Polarised Infrared Spectra Obtained from a Single Crystal of Cu-STA7 Heated in Flowing Air Sequentially from 100 to 400 °C. Solid Lines are Measured with Polarisation Parallel to the Crystal c-axis; Dotted Lines Perpendicular to the c-axis. (Reproduced with Permission from Reference)

performance of a solid adsorbent for carbon dioxide adsorption is to measure adsorption isotherms as a function of temperature either in a gravimetric microbalance or chromatographically. In both methods, relatively large amounts of a sample are employed, and a full set of data requires several days of measurement to achieve equilibrium at each partial pressure and temperature. A further limitation of such measurements is that carbon dioxide uptake in the presence of competing gases (conditions that would typically exist in a practical gas separation) cannot be easily determined.

It has recently been shown that infrared microspectroscopy on individual crystals of an MOF carbon dioxide adsorbent can provide a full set of uptake and thermodynamic data in a few minutes. Furthermore, the spectroscopic observation of the adsorbed carbon dioxide provides direct information regarding the interaction between the carbon dioxide and the adsorbent at a molecular level, and it can be undertaken in the presence of other competing gases [9].

Figure 4 shows a set of spectra measured from one crystal of the MOF $\text{Sc}_2(\text{BDC-NH}_2)_3$ exposed to a 10% carbon dioxide in helium stream at different temperatures. The sample was equilibrated at each temperature for 5 minutes before spectra were collected (~ 1 -minute collection time). At lower temperatures, there was a strong band due to the asymmetric stretching vibration of adsorbed carbon dioxide at 2333 cm^{-1} , which is 15 cm^{-1} below the frequency of gas phase carbon dioxide. At a higher frequency, there were C-H

stretching bands of the benzene dicarboxylic acid ($\sim 3000\text{ cm}^{-1}$), and at $\sim 3500\text{ cm}^{-1}$, N-H stretching bands of the amine functional groups attached to the benzene rings in the MOF structure. The changes in the intensity of the adsorbed carbon dioxide band with temperature occurred due to the temperature dependence of the coverage; the data in Figure 4 constitute an adsorption isobar. These changes were completely reversible, and replacing the carbon dioxide stream with pure helium removed the carbon dioxide completely within a few tens of seconds, indicating a rapid diffusion of carbon dioxide in and out of the pores of the MOF.

By measuring the integrated intensity of the band due to adsorbed carbon dioxide relative to that of the N-H stretching band, relative amounts of adsorption as a function of temperature could be calculated. These calculations could be converted to an absolute scale by calibrating against a single data point measured with a gravimetric microbalance. Adsorption isobars could then be measured at different partial pressures of carbon dioxide. Figure 5 shows the data obtained. The different points shown on the graph were measured in different regions of the single crystal (see inset to Figure 4). From these data, an enthalpy of adsorption was estimated of $\sim 31\text{ kJ mol}^{-1}$, which agrees well with that previously determined for the same material from gravimetric adsorption isotherm measurements. The infrared microspectroscopic measurement was completed within several hours as compared with several days for the gravimetric data.

