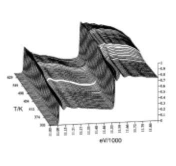
Bringing time resolution to EXAFS: recent developments and application to chemical systems



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Received 4th August 2001
First published as an Advance Article on the web 29th January 2002

The currently available methodologies for applying extended X-ray absorption fine structure (EXAFS) spectroscopy to the interrogation of dynamic chemical systems are critically reviewed. Particular regard is paid to applicable experimental timescales, extraction of structural information, sample presentation, and simultaneous pairing with complementary techniques; the potential for further developments in this area is also assessed.

1 Introduction

The relationship between structure and reactivity is a fundamental and unifying thread that runs through the entire canon of chemical disciplines. Experimental techniques (or combinations of techniques) that are quantitative in terms of structural information, whilst at the same time yielding dynamic information regarding the reactivity of the system under study, are therefore highly sought.

X-Ray absorption (XAS) spectroscopies have developed over the last three decades to become one of the most widely used and powerful probes of local molecular structure. X-Ray absorption fine structure spectroscopy (XAFS) provides a way of investigating the locality of an element. The elemental specificity arises from the differing energies of their core orbitals. Normally either the 1s or 2p orbital is probed and an X-ray of appropriate energy is used to cause core to valence and core–continuum transitions. The former provide features (XANES) close to the absorption edge and can fingerprint a co-ordination geometry. The latter generate photoelectrons that are scattered back by nearby atoms (EXAFS). This modulates the intensity of the X-ray absorption. The periodicity of the modulation provides interatomic distances (to *ca.* 1.5% precision), and the intensity the number of atoms (10–20% precision); the intensity profile over the spectrum indicates the atomic number of the neighbouring atom (identifies its row in the periodic table). Being a spectroscopy, XAFS can be applied to disordered as well as ordered phases. This means that it is applicable to metal catalysts both in solution and also in heterogeneous catalysts. For most transition elements the

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DOI: 10.1039/b100115a

penetration depth of the X-radiation is sufficiently long that *in situ* cells can be constructed.

EXAFS provides information complementary to other common probes such as infra-red, NMR and X-ray diffraction. Infra-red spectroscopy can identify functional groups and in favourable cases, local symmetry and bond angles. NMR provides excellent speciation, can fingerprint structural units from their characteristic shifts, and establish connectivities in structures through coupling patterns. EXAFS gives direct structural parameters more clearly, and is not restricted to the range of elements that possess accessible NMR nuclei.

Since XAFS is a form of electronic spectroscopy, the transition is faster than a molecular vibration. So the observed interatomic distances for a particular atom pair are a summation of both variations in the equilibrium bond length (static Debye Waller factor) and also those due the vibrational envelope (dynamic Debye Waller factor). This damping effect can be very large at room temperature for structural units linked by low frequency, high amplitude vibrations, such as an M–I–M bend. This has the effect making many local nonbonding interatomic distances invisible, but simplifies the task of spectral analysis.

When mixtures of chemical species are present incorporating the same absorbing element then XAFS will again detect the summation of the species present. This is not a major problem when different scattering elements are involved with different interatomic distances, *e.g.* replacement of M–I by M–C, although even then minor species ($<10\%$) may be difficult to detect. However, if these species have the same neighbouring atoms, identification of minor components is highly problematical; their effect is to increase the static disorder and so dampen the scattering from this shared shell of neighbours. Nevertheless, when used judiciously, XAFS can illuminate the structures present in catalytic systems in a unique way, the more so when used in conjunction with other techniques; in heterogeneous catalysis at least it is probably seen as an essential component of characterising a catalyst in its resting state. If it can be carried out on a rapid timescale, it offers the potential of structural detail on reaction intermediates, hitherto normally only fingerprinted by UV–visible spectroscopy in homogeneous systems.

The traditional (and still predominant) application of EXAFS has however been rooted in the steady state with data acquisition times measured in thousands of seconds. 'Standard' EXAFS has therefore not been generally applicable to the *in situ* study of dynamic chemical systems in non steady-state environments, and, for instance, the elucidation of the structure of intermediates involved in chemical processes. Examples do exist however of 'standard' EXAFS being used to derive structural and kinetic information concerning the progress of suitably slow reactions.[1]. Fig. 1 shows one such case of Pt L_{III} edge EXAFS being collected during the rearrangement of one PtRu cluster to another (Scheme 1). Over a period of twelve hours, ten separate EXAFS measurements allow a quasi-continuous but detailed assessment of the average local Pt coordination. Further, through measurement of the intensity of the EXAFS features indicated, a rate constant for this process can be derived directly and shown to be comparable to that derived from other techniques ($\sim 1 \times 10^{-4}\, s^{-1}$ at room temperature).

The quality of data obtained from this standard experiment is very high and therefore permits detailed extraction of structural information; it is also correspondingly slow but neatly illustrates both the potential power and the intrinsic limitations of standard EXAFS for probing dynamic reactions from both structural and kinetic points of view.

It does however provide a suitable starting point for our consideration of the methodologies that may be employed to make EXAFS applicable to the detailed study of structural change occurring during reactions proceeding on timescales of several minutes to sub-second or less. From this we will consider how time-resolved EXAFS may be simultaneously combined with other techniques to provide powerful analytical strategies for interrogating the relationships between chemical structure and reactivity. In doing so we will only consider approaches that may result in EXAFS data (and therefore the potential for structural determination), rather than those that result in very rapid (<50 ms) acquisition of near-edge structure (*e.g.* piezo-XAFS),[2] the interpretation of XANES structure being generally rather qualitative, and/or requiring reference to known standards. Further, in this review we shall concentrate on the chemistry that may be elucidated using these techniques. Therefore, and due to limitations of space, we will not enter into detailed discussions regarding more physical aspects of the experiments (*e.g.* beamline construction or the physical properties of detector systems used in EDE) as these are described elsewhere.[3]

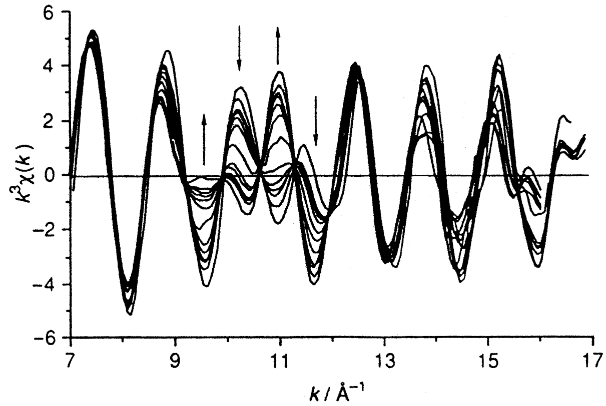
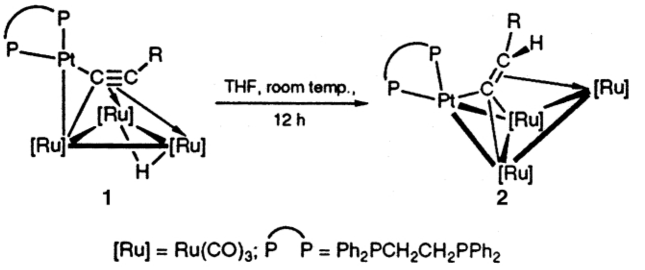


Fig. 1 k^3 Weighted Pt L_{III} edge EXAFS in the range of 7–17 Å^{-1} for the rearrangement of **1** into **2** in 80 mmol dm^{-3} THF solution. Measurements were made hourly over a 12 h period. Arrows indicate the direction in which a feature develops during this time. (Reproduced from ref. 1.)



Scheme 1

2 Methods for time resolved XAS

2.1 Experimental approaches to time resolution in EXAFS

The central barrier to inducing increased time resolution in EXAFS lies in obtaining the range of X-ray energies that comprise the spectral width and also in obtaining the accuracy of their intensities. It is these factors that are the chief determinants of the degree with which any EXAFS data may be extracted to yield detailed structural information.

Two strategies have been developed to address the problem of sampling the energetic range required for EXAFS measurements rapidly and provide the delineating factor between the major time-resolved EXAFS variants, quick EXAFS (QEXAFS)[2,4] and energy dispersive EXAFS (EDE or DEXAFS)[5]; Fig. 2a and b illustrate the differing experimental arrangements used in each case. A third, hybrid approach, 'Turbo' or T-EXAFS has also recently been demonstrated.[6,7]

The experimental requirements of QEXAFS are a derivative of the 'standard' experiment, the central concept of QEXAFS being the optimisation of the movement of a conventional double crystal monochromator system. QEXAFS therefore retains the 'point by point' mode of data acquisition of the standard experiment but utilising high geared stepper motors, or a dc motor with encoder, to continuously drive the monochromator through the desired energetic window. In this configuration simultaneous background acquisition, and therefore intrinsically accurate data normalisation, is achieved as in the standard experiment.

The energy dispersive approach to time-resolved EXAFS is based upon a completely different, and arguably more elegant, solution to the question of speed of data acquisition that actually pre-dates[5] the first QEXAFS experiments.[4] Indeed, the principle of using a bent monochromator, albeit for differing ends, can be traced back to the very earliest days of X-ray absorption spectrometry in the pioneering work of Yvette Cauchois.[8] The principal notion in EDE is the elimination of the stepwise progression through the X-ray window of interest by using a 'bent' monochromator crystal to instantaneously illuminate the sample with a focussed X-ray beam containing the desired spread of energies. This removes any temporal components resulting from the physical movement of the monochromator and therefore data acquisition times are limited, in principle, only by the time required to obtain acceptable statistics.