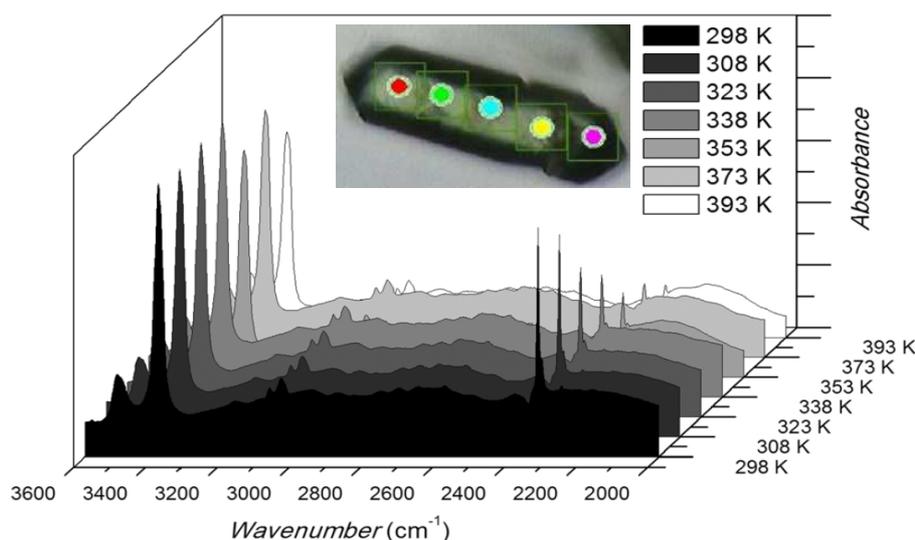


Figure 4. Infrared Spectra Measured from an Amine Functionalised Scandium Benzenedicarboxylic Acid MOF Single Crystal (Shown in the Inset) Exposed to a Gas Stream of 10% Carbon dioxide in Helium as a Function of Temperature. Spots Marked on the Crystal Show where Spectra were Measured (Reproduced with Permission from Reference)

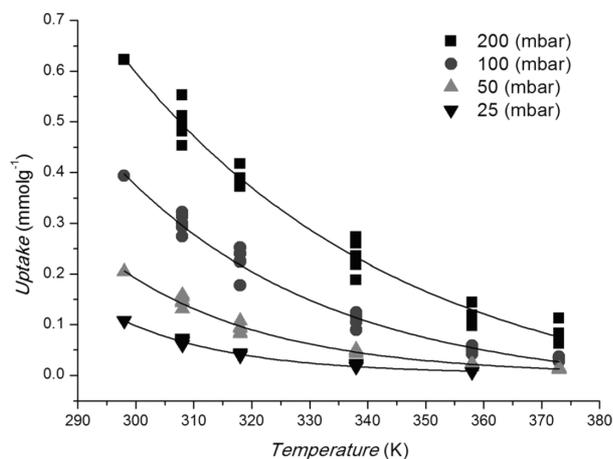


Figure 5. Adsorption Isobars Measured at Different Partial Pressures for Carbon dioxide Uptake in $\text{Sc}_2(\text{NH}_2\text{-BDC})_3$. The Lowest Temperature Point at each Pressure is a Calibration from a Gravimetric Experiment. All other Points were obtained from the Infrared Microspectra Measured from Different Spots on the Single Crystal Shown in the Inset to Figure 4 (Reproduced with Permission from Reference)

The enthalpy of adsorption in the amine functionalised MOF was $\sim 8 \text{ kJ mol}^{-1}$ higher than that in the corresponding unfunctionalised Sc_2BDC_3 MOF, suggesting that the amine groups are important in enhancing the carbon dioxide uptake. This was confirmed by the infrared microspectroscopy. The N-H stretching frequencies of the amine functionalised MOF were shifted down by $\sim 5 \text{ cm}^{-1}$ in the presence of carbon dioxide. Furthermore, polarised infrared spectra of the adsorbed carbon dioxide measured from crystals with different orientations showed that the carbon dioxide molecules were aligned approximately along the channel axes in the MOF structure and that this alignment was close to that of the N-H groups. In further work not yet published, it has been shown that adsorbed carbon dioxide can also be observed in the presence of other co-adsorbed gases, such as ethane.

The microspectroscopic method also has the potential to follow temporal and spatial variations of carbon dioxide over a single crystal and to determine adsorbate diffusivities. In the particular MOF described here, which has a relatively open pore structure, diffusion was too rapid to permit this, but it may be possible in other adsorbents with smaller pores. These initial experiments have certainly demonstrated that infrared microspectroscopy is an important new tool for investigating adsorption processes at the microscopic level.