The first monochromators developed for dispersive EXAFS were generally triangular, manipulated *via* a three-point bending mechanism and utilised in a Bragg configuration. These systems have generally been replaced by four-point bending mechanisms[9,10] that demonstrably reduce aberrations in the monochromator due to the bending process. Further, it has been shown that both Bragg and Laue configurations may be used, with the Laue configuration preferred at higher X-ray energies.[9]

In the absence of other factors, EDE will always provide a greater potential speed of acquisition over the energy range required for EXAFS. Practically speaking, however, the EDE pays heavily in other areas of the experiment, as a result of simultaneously illuminating the sample with a broad bandwidth of X-rays.

2.2 Experimental considerations and limiting criteria

2.2.1 QEXAFS. As quick EXAFS is an optimised version of the standard experiment the experimental design criteria are broadly well known: the standard experiment being well developed and the subject of numerous reviews (for example, ref. 11). Importantly, reference measurements, which take account of fluctuations in beam intensity, are intrinsically part of the absorption measurement in the sample. Further, as QEXAFS samples only one X-ray energy at any one time, the spatial uniformity of the sample, or small changes in X-ray beam position (relative to the size of the sample), should not be significant issues in determining the practicability of an experiment.

Therefore QEXAFS is limited by the speed of stepwise monochromator movement attainable, the integration time required per point to achieve acceptable statistics, and the reproducibility of monochromator movement in both forward and reverse directions. As the complete elimination of backlash in mechanical systems is difficult this last point is important as the failure to scan reproducibly in both monochromator directions will effectively halve the time resolution available. Further, since the sample should not change during the acquisition of a single spectrum the time resolving power of QEXAFS is limited such that $t_{1/2}^{\text{reaction}} \gg t^{\text{spectrum}}$. As we shall see, t^{spectrum} is generally of the order of > 30–60 seconds.

Lastly all the methods available for detection in the standard configuration, such as transmission, X-ray induced fluorescence, and total, partial or Auger electron yields, are available to QEXAFS. As such, QEXAFS can deal easily with dilute samples for which fluorescence yield detection is favoured. Further, the ability to use a fluorescence detection mode means that deleterious contributions from X-ray scattering (where they occur) can be minimised through the use of multi-element solid state detectors or Z-1 filters (in the case of simple diode detectors).

As such, QEXAFS should be readily applicable to surface science based single crystal studies (quick surface EXAFS) and it is surprising that only one example of such a usage[12] (studying the growth of thin Cu films evaporated onto a W covered Si wafer) exists in the literature.

Further, the surface sensitive, high pressure secondary electron detection techniques developed by Rayment *et al.*, [13] should also be amenable to the QEXAFS approach, though as yet there have been no reports to this end.

2.2.2 Energy dispersive EXAFS. By illuminating the sample with a range of X-ray wavelengths the energy dispersive approach becomes far more demanding in terms of temporal and spatial beam stability and sample presentation than QEXAFS. Firstly, the polychromatic X-ray beam used in EDE means that the only mode of detection currently available is transmission using a highly linear detector with spatial discrimination (such as a photodiode array or a CCD). As fluorescence detection is not available the concentration limit of the experiment is effectively raised, and contributions from unwanted X-ray scattering due to the sample under study cannot

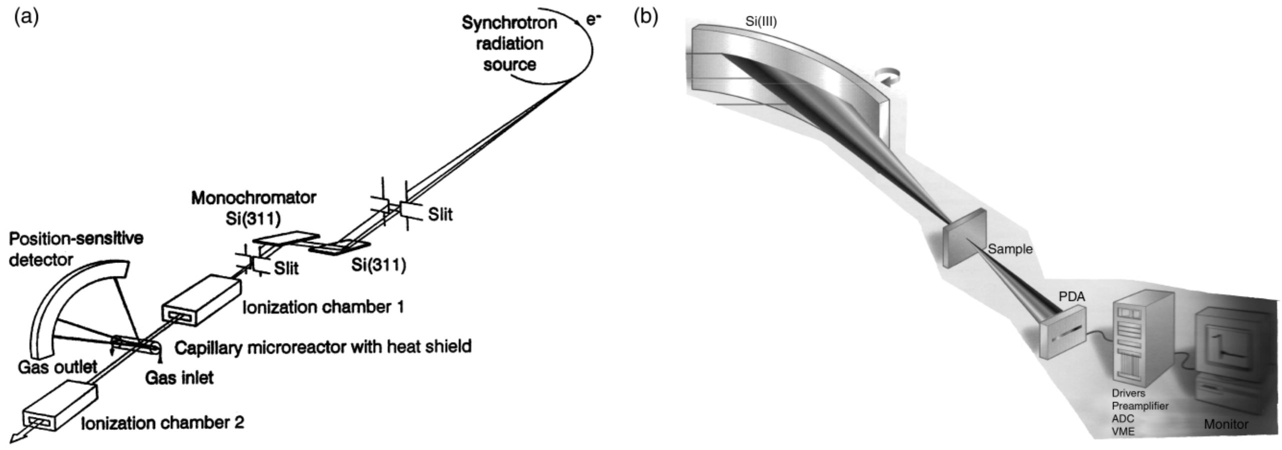


Fig. 2 Typical experimental arrangements for QEXAFS and dispersive EXAFS. (a) Quick EXAFS, in this case configured for 'combined' QEXAFS and X-ray diffraction. (Reproduced from ref. 16*a* with permission of the Academic Press.) (b) A general schematic for dispersive EXAFS with a curved Si[111] monochromator in a Bragg configuration.

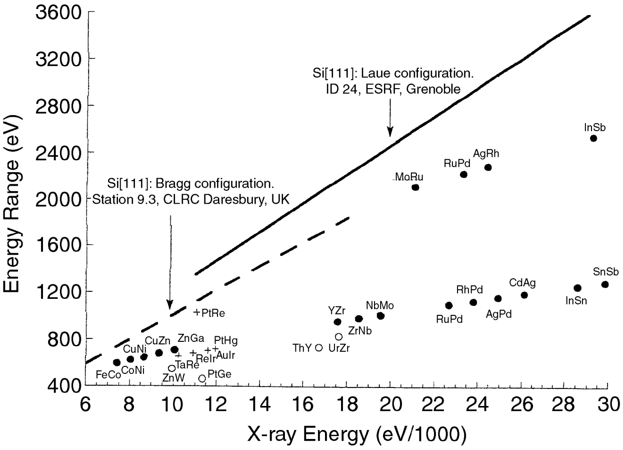


Fig. 3 Energetic windows available as a function of X-ray energy for dispersive configurations currently in operation at CLRC Daresbury (station 9.3) and at the ESRF Grenoble (ID 24). Energy ranges are shown for both the Bragg and Laue configurations. The Laue configuration is currently only available at the ESRF. The energy ranges provided by Si[111] monochromators in the Bragg configuration at both ID 24 and station 9.3 are very similar. The curve shown, though derived for 9.3, therefore serves as a good guide for ID 24. Also shown are K–K (filled circles), K–L_{III} (open circles) and L_{III}–L_{III} (crosses) edge combinations accessible within the energy ranges provided by the dispersive arrangements. (Adapted from ref. 15.)

easily be minimised; further, the possibility of utilising electron detection techniques is also at present ruled out.

In addition, the X-ray beam will not be perfectly focussed through the sample and therefore each wavelength within the beam samples a slightly different area. As such, for a successful experiment the sample itself must be spatially uniform over at least the dimensions of the focussed beam [*ca.* 20–200 µm (horizontal) × 100 µm (vertical)]. If we also recognise that in reality the X-ray beam itself will never be completely stable spatially, this sample uniformity needs to extend beyond the physical size of the beam focus.

Lastly the simultaneous sampling of a broad band of X-ray energies currently means that the use of a single detector to account for variations in beam flux during the experiment, through a simultaneous background acquisition (I_o), is not applicable. In practice, this means that before and after single or multiple sample measurements the sample must be moved out of the X-ray beam to allow a suitable reference measurement to be made (in a similar way to a Fourier transform infra-red spectrometer). Further, in the case of multiple measurements, an interpolation made between the starting and final reference measurement has to be made. This means that EDE places stringent constraints on the stability of the X-ray beam over the timescale of any given experiment.

However, as the whole spectral energy range is simultaneously acquired the effective time resolution of the EDE experiment is the integration time for the single accumulation. EDE therefore potentially allows sub-millisecond time resolution—a prospect that is tantalising and being actively developed. Beyond this there is one further ramification of the dispersive approach that is unique and potentially extremely useful. As a given sample is illuminated with a broad band of X-ray frequencies the possibility of probing the local order of more than one element in a multi-component system in a genuinely *simultaneous* manner arises. As QEXAFS retains the stepwise approach to sampling, multi-edge sampling can only be achieved in a sequential manner rather than instantaneously. This 'multi-edge' possibility was implicitly recognised by Matsushita and Phizackerley[5] in 1981, and by Couves *et al.*[14] in 1991; only recently, however, has a practical application of this unique property of the dispersive experiment been demonstrated[15] (see below). The energetic width of the X-ray window that may be obtained from a dynamic bending of a single crystal monochromator depends on a number of factors related to the beamline and experiment geometry, and is calculable from the known experimental geometry (for instance, refs. 4 and 15). Fig. 3 shows the operational energy ranges, and X-ray energy windows obtainable, for current dispersive configurations at line 9.3 at the Daresbury SRS (monochromator in Bragg configuration) in the UK, and at ID 24 at the ESRF in France [Bragg (not shown) and Laue configurations]. As can be seen, a considerable number of elemental combinations fall within the energetic windows derived from the differing monochromators and are therefore amenable to simultaneous, twin-edge experiments: an example of such an application will be detailed below.