A third example of the application of synchrotron microspectroscopy is the study of methanol conversion over single crystals of the zeolite ZSM-5. The so-called

MTG process converts methanol made from natural gas or coal into gasoline range-hydrocarbons over a ZSM-5 catalyst. The process was first introduced commercially by Mobil in New Zealand in the 1980s, utilising natural gas. More recently, plants have been constructed in China in which the methanol is produced from coal. The question of how methanol reacts over the acid zeolite ZSM-5 to produce the observed products has attracted widespread attention over the intervening 30 years (see reference [10] for a recent review). There is a clear consensus that methanol initially methylates the zeolite by replacing zeolite OH groups with OCH_3 . Dimethylether is the first reaction product detected. At higher temperatures, a so-called hydrocarbon pool is formed within the zeolite, comprising a complex mixture of adsorbed olefins and aromatics, and under steady-state working conditions, this hydrocarbon pool provides the reaction pathway for forming a high aromatic gasoline. Infrared spectroscopy has been used by a number of groups to observe species formed in the zeolite and exposed to methanol at different temperatures [11-14]. These studies have shown the formation of methoxy groups and the ability of these methoxy groups to methylate other molecules. A key mechanistic issue still unresolved is how the first carbon-carbon bonds are formed from methanol, dimethylether, or methoxy groups.

A similar chemistry occurs over the smaller pore aluminophosphate zeolite SAPO-34, but in this case, the reaction products are mostly light olefins (the so-called MTO process). A recent report [15] described conventional infrared studies of this reaction and presented evidence for the formation of methoxymethyl cations, which react with methanol or dimethylether to form the first carbon-carbon bonds. Qian et al. have used synchrotron infrared microspectroscopy (combined with UV-VIS and fluorescence microspectroscopy) to observe methanol and ethanol reactions in single crystals of SAPO-34 [16]. Their infrared spectra showed the formation of alkylated aromatics (more from methanol than from ethanol). The authors exploited the spatial resolution of the infrared microscope to show that although the acidic hydroxyl groups that are the active sites in the zeolite are distributed uniformly throughout the crystals, the alkylated aromatic species that are formed from methanol or ethanol are concentrated at the edges of the crystals. This was attributed to the higher local concentrations of methanol or ethanol in the outer regions of the crystals.

Stimulated by this intriguing microspectroscopic study we have begun an investigation of the same chemistry in single crystals of ZSM-5 [17]. In the first part of this study, the spatial resolution of the microscope was used to confirm that as in SAPO-34, the acidic hydroxyl groups are uniformly distributed throughout the crystals. Using polarised radiation, it was observed that the

hydroxyl groups were not randomly distributed throughout the crystal structure. Figure 6 shows polarised spectra from different spots on one crystal measured with radiation polarised parallel to, perpendicular to or at 45 degrees to the crystal c-axis. It is known [18] that ZSM-5 crystals of this morphology are not in fact single crystals but intergrowths of two different orientations. Both orientations have their c-axes aligned along the long axis of the crystal, but their a and b axes differing by ninety degrees. The pore structure of ZSM-5 comprises intersecting linear and zig-zag channels. The linear channels run along the direction of the b-axis, and the zig-zag channels along the a-axis. Thus, in both intergrowths, the c-axis lies

perpendicular to the channel directions. For the crystal shown in Figure 6, the 3610 cm^{-1} band, which is the O-H stretching vibration of the acid sites, had a maximum intensity when the radiation was polarised parallel to the c-axis, i.e., perpendicular to the channel directions in both intergrowths, and a minimum intensity when the radiation was polarised parallel to the channel directions. Furthermore, these polarisation effects were the same regardless of where on the crystal the spectra were measured, i.e., independent of the particular intergrowth orientation. To the authors' knowledge, this is the first demonstration that the hydroxyl groups in ZSM-5 are not randomly distributed.

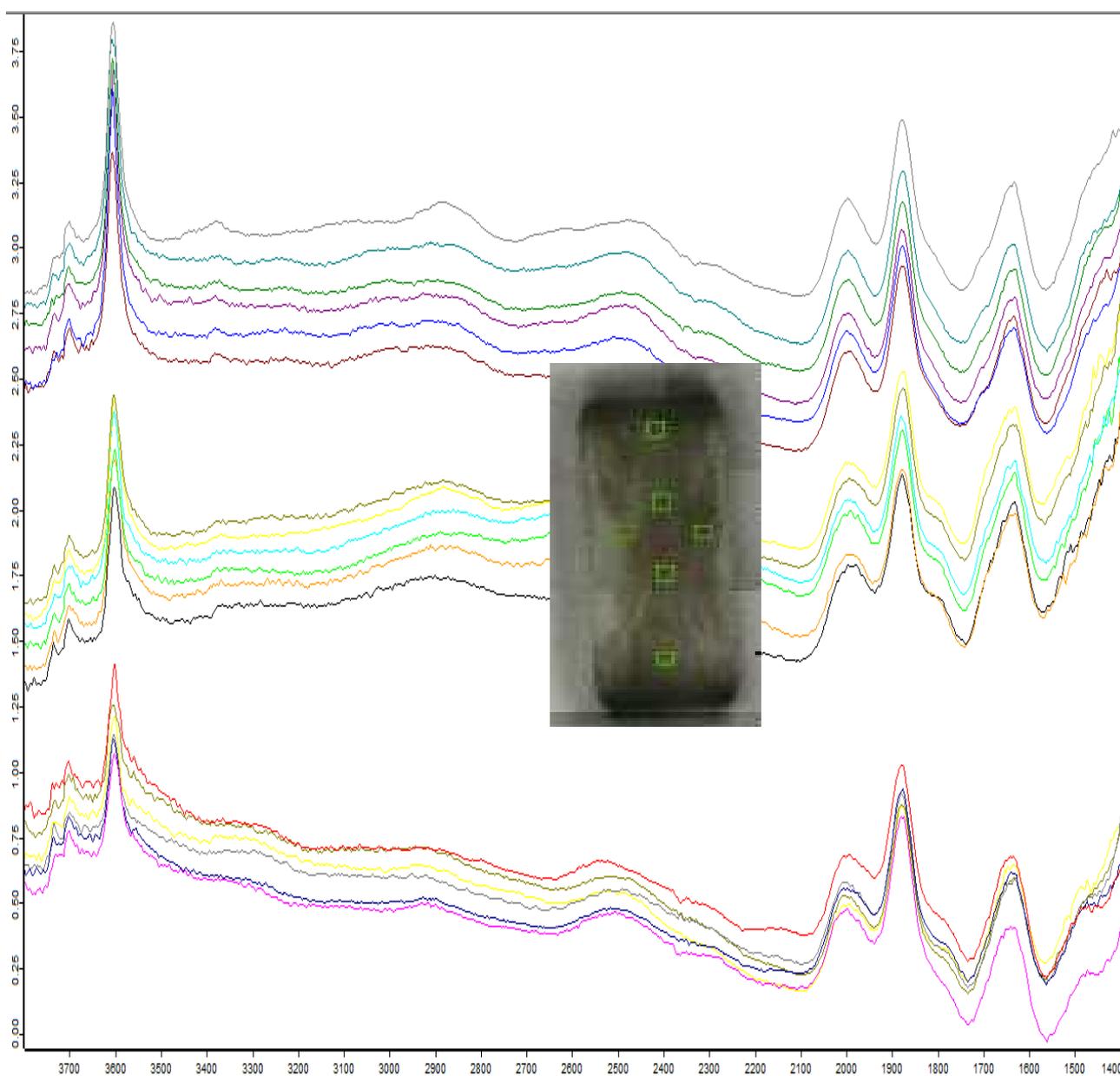


Figure 6. Polarised Infrared Spectra of a Dehydrated Crystal of ZSM-5 Measured from the Spots Shown in the Inset with Polarisation Perpendicular (Bottom), Parallel (Top) and at 45 Degrees (Middle) to the Long Axis (c-axis) of the Crystal

Space limitations in this review prevented a detailed presentation and discussion of spectra obtained when methanol or dimethylether were injected into the ZSM-5 crystals. Below 473 K, both molecules were hydrogen bonded to the acidic hydroxyl groups. Above 473 K, the methoxy groups were formed by the dissociation of the reactants. At 523 K or above, the first C-C bonds were formed, as evidenced by the appearance of C-C stretching vibrations of olefinic and aromatic hydrocarbon species as well as characteristic C-H stretching vibrations of these. An unexpected consequence of the brightness of the synchrotron infrared source was the ability to collect spectra from individual crystals very quickly. This allowed for real-time observation of the evolution of hydrocarbon species within the catalyst pores. For example, Figure 7