However, it is also clear that the energy windows provided by these currently available monochromators at X-ray energies of *ca.* < 5 keV will not be wide enough to provide the post edge data length required for EXAFS analysis; this situation will be magnified in the case of a Bragg configuration at ID24 (ESRF, Grenoble), due to the limited bandpass of the beamline undulator at these energies. As such, for softer edges EDE will only be able to provide time-resolved XANES information. In principle, QEXAFS does not suffer from this limitation and therefore will be the method of choice in the derivation of EXAFS data from such 'soft' systems.

2.2.3 Turbo EXAFS. As we have seen, the potential time resolution of EDE is extremely desirable, but the dispersive approach is correspondingly demanding in all areas of the experiment. A third, hybrid, approach to time-resolved XAS, has recently been demonstrated in specific response to early beamline instabilities experienced on the dispersive EXAFS line (ID 24) at the ESRF Grenoble.

Turbo EXAFS, developed by Pascarelli *et al.*[6,7] at the ESRF, incorporates a slit that scans across the broad band of X-ray energies provided by a dispersive monochromator. This arrangement allows a sequential scanning of the energy window required (as in QEXAFS) but with no associated monochromator movement. Further, as at any one time a single X-ray energy is sampled, both sample and reference measurements can be made simultaneously, and fluorescence detection becomes possible. Thus a big bugbear of the EDE experiment (normalisation) is removed and with it sensitivity to temporal changes in beam flux. The sample uniformity and spatial beam stability requirements of EDE remain, but the small number of studies using this hybrid approach to time-resolved EXAFS are promising[6,7] with a time resolution of a few seconds. Until such time as simultaneous normalisation can be achieved in EDE it will remain a practical manner in which to circumvent some of the problems associated with beam instability.

2.2.4 Coupling time-resolved EXAFS with secondary spectroscopic techniques. No single spectroscopic technique will completely characterise a given chemical system in all its aspects, and it is logical that a variety of experimental probes need be applied to a system in order to unravel all the chemistry at work in any given process. As such, the capacity to augment time-resolved EXAFS with secondary techniques providing complementary information *in situ*, and on a comparable timescale to the EXAFS acquisition, is an important consideration.

An ever increasing array of adjunct probes have been successfully coupled with time-resolved EXAFS. The most widely used has been the combination of X-ray diffraction with QEXAFS and EDE in the study of solid and powder systems. From the former, information in relation to the local atomic environment of the absorbing atom is obtained, and from the latter information pertaining to the overall structural integrity and phase identification is obtained. This 'combination' has been used extensively in the *in situ* structural study of heterogeneous catalysts and the reader is referred to the literature for extensive reviews.[16]

A diverse array of techniques can be married to time-resolved XAS: from the use of mass spectrometry in gas–solid systems,[17–21] through cyclic voltammetry[22–27] in electrochemical systems, to differential scanning calorimetry[28] and chemiluminesence.[29] We shall now consider a few informative examples, representative of the current state of the art, and/or indicative of promise for the future.

3 Applications of time-resolved EXAFS to dynamic chemical systems

3.1 Direct comparison: QEXAFS *vs.* EDE

To our knowledge, and somewhat surprisingly, there exists only one report[24] that directly compares QEXAFS and EDE in their potential application to a dynamic chemical system. Some illustrative k^3 weighted Pt L_{III} edge EXAFS from this laudable exercise, designed to test the applicability of time-resolved EXAFS in studying the electrochemical oxidation of Pt under potential (cyclic voltammetric) control, are shown in Fig. 4.

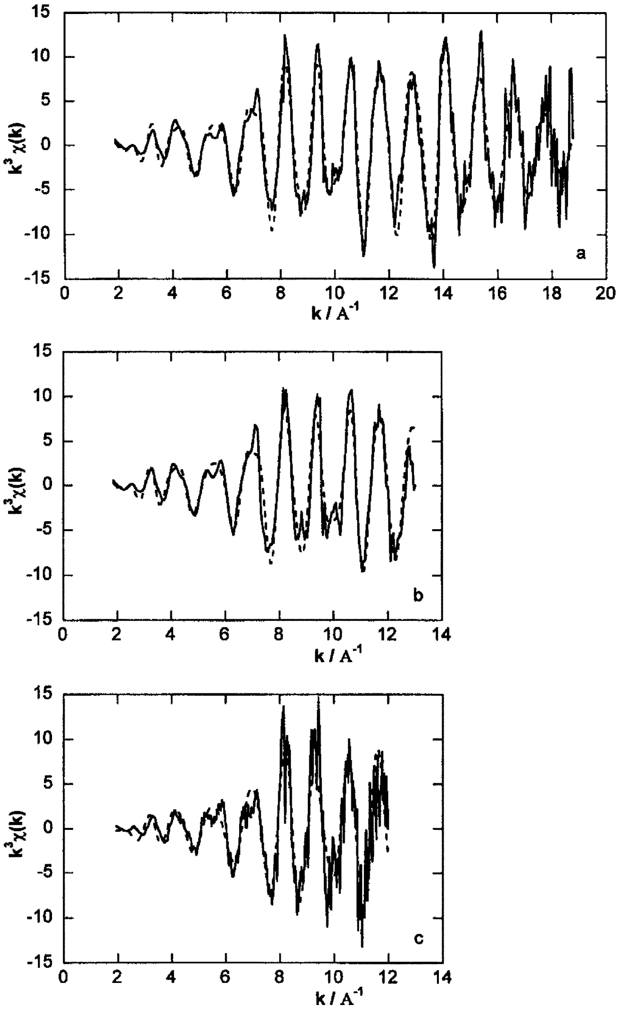


Fig. 4 k^3 Weighted $\chi(k)$ spectra derived from 40 wt% Pt/XC-72R catalyst suspended in Nafion spread over carbon cloth or carbon paper. Top spectrum = standard EXAFS collected in *ca.* 2400 s; middle spectrum = QEXAFS collected in 60 s; bottom spectrum = EDE with 5 s total acquisition time. (Reproduced from ref. 24 by permission of Kluwer Academic Publishers.)

This system comprises a 40wt% Pt catalyst suspended in Nafion and water and pressed (on carbon paper or cloth) and cut into electrodes.[20] The path length through the Pt containing layer is *ca.* 1–1.5 mm. As can be seen both the QEXAFS (60 s; Δk = 1.90–13 Å^{-1}) and the EDE (5 s; Δk = 1.9–12 Å^{-1}) result in considerably truncated analysable data ranges compared to the standard experiment (2400 s; Δk = 1.9–18.8 Å^{-1}) even though the energetic window provided by the dispersive, Bragg configured, monochromator will be of the order of (1100–1200 eV) (Fig. 3[15]).

As might be expected from our discussions (above) of the limiting criteria for the differing time-resolved approaches, the order of magnitude gained in time resolution in the EDE experiment may be paid for in increased noise levels and a significantly shorter analysable data range. The major ramifications of this are that only two shells of co-ordination data may be confidently extracted from the EDE (as opposed to three from the QEXAFS). The curtailed data range increases the error associated with the derived co-ordination number from 10% for the standard EXAFS to nearer 20% for the EDE. Bond length determination is more robust varying by only ~1% between EDE and QEXAFS.

From a practical point of view, though the QEXAFS experiment provides the sturdier data set, a 60 second acquisition time is extremely restrictive in terms of following electrochemical oxidation processes in any kinetic detail (typical sweep rates). Whilst the EDE provided less information, the acquisition timescale is sufficient to follow such rapid processes, where the significant white line changes (which, in fairness, could also be achieved using the rapid acquisition of XANES data in QEXAFS mode recently demonstrated by both Als-Nielsen[30] and Frahm[2]), or where significant changes in co-ordination are occurring.

Though, as we will see, these data are not representative of the highest quality that can be achieved in either technique, the comparative analysis undertaken by Mathew and Russell[24] illustrates well the currently pervasive trade off between data quality and time resolution.

3.2 Time-resolved studies as applied to homogeneous chemical systems

A survey of the application of time-resolved EXAFS to homogeneous systems reveals a marked preference for a given experimental variant according to the material phase under study. QEXAFS is found to predominate in the solid state, EDE in the liquid phase: it is in the liquid phase, with its intrinsic spatial homogeneity, that the constraints of the dispersive approach are least problematical.

3.2.1 Reactions in the solid state. Several solid state processes have been studied using QEXAFS from solid combustion reactions,[31] polymerisation,[28] precipitation[32] and crystallisation processes.[33] The first case illustrates a situation where the transmission limited EDE approach is not applicable due to the volume required to sustain these explosive reactions and the capacity for QEXAFS measurements to be made in fluorescence mode comes to the fore. The other cases demonstrate the successful combination of differential scanning calorimetry (DSC) with QEXAFS having an acquisition time of *ca.* 135 s. In all these cases the obtained post edge data range has been somewhat short (< 9 Å^{-1}) and representative data from ref. 18*a* are shown in Fig. 5 for the solid state elimination from sodium bromoacetate to form polyglycolide and NaBr. The important conclusions from this combination of techniques are that this process proceeds with no long lived (within the temporal resolution of the experiment) intermediates and that the structural changes observed relate directly to the enthalpic changes measured by DSC.