shows a set of spectra collected over a 15-minute period after beginning a flow of dimethylether at 573 K. The bottom spectrum was recorded after the injection of a dimethylether at 523 K and subsequent heating in helium to 573 K. It showed predominantly adsorbed methoxy groups. Upon exposure to a dimethylether at 573 K, the hydroxyl group band at 3610 cm^{-1} was dramatically reduced in intensity, and complex changes occurred in the C-H stretching ($2800\text{-}3200\text{ cm}^{-1}$), C-C stretching ($1500\text{-}1600\text{ cm}^{-1}$), and CH deformation ($1300\text{-}1500\text{ cm}^{-1}$) regions. In broad terms, these changes are consistent with the gradual interconversion of olefinic and methyl substituted aromatic species within the zeolite pores. In other words, the microspectroscopic experiment is able to see in real time the changes occurring in the hydrocarbon pool with time on stream.

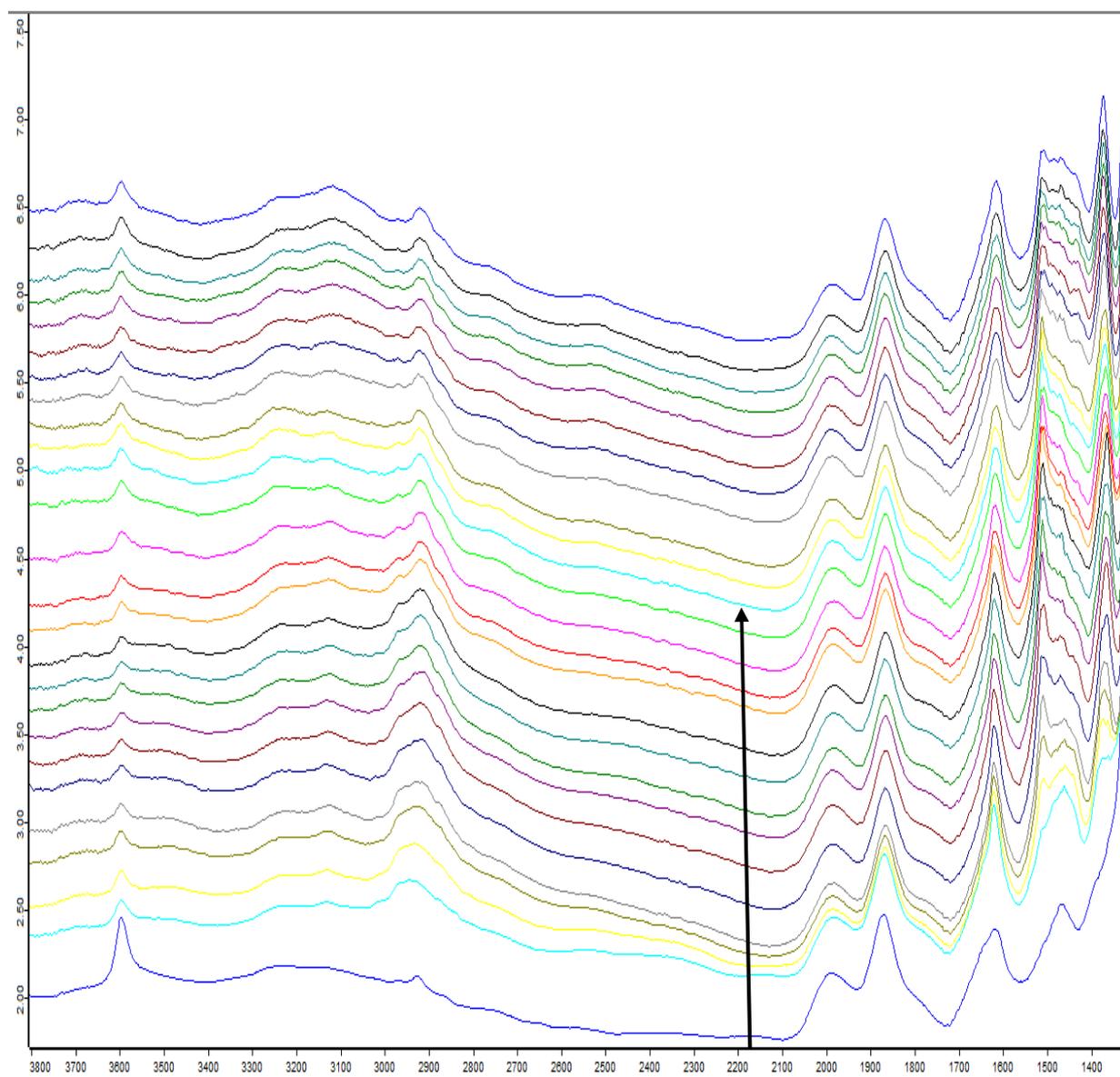


Figure 7. Infrared Spectra Measured as a Function of Time from a Crystal of ZSM-5 Following Exposure to Dimethylether at 573 K (Bottom to Top). Total Time Elapsed 15 Minutes

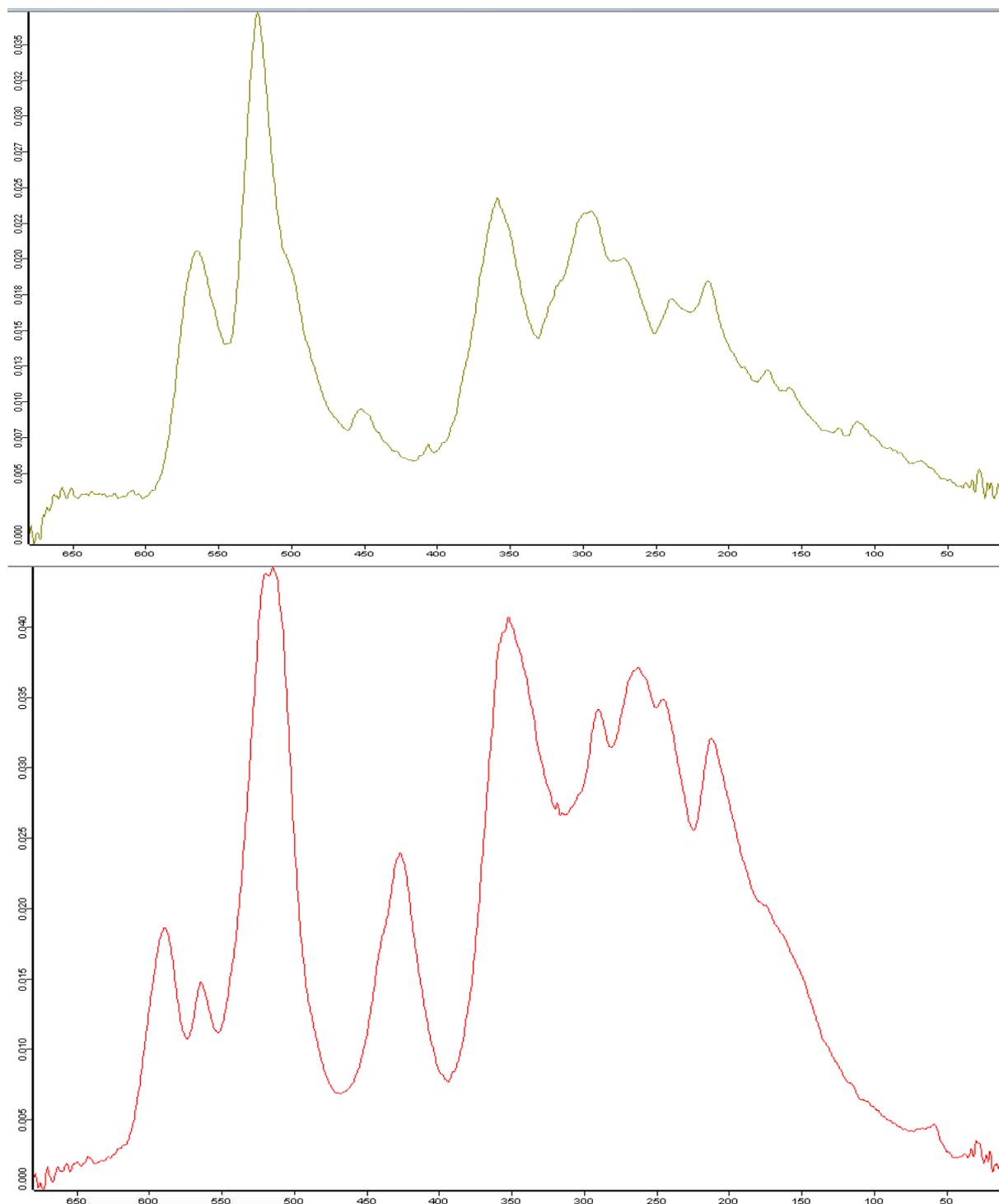


Figure 8. Far Infrared Spectra of $\text{Sc}_2(\text{BDC})_3$ (Top) and $\text{Sc}_2(\text{BDC-NH}_2)_3$ (Bottom)

Far infrared (Terahertz) spectroscopy of microporous materials. The infrared spectrum below 500 cm^{-1} has received little attention in catalyst literature. The interpretation of bands in this region is not straightforward, but laboratory far-infrared spectrometers also struggle to achieve reasonable signal to noise. The Ozin group published a number of papers in the 1980s

showing that the far infrared spectra of zeolites contain bands that occur due to vibrations of zeolite cations within the zeolite structure. They were able to correlate the vibrational frequencies with different cation sites and to observe the effects of adsorbates [3]. The method has not attracted further attention since the papers were published.

As noted, the increased brightness of the synchrotron infrared source in the terahertz region makes far infrared spectroscopy experimentally easier. A second new development is the availability of diamond ATR (attenuated total internal reflectance) cells for sampling. In this method a small amount of sample is pressed against the face of a diamond ATR crystal. The infrared beam passing through the crystal is internally reflected at the top face, but passes several microns into the sample external to the top face of the crystal. This sampling method works much better in the far infrared than conventional transmission measurements through pressed disks of powdered solids.

The combination of synchrotron radiation and diamond ATR sampling to obtain far infrared spectra from metallo-organic framework materials was first described by Ryder et al. [19]. These authors were able to identify all of the low frequency vibrations in the imidazole based metallo-organic porous frameworks ZIF-4, ZIF-7 and ZIF-8, by combining synchrotron far infrared spectra with inelastic neutron scattering and ab-initio DFT calculations