In what is a unique example of amalgamating further experiments the enthalpy change and short range order studied *in situ* by DSC-QEXAFS[28*a*] was united with combined XRD-EXAFS.[28*b*] Thus, the incomplete knowledge of the reaction

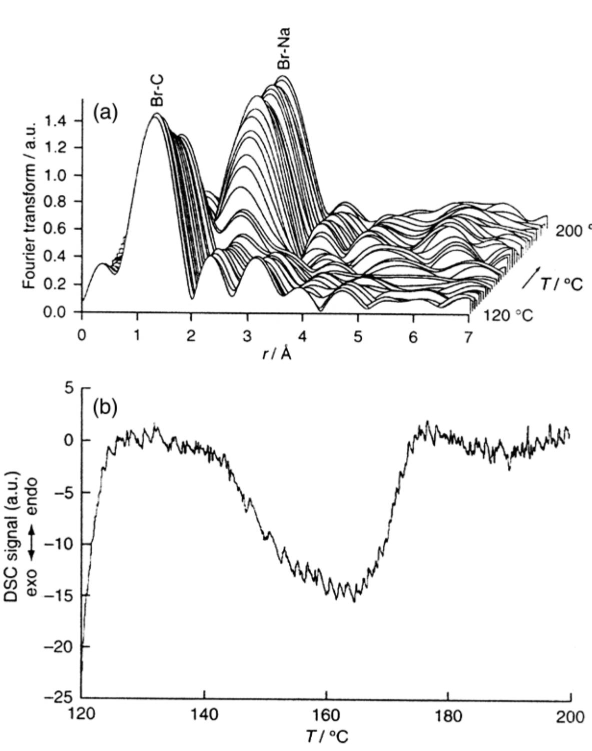


Fig. 5 (a) Radial distribution functions (not phase corrected) derived from Br K edge QEXAFS during the solid state elimination of sodium bromoacetate (see text) in the temperature range 393–473 K (heating rate = 1 K $\min^{-1}$). Spectra recorded every 135 s. (b) Baseline corrected DSC data collected simultaneously with the QEXAFS shown in (a). (Reproduced from ref. 28*a*.)

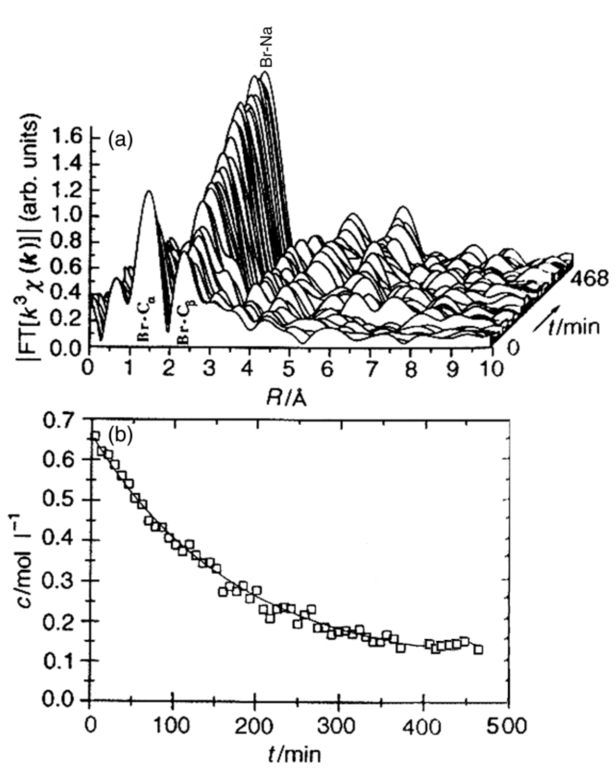


Fig. 6 Radial distribution functions derived from Br K edge QEXAFS during the 'Finkelstein' reaction at 328 K. At $t = 0$ the spectrum corresponds to that of 2-bromopropane, at $t = 468$ min to (predominantly) dispersed NaBr. (b) Temporal variance of 2-bromopropane concentration derived from QEXAFS data shown in above in (a). The solid line represents the computed second order reaction kinetics. (Reproduced from ref. 34.)

pathway was supplemented with long range order information. This showed that all changes occurring during the reaction (enthalpic, short range, and long range) take place simultaneously and, therefore, that the reaction occurs in one step and without a crystalline, liquid or amorphous intermediate observable on the experimental timescale.

Applications of EDE to reactions in the solid state are scarcer but again Hilbrandt and Martin[32] and D'Acapito *et al.*[33] have both applied EDE to 'kinetic' studies of solid state processes; namely the precipitation formation/dissolution of spinels[23] and the crystallization of amorphous metal alloys.[24] In both of these cases acquisition times of ~ 1 s were achieved for bulk materials at Ni K, Fe K and Cu K edges. Hilbrandt and Martin[32] clearly demonstrate the potential of the dispersive technique but do not derive quantitative kinetics as they have done in other systems.[18a,34] D'Acapito *et al.*[33] however do derive data pertaining to nucleation processes occurring during heating of a $Ni_{60}B_{40}$ amorphous alloy that are verified as consistent with the expectation of nucleation and growth theories currently used to describe such processes.

3.2.2 Reactions in the liquid phase. As mentioned above, the natural homogeneity of the liquid phase makes it the ideal environment for EDE and, as early as 1990, millisecond time-resolved XANES was demonstrated and applied to determination of the rate constants for electron transfer between iron(III) nitrate and hydroquinone in solution.[35]

However, one of the few examples of QEXAFS being applied to liquid phase chemistry, the study of Epple *et al.*[34] of the 'Finkelstein' reaction, is currently unique (from a homogeneous perspective) in that the QEXAFS is used to derive quantitative kinetic data regarding this reaction. Fig. 6 shows representative Fourier transforms derived from the Br K edge during this reaction and the resulting kinetic plot and second order fit. The kinetic data are derived under the assumption that the relative intensities of the Br–C and Br–Na features present in the radial distribution functions are proportional to the concentrations of product and reactant, and this assumption is borne out through reference to the well known kinetics of this reaction.

It is instructive to compare the data sets shown in Fig. 1 with those in Fig. 6. The standard experiment in Fig. 1 is vastly superior in terms of analysable data range. However, the QEXAFS is clearly good enough to be used to restore accurate and bonding specific kinetic data with a time resolution nearly two orders of magnitude higher than the standard XAFS measurement (*cf.* Fig. 1). The authors themselves point out that the reactant concentrations used in this study are somewhat higher (1.33 M for each reactant) than would generally be used in kinetic studies (in order to obtain sufficient absorption contrast). However, this study clearly shows the potential of such an approach, particularly in light of the development of high brilliance, third generation, light sources.

Whereas the above experiment utilised a premixed solution of reactant and a 'temperature' jump (using a DSC heat-flux calorimeter) to initiate reaction, the more common approach to studying rapid reactions in solution is *via* 'stopped flow' techniques that potentially yield millisecond time resolutions.

As has been delineated above, only EDE currently holds the promise of obtaining EXAFS data (rather than just XANES) on such timescales. Though, as mentioned above, millisecond XANES was demonstrated as early as 1990,[35] this potential for extremely rapid and structurally deterministic studies has yet to be realised. However, a number of workers have pursued the development of stopped flow EDE measurements. Principal amongst these have been Ohtaki and co-workers[36,37] who, since 1993, have pursued this objective with some considerable success: a success all the more remarkable when one considers that, up until 1997, their work had been conducted using a laboratory based rotating anode X-ray source rather than a storage ring.

Amongst the numerous systems[36] to which they have applied their laboratory based stopped flow EXAFS methodology we will consider here only one as an example: the substitution of Cu at the expense of Hg in a 5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin (tpps).[37] In contrast to the example shown in Fig. 6, the aim of this study was to probe the structure of a short lived intermediate involved in this substitution reaction by making use of the known kinetics of this process, rather than to demonstrate the derivation of kinetic data from the EDE itself.

Any form of EXAFS is a probe of average local order. As such, measurements made upon reaction mixtures, which at any point during the reaction contain reactant, intermediate, and product molecules, will result in XAFS that is a convolution of the local order of all species present. The true structural parameters of the target species (usually the intermediate) are therefore obfuscated. Whilst it is analytically possible to disentangle these competing contributions to the EXAFS, for any such exercise to be undertaken with any confidence, high quality data and/or information from auxiliary techniques (an example of this will be given later), are required . Ohtaki and co-workers circumvent these difficulties by using the known kinetics and pH dependence of the substitution reaction to ensure that after mixing solutions, and when sampling the Cu K edge (for 10 seconds at a time), practically all the Cu exists in the intermediate state. Due to the limitations of the rotating anode source this measurement had to be repeated 180 times to obtain the data shown in Fig. 7. The absolute time resolution is relatively poor, but the combination of both stopped flow and EDE results in a means of effectively quenching the reaction to reveal the transitory formation of an extended Cu–N bond just prior to Cu incorporation into the porphyrin framework.

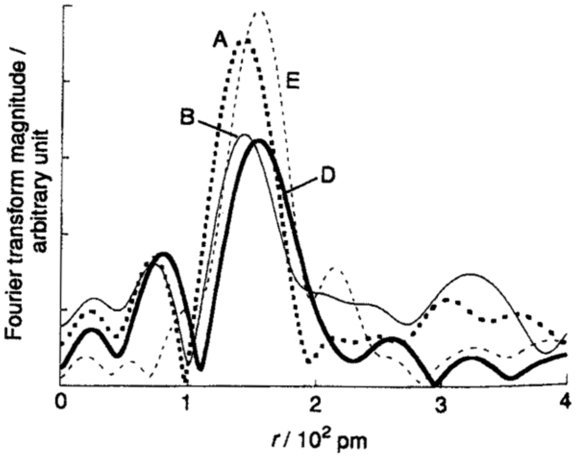


Fig. 7 Fourier transforms of dispersive EXAFS derived from solutions of (A) Cu(acetate)$_2$, (B) [Cu(tpps)]$^{4-}$ complex, (D) the intermediate species [Hg(tpps)Cu]$^{2-}$, and (E) [Cu(OH$_2$)$_6$]$^{2+}$. (Reproduced from ref. 37.)

Despite the resourcefulness of Ohtaki *et al.*, and their 'proof of concept' in respect of studying the structures of true intermediate species using EDE, it is clear that the numerous benefits of synchrotron light (especially in the high flux of the third generation sources) need to be brought to bear on such problems. Fig. 8 shows k^3 weighted Ni K edge EDEXAFS, obtained on station 9.3 at the SRS at Daresbury with a total acquisition time of 2 s, during the mixing of Ni(acac)$_2$ (140 mmol dm^{-3}), hex-1-ene (Ni–hex-1-ene = 1 : 20) and AlEt$_2$(OEt) (280 mmol dm^{-3}), resulting in rapid ethyl trans-metallation between the Al and Ni centres[38] shown in Scheme 2. The extent and quality of this data are greatly superior to those of the previous example, despite the magnitude increase in dilution of the element under study), and the experiment is time-resolved in a more traditional sense with spectra being taken every 10–15 seconds. Whilst no quantitative kinetic data are derived in this case the EDE shows that equilibration between the Al and Ni centres occurs within 40 seconds of mixing at 273 K, and also allows *a priori* EXAFS analysis to be undertaken. Further, using a stopped flow system for faster reactant mixing[38b] the Ni(acac)$_2$ with AlEt$_2$(OEt)–hexene (Scheme 2) conversion could be monitored at intervals of 6 s in an early experiment made at ID 24 at the ESRF Grenoble.

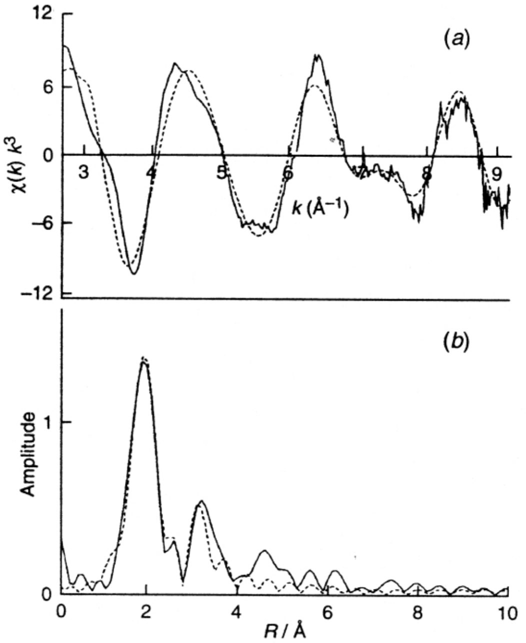
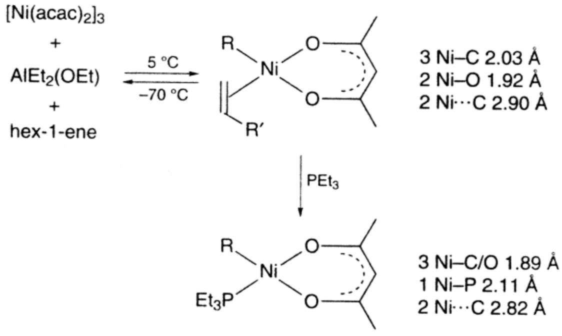


Fig. 8 k^3 EXAFS (a) and (b) experimental and calculated Fourier transforms derived from Ni(acac)$_2$–AlEt$_2$(OEt) (Ni–Al = 1 : 2) in hex-1-ene (Ni–hexene = 1 : 20) after 285 s at 273 K. The acquisition time is 2 s. (Reproduced from ref. 38*a*.)



Scheme 2

The above examples demonstrate that time-resolved EXAFS in its two predominant variants are versatile and potentially powerful tools in the study of chemistry occurring in homogeneous systems. However, it would seem fair to say that, the real impact of these developing methodologies has yet to be felt widely in these arenas, despite the growth in potential applicability arising from (for instance) diminishing dilution limitations due to improvements in synchrotron, beamline and detector technology.

In contrast, application of both QEXAFS and EDE to heterogeneous systems is growing rapidly and it is to these areas of surface based chemistry that we now turn.

3.3 Application of time-resolved EXAFS to heterogeneous systems

In Section 3.1 we touched upon one area where time-resolved EXAFS studies have been applied and compared:[24] the study of a heterogeneous electrochemical system. Now we consider in more detail other examples of time-resolved methodologies, as they have been applied to both solid–liquid and gas–solid systems, with particular regard to both the genesis and reactivity of complexes and the often highly fluxional behaviour of supported metal catalysts.

3.3.1 Applications to surface mediated electrochemical processes. Processes occurring at electrode surfaces have been the subject of a range of time dependent EXAFS examinations[22–27] designed to probe the local structural changes occurring in tandem with redox processes under voltage control.

QEXAFS. QEXAFS has been applied with some considerable success during cyclic voltammetric oxidation and reduction of Ni electrodes using a conventional transmission mode of detection.[25] However, the example we shall consider here is the application of QEXAFS in a manner that has yet to be achieved using EDE: the study of electrochemical (anodic) silver oxide formation by Hecht *et al*.[26] The unique feature of this study is that it utilises a total reflection mode of acquisition to imbue the experiment with a high sensitivity to local order changes occurring at the surface of the anode rather than the bulk. Fig. 9 shows both raw reflectivity data and Fourier transforms, and the simultaneously measured transient current, derived from a voltage jump from −0.3 to 0.4 V as the Ag surface is oxidised. From these data the temporal response of Ag–Ag and Ag–O co-ordination to the voltage jump can be extracted to yield the rate of growth of the oxide film thickness for various final applied voltages. From this the rate law describing this process can be determined at each voltage. This reveals a rate of growth proportional to $t^{1/2}$, indicative of growth being limited by diffusion processes occurring through the growing adlayer, and, through charge balance calculations, indicates that only $\sim \frac{1}{3}$ of the total charge appears in the form of a surface oxide.

EDE. The first experiments to couple time-resolved EXAFS to cyclic voltammetry utilised EXAFS in dispersive mode to investigate redox processes occurring at Ni electrodes.[23] These have subsequently been followed by further work regarding the behaviour of both bulk and Pt/C electrodes.[24,27] In each case the application of fast EXAFS in the dispersive mode and under CV control has revealed considerable differences in the behaviour of bulk *versus* dispersed (Pt/C) electrodes, and/or in the stages involved in oxidation and reduction.

Fig. 10a shows Fourier transform moduli derived from (A) oxidation and (B) reduction of carbon supported Pt particles (~20 Å) during 'voltage jump' relaxation experiments.[27] As with the previous QEXAFS example the sample was equilibrated at a given voltage before the voltage (0.1 V for oxidation; 1.2 V for reduction) is switched to a new value (1.2 and 0.1 V respectively) and the resulting response of the system monitored using time-resolved XAFS. 30 accumulations resulting in 1 spectrum are collected every ten seconds during this process resulting in Fig. 9. These results may be explicitly analysed for Pt–Pt and Pt–O co-ordination to reveal both the kinetic form that describes each process, and the net rate constants (Fig. 10b).

3.3.2 Time-resolved studies of heterogeneous, gas–solid systems. The intrinsic spatial heterogeneity of supported metal or metal oxide catalysts has, for the manifold reasons discussed in Section 2.2, led to QEXAFS being the method of choice[16] for time-resolved studies in such systems. However, many of the considerable technical difficulties that EDE presents in this arena are being surmounted[15,17,19–21,39] and its application more widespread.