Figure 8 shows the spectra measured of two other MOF materials in this study, $\text{Sc}_2(\text{BDC})_3$ and $\text{Sc}_2(\text{BDC-NH}_2)_3$ (the MOF used in the CO_2 adsorption studies described above). The bands could not be assigned to specific vibrations without undertaking modelling calculations of the type described in [20]. Nevertheless, comparison of the two spectra suggests that the band around 430 cm^{-1} in the spectrum of the amine functionalised MOF is associated with the NH_2 group (a deformation vibration), whereas the remaining features, which are common to both, are associated with the ScO_6 octahedra and benzene dicarboxylic acid linker groups.

Conclusions

This short review has attempted to show by means of selected examples how synchrotron infrared spectroscopy can offer significant advantages over conventional laboratory infrared spectroscopy in studying catalytic materials. Aside from the obvious advantages of microspectroscopy in observing spatial distribution and orientation of species within crystals of microporous materials, the speed with which data can be collected has opened the possibility of real time operando measurements of adsorption, diffusion and catalytic reactions. Applications of far-infrared spectroscopy are much less well developed. Interpretation of spectra requires theoretical modelling, and the practical problem of how to undertake in-situ operando measurements in the far infrared with the diamond ATR technique has not yet been solved. Nevertheless, this is an area where the method shows real potential for future application.

Acknowledgements

The author's work with synchrotron infrared spectroscopy was a collaborative project with Professor Paul Wright's group at the University of St. Andrews. Students and postdoctoral fellows involved include Dr. Alex Greenaway, Dr. A. Lorena Piccone, Eike Eschenroeder, Alessandro Turrina, and David Price. The Diamond Light Source is acknowledged for providing beam time on BM22, and the work would not be possible without the support of the beam line staff of Dr. Gianfelice Cinque and Dr. Mark Frogley.

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