These differing approaches, rather than being directly competitive, are currently somewhat discrete in terms of the arenas in which they are best exploited. In terms of the study of supported catalyst systems the most significant differences in approach to specific problems seem not to be in the choice of QEXAFS or EDE, but in the matter of sample presentation: pressed disks *versus* packed tubular flow reactors. The former being currently favoured by Prins and co-workers (QEXAFS)[40–42] and the groups of Schlögl,[19] Ressler[20] and recently Iwasawa[21] (EDE); the latter by Clausen *et al.* (QEXAFS),[2a,16,30] and our own group.[15,17,39]

QEXAFS. The work of Prins' group[40–42] on a number of catalytically important systems demonstrates well the type of measurement for which QEXAFS is currently demonstrably a

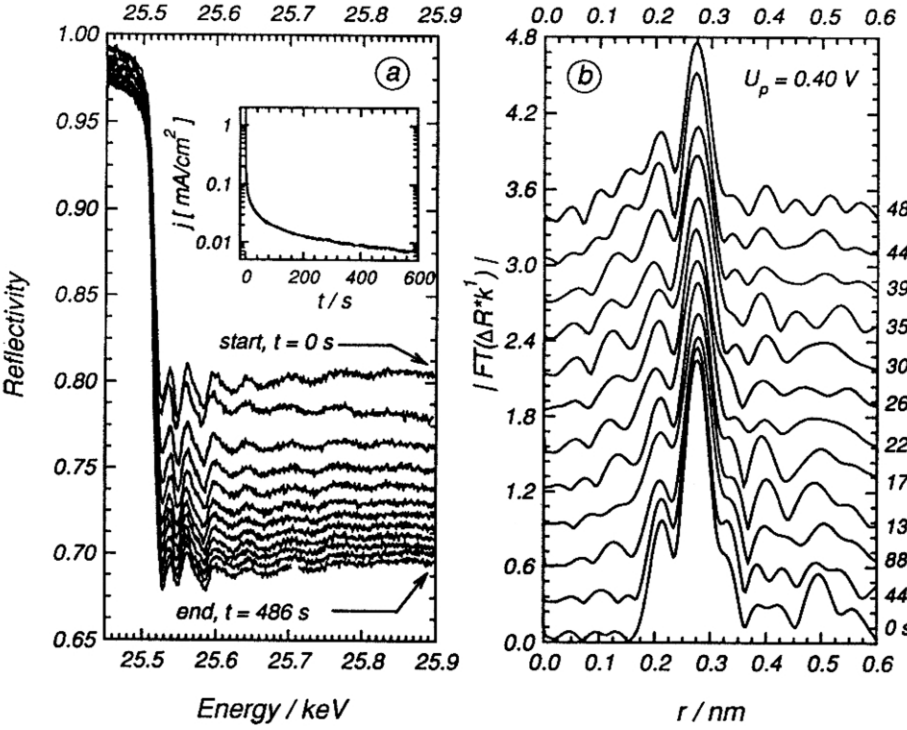


Fig. 9 (a) QEXAFS data collected in total reflection geometry during voltage jump (−0.3–0.4 V) induced oxidation of a silver electrode surface. Each spectrum was collected in 44.2 s. The insert shows the corresponding current associated with the oxidation process. (b) The corresponding Fourier transform magnitude derived from k^1 weighted EXAFS derived from the spectra shown in (a) (Reproduced from ref. 26 by permission of the American Chemical Society.)

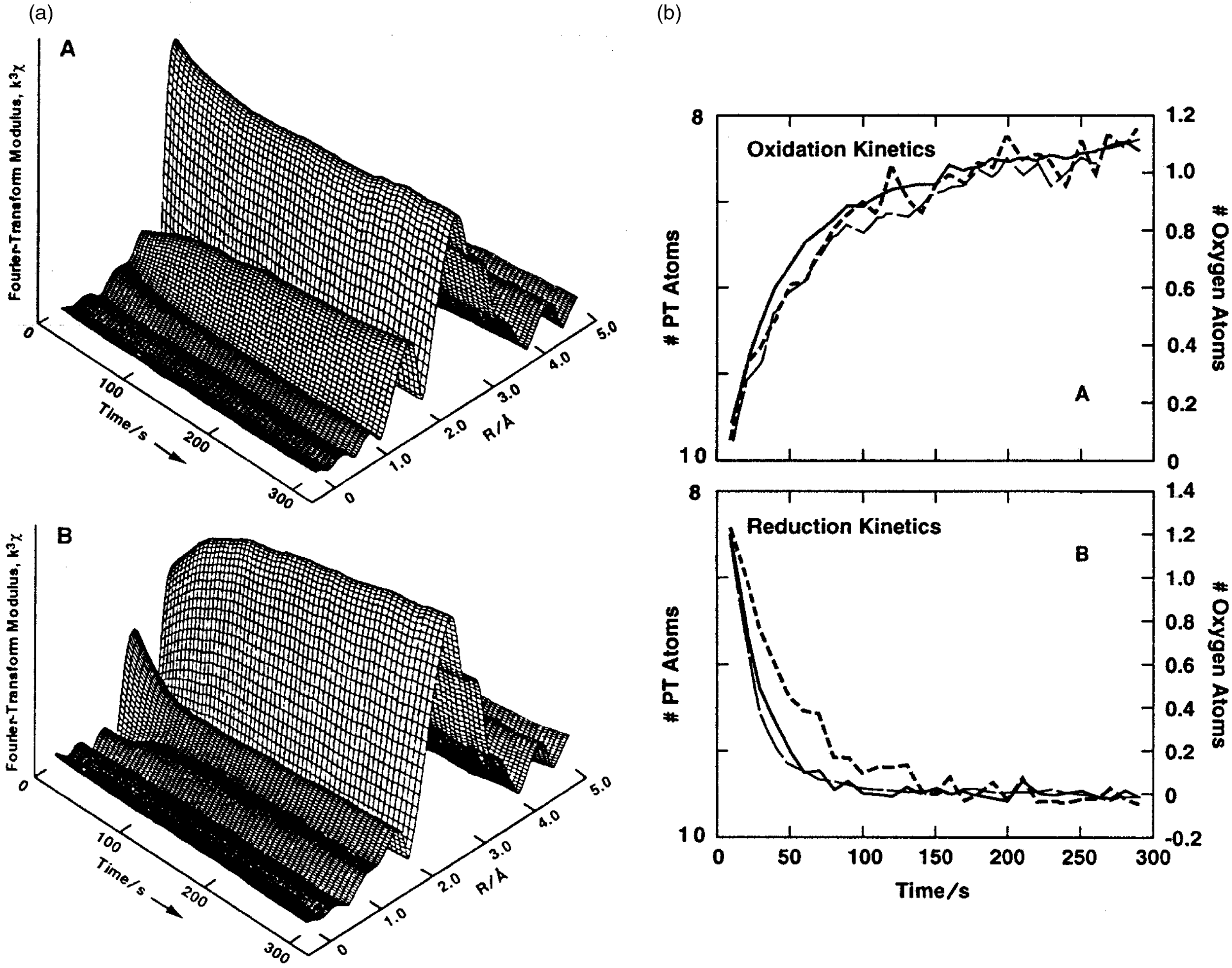


Fig. 10 (a) Fourier transforms derived from Pt L_{III} EDEXAFS from carbon supported Pt catalysts during voltage jump relaxation experiments: (A) during oxidation ΔV = 0.1–1.2 V; and (B) ΔV = 1.2–0.1 V. The feature at *ca.* 2.7 Å is due to Pt–Pt co-ordination. The feature at *ca.* 1.5 Å is due to a combination of a side lobe due to Pt–Pt structure and the changing Pt–O co-ordination. (Reprinted from ref. 27*a* with permission from Excerpta Medica Inc.) (b) Kinetics of oxidation and reduction derived from analysis of data shown in Fig. 9b. Long dash line = oxygen co-ordination; short dash = Pt–Pt first shell co-ordination; solid line = adsorption peak intensity.

superior approach to EDE and Fig. 11 shows some typical results concerning the growth of alloyed PtRh clusters in NaY Zeolite.[40] The data shown in Fig. 11a were obtained from samples with relatively low loadings (Pt = 2.6wt% and Rh = 1.3wt%) in 60 seconds. The data obtained are of both good quality (signal to noise) and length (12–13 Å^{-1}) for both edges studied, and over a three-hour (5 K min^{-1} to 573 K + 2 h at 573 K) reduction period a total of 180 separate spectra were collected. Fig. 11b shows the derived evolution of both elemental and alloy coordination obtained from both Pt L_{III} and Rh K edges.

Clearly as long as the processes at work are slow, as in the PtRh system, QEXAFS provides a stable and very detailed window into the evolving elemental particles. Indeed, the above example illustrates well the predominant usage of QEXAFS in application to heterogeneous catalytic systems, with processes such as the temperature resolved reduction of catalysts precursors and sulfidation being studied in some considerable detail.

Moreover, QEXAFS provides this detailed information even at the relatively low metal loadings used in this study, and the potential for fluorescence based detection inherent in QEXAFS, makes it the method of choice for time-resolved studies in dilute heterogeneous systems. Though EDE cannot compete with QEXAFS in this respect, even the fastest reported QEXAFS experiments made on heterogeneous systems[30] (3.2 seconds per scan, but in one scanning direction only *i.e.* net 6.4 s between scans) were only able to restore near-edge data. As such these could only provide qualitative information *via* reference to known standards. In this respect, and others, EDE comes into its own.

EDE. The pioneering work of Thomas *et al.*[14,43] and Keegan *et al.*[44] regarding the application of EDE (and, in the former cases, its combination with XRD[14,16,43]), in the study of heterogeneous systems showed such experiments, despite their extreme technical demands, were possible on pressed samples. Since then numerous advances in SRS sources, dispersive X-ray detectors, and monochromators, have begun to make EDE measurements on such systems possible on timescales that can easily outstrip standard QEXAFS whilst retaining a quality of data retrieval that permits useful structural analysis.

Fig. 12 considers the application of EDE to the study of the *in situ* reduction of 5wt% $Pt(acac)_2$–H_1SiO_2[33] and 5wt% $Pt(acac)_2$–5wt% $GeBu_4$–H_1SiO_2[15] catalyst precursors. Fig. 12a shows a representative raw data set for the reduction of the latter system illustrating the utilisation of the dispersive EXAFS X-ray window to the simultaneous sampling of more than one elemental edge. The analysis of the Ge K edge EXAFS is intrinsically limited to 9 Å^{-1} by the proximity of the Pt L_{III} edge which itself yields ~ 11 Å^{-1} of useable data (much as in Fig. 4 but for a system considerably more dilute in Pt). Fig. 12b presents a plot analogous to that shown in Fig. 11 but showing data derived from both Pt only and PtGe systems. The total acquisition time in these cases was 5–8 s per spectrum, and the repetition rate was chosen to 2–3 spectra per minute. A faster timescale can be employed if the speed of the processes under study demands it, since clear EXAFS features are already easily observable after only 500 ms acquisition time.[39]

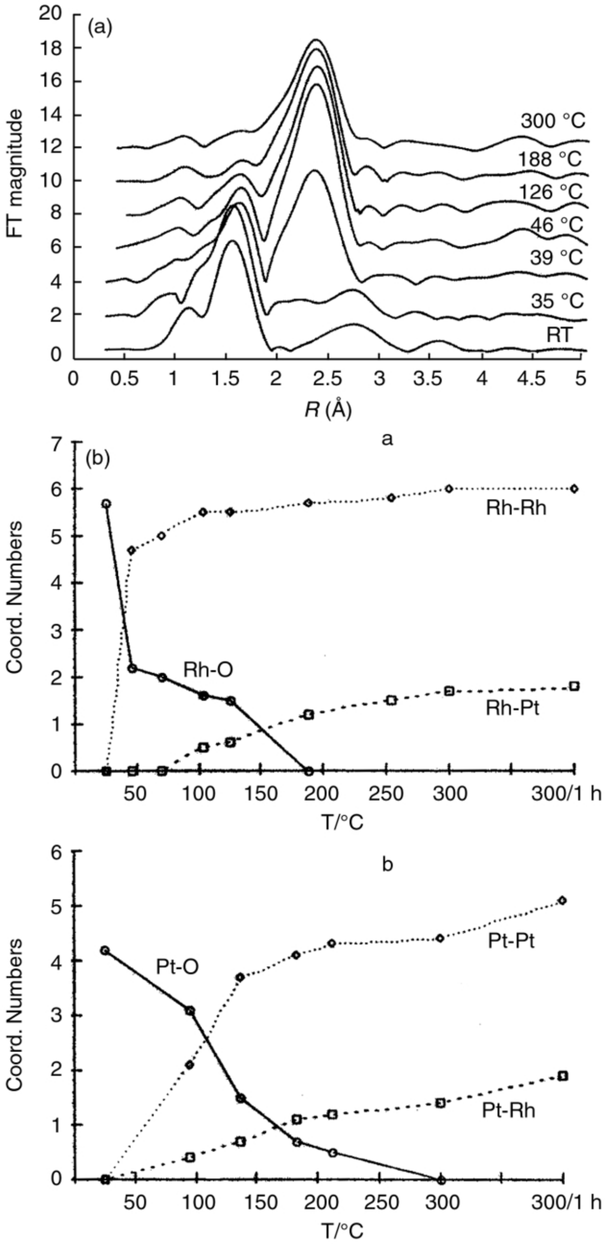


Fig. 11 (a) Representative Fourier transforms derived from Rh K edge QEXAFS spectra (60 s acquisition time) obtained during the reduction of calcined 2.6wt% Pt–1.3wt% Rh–zeolite Y catalyst precursors. (b) Evolution/diminution of elemental (Pt–Pt, Rh–Rh), metal–O and alloy (Pt–Rh) co-ordination during temperature programmed reduction derived from QEXAFS measurements made at the Rh K edge and Pt L_{III} edges. (Reproduced from by ref. 40 by permission of the American Chemical Society.)

Whilst the analysable data length is reduced relative to the Pt and Rh data derived from QEXAFS by Cimini and Prins,[40] the increased speed of acquisition in EDE permits the detection of much faster reductive processes. In this case this results in a window into the autocatalytic collapse (Fig. 12b) of the supported $Pt(acac)_2$ precursor to yield large Pt clusters (N_1 ~ 9) within a temperature range of only 15–20 K. Moreover, a kinetic damping of this Pt particle evolution in the presence of $GeBu_4$ is observed despite the fact that no observable PtGe interactions are detectable in the EDE below temperatures of *ca.* 525 K.

The application of EDE to relatively fast, transient processes occurring in heterogeneous systems has started to burgeon. Ressler and co-workers[20] have used this approach to investigate the relationship between oscillatory kinetics occurring in CO oxidation over supported Pd catalysts and the degree of oxidation of the surface of the supported particles. Further, through the use of pulsed flow techniques, the effects of *in situ* reduction of bulk MoO_2 to MoO_{3-x} on the activity and selectivity of propene oxidation occurring over these materials have also been investigated.[19] These latter measurements postulate that oscillations in the oxidation of propene at high temperatures are due to an identifiable variability in the degree of distortion observed in the active MoO_6 octahedra.

However, it is only more recently that *a priori* structure determination, in tandem with detailed kinetic data pertaining to the chemistry of supported, catalytically relevant systems, has been derived directly from EDE.[17] Fig. 13 shows k^3 weighted Rh K edge EXAFS derived in two seconds from the starting and end points in the reversible reaction of a supported $Rh^I(CO)_2$ (derived from vapour deposition of $[Rh(CO)_2Cl]_2$ to hydroxylated Al_2O_3) with NO, together with the calculated fit derived from multiple scattering, spherical wave analysis. Analysis of these spectra leads to quantitative structural determinations. The starting Rh species is confirmed as a supported $Rh(CO)_2$ species and the EDE confirms the retention of the Rh–Cl bond in this species and the formation of a single Rh–OAl linkage. The product of this species' reaction with NO is determined to be a 'bent', square planar NO^- species (∠RhNO ~ 134°). Again the Rh–Cl bond is retained in this conversion but the single Rh–OAl linkage augmented by a second that compensates for the net loss of a ligand by the replacement of two CO species with a single NO.

The total data acquisition time for these spectra was *ca.* 2 s, though detector readout limited sequential spectrum acquisition to one every 7.2 s. By acquiring the EDE spectra synchronous to a gas switch from He to a dilute He–NO mix, the reaction may be followed *in situ* and as a function of temperature. Fig. 14 shows the temporal variations observed in both white line and an EXAFS feature observed to increase and diminish in intensity during the reaction, as well as the observed variation in the production of CO measured using a downstream mass spectrometer. These data allowed us to show that this reaction proceeds *via* the transient formation of an intermediate species (from the temporal displacement of the CO production from the changes in EXAFS) that subsequently converts to the product nitrosyl at a slower rate. As the EXAFS, especially at low reaction temperatures, appears not to change (despite the obvious initial reaction) we are also able to infer that the local order and symmetry of this intermediate are very close to those derived from the starting material. Further, from other mass spectroscopic considerations, it can be suggested that the intermediate species is a supported $[Al(O)Rh(NO)_2Cl]$ species. This subsequently decomposes to yield N_2O and, with the addition of a third NO from the gas phase, forms the final 'bent' nitrosyl species. Further, the data shown in Fig. 14 can be kinetically modelled using a simple two-step reaction sequence[15] to reveal the kinetic parameters intrinsic to each step in the conversion.

This example, along with the others referred to above, shows well the types of measurement for which EDE is far better suited than currently available QEXAFS. However, as has been mentioned above, when processes are relatively slow (such as in refs. 16 and 40–42) QEXAFS may produce the more extensive data set and therefore a more detailed local order determination.

4 Future developments and outlook

A comparison between Figs. 1, 6b, and 13 shows that quantitative structural and kinetic data can be restored for a variety of systems and using different approaches to time-resolved EXAFS. From Fig. 1, the application of standard EXAFS[1] yields a data point frequency for kinetic determinations of ~2.8×10^{-4} s^{-1}; the QEXAFS shown in Fig. 6b[34] one

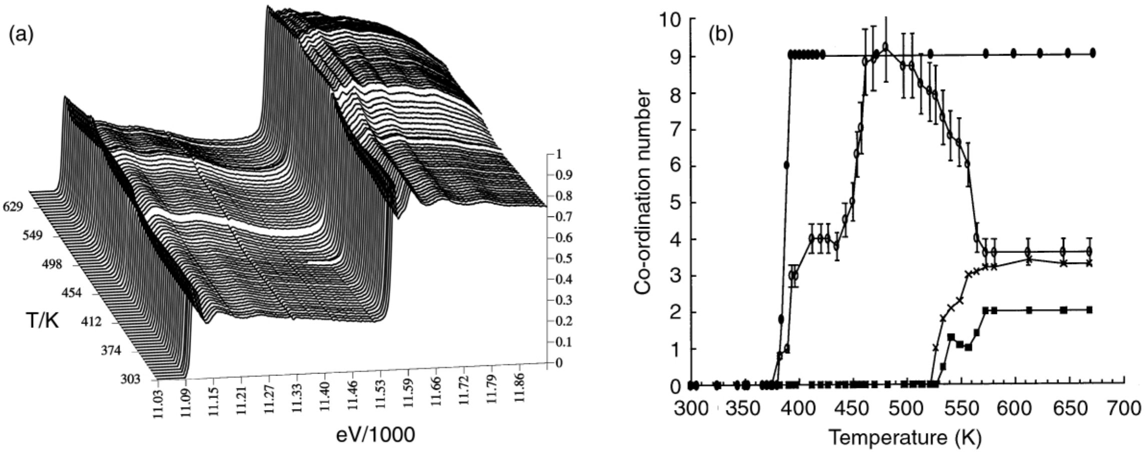


Fig. 12 (a) EDEXAFS spectra for the Pt L_{III} and Ge K edges in the temperature range 298–670 K. Each spectrum has a total acquisition time of 8 seconds (1000 acquisitions at 8 ms per acquisition). (Reproduced from ref. 15.) (b) Temporal variation in Pt–Pt and Pt–Ge coordination derived from analysis of EDE derived during the reduction of $Pt(acac)_2$ and $Pt(acac)_2$–$GeBu_4$–H_1SiO_2supported catalyst precursors. Open circles Pt–Pt, $Pt(acac)_2$; filled circles Pt–Pt, $Pt(acac)_2$–$GeBu_4$; crosses Pt L_{III}(Ge), Pt–Pt, $Pt(acac)_2$–$GeBu_4$; filled squares Ge_K(Pt), Pt $Pt(acac)_2$–$GeBu_4$. Representative errors in co-ordination are shown in one case. (Data drawn from refs. 39 and 15.)

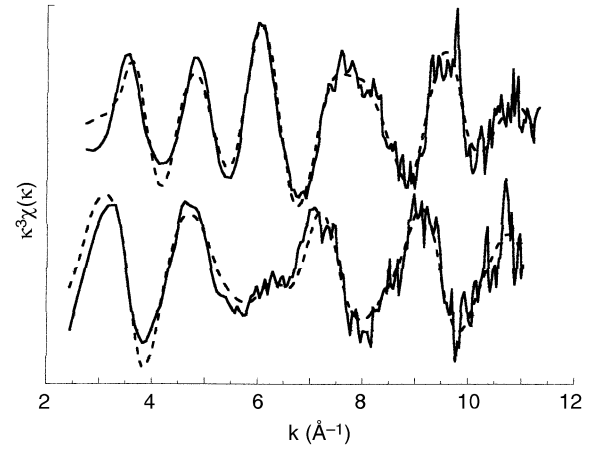


Fig. 13 k^3 Weighted EDEXAFS derived from (a) $Rh(CO)_2Cl$ species supported upon hydroxylated Al_2O_3 and (b) from the nitrosyl adduct of the reaction of that species with NO. The acquisition time for each spectrum is ~2 s. (Reproduced from ref. 17 by permission of the American Chemical Society.)

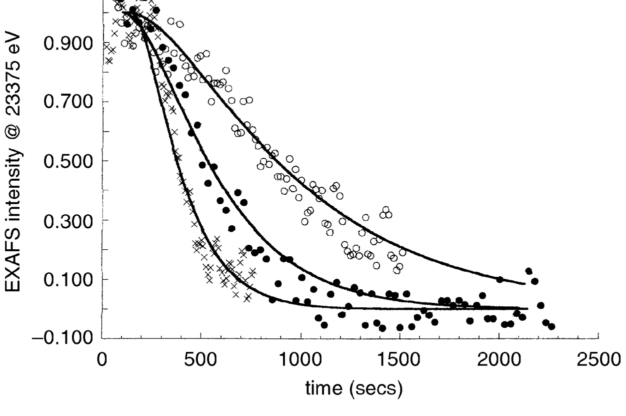


Fig. 14 Temporal dependence of CO evolution in the gas phase during a switch from He to NO gas flows and the corresponding variation observed in white line/EXAFS (at 155 eV post edge) intensity. The temporal mismatch between the two observables indicates the formation of an intermediate species having a local order akin to that of the starting Rh species (see text). (Reproduced from ref. 17 by permission of the American Chemical Society.)

of ~2×10^{-3} s^{-1}; the last example[17] (by EDE) ~0.14 s^{-1}; and others[21,32,33], *ca.* 1 s^{-1}. As such, we can gauge that the capacity for EXAFS measurements to be used in quantitative structural-kinetic investigations in a wide range of chemical areas has increased by factors in the region of 100–3000 in the last 10 years, greatly widening the scope of such investigations.

In terms of QEXAFS the time regimes that may be accessible using this approach will depend greatly on the practical limitations and reliability of fast monochromator movement. Frahm and co-workers have recently demonstrated the use of piezo based systems capable of sampling near edge structure in milliseconds.[2] They have also shown that with direct high speed readout from ionization chambers, energetic windows of *ca.* 3 keV can be collected in ~ 140 seconds;[45] it will be interesting to see how this new technology may be applied to obtain EXAFS from dynamic chemical systems. The advent of third generation, high brilliance beamlines, and the capacity for fluorescence detection inherent to QEXAFS will continue to make this the method of choice for time-resolved studies of extremely dilute systems. As such, intrinsically dilute arenas, such as those involving biological molecules (*e.g.* enzymes[46]), as well as adsorbates on single crystal samples (quick surface EXAFS), are obvious areas for development.

EDE has always given the promise of sub-millisecond time resolution. The realisation of this promise will depend not only on the development of more stable (spatially and energetically) X-ray sources but also on the continuing improvement in detector technology and experimental methodology. In the former case the past ten years have seen considerable advancement and the recent and ongoing development of silicon microchip based (XSTRIP) detectors[47] holds great promise for a new generation of robust, linear, and extremely fast detector systems.

The biggest challenge in respect of realising the potential of EDE is however the development of methodologies for circumventing the less than desirable normalisation procedures that are currently utilised, which make the experiment extremely susceptible to the vagaries of the X-ray source and heighten the requirements for sample uniformity. The resolution of this problem, in tandem with the emergence of new detector technology, will mean that, sub-millisecond, kinetic, and simultaneously structurally determining, experiments will become possible in the relatively near future.

Homogeneous liquid phase chemistry, using stopped and continuous flow methodologies and millisecond resolved EDE, are the most obvious systems in which this possibility will be first demonstrated and brought into more general usage. In the solid state, and in heterogeneous systems, it has already been shown that the extreme sample uniformity issues attendant with EDE can be overcome, and as such there seem to be no intrinsic reasons why these areas of chemical research should not also benefit from such a timescale.

The genesis of combined *in situ* and simultaneous experiments, providing complementary information, can only enhance the degree of understanding obtained from any dynamic system.

The most notable absentees from the list of techniques that have been integrated with time-resolved EXAFS are spectroscopies such as ultraviolet and infra-red. Both of these techniques are powerful probes of functionality and electronic structure. Indeed, correlation of QEXAFS/XRD and *ex situ*, static, infra-red measurements has already been shown to yield a significantly higher degree of characterisation than any of the three techniques applied on their own. The study of the active site in CoAlPO-18 solid acid catalysts for the conversion of methanol to light olefins by Thomas *et al.*[48] being a prime example of such a combined approach. Further, modern IR and UV instruments may be operated with a significant time resolution (ms).

Following this lead,[48] the combination of time-resolved EXAFS with Fourier transform infra-red spectroscopy (in both transmission and diffuse-reflectance modes) is currently being developed within our group. The ultimate aim of this development being the attainment of both structural and vibrational spectroscopic information from a given system, simultaneously and with a time resolution of *ca.* 10–100 ms.

5 Summary and conclusions

Time-resolved EXAFS in all it forms, and either alone or in combination with adjunct techniques, is an extremely useful and powerful probe of a diverse range of chemical systems. Moreover, beamlines supporting time-resolved studies are becoming more widespread (see Addendum) and are being continually developed. Timescales of a few seconds to a minute are becoming more and more routine, affording the potential researcher with considerable experimental scope.

The prospects for making structurally deterministic measurements with timescales of 1–50 milliseconds, both alone and in tandem with equally fast and complementary techniques, are extremely good. Indeed, it may quite reasonably be expected that these sorts of timescales will themselves become routine, shedding new light upon important chemical problems existing within a wide range of areas and disciplines.

There seems little doubt that widening areas of application, combined with increasing data quality, and sub-second timescales will produce new, significant, and sometimes unexpected, insights into many old and new areas of chemistry.

6 Addendum

Table 1 Beamlines supporting time-resolved EXAFS facilities

	QEXAFS	Dispersive EXAFS
CLRC Daresbury	Stations 9.3, 9.2, 7.1, 16.5	Station 9.3
ESRF Grenoble	ID 26, BM 29	ID 24
Hasylab	BW1, D4, X1(ROMO II)	
LURE		DCI-DW11A
Photon Factory		BL-9C
Brookhaven NLS	X9B	
APS, Chicago	DND-CAT, BioCAT	SRI-Cat (1-BM-B)
Stanford SRL	10-2	

7 Acknowledgements

The authors are indebted to Drs Sakura Pascarelli, Sofia Diaz Moreno, and Thomas Neisius of the ESRF (Grenoble, France); Drs Fred Mosselmans and Ian Harvey, and Mr Guiseppe Salvini, of the CLRC Daresbury Laboratory; and Dr Andrea Russell, University of Southampton. We would also like to take this opportunity to thank Bruce Hancock, Mike Caplin, Melanie Hill, and John James (University of Southampton), along with Sebastian Pasternak and Ralph Wiegel (ESRF), whose technical skills and patience have contributed significantly to our own research in this area. We would like to acknowledge the financial support of the EPSRC under the *Catalysis and Chemical Processes* initiative. The ESRF, Grenoble, France, and CLRC Daresbury laboratory, UK are also thanked for access to facilities.

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