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# In situ probing of the near-surface properties of heterogeneous catalysts under reaction conditions: An introduction to total electron-yield XAS

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## Abstract

Over the last two years, our understanding of gas-flow total electron-yield (TEY) detection for in situ X-ray absorption spectroscopy (XAS) has rapidly progressed. A short summary of recent developments is presented with a particular view to applications in the field of heterogeneous catalysis. For the first time, true in situ TEY data (of Ni- and Cu-based systems) acquired in reactive gas atmospheres and at pressures up to 40 atm are presented. The salient physical principles underlying the formation of the TEY signal are briefly introduced. Previously unexplained 'self-absorption' distortions in the TEY signal are explained by photoelectrons excited by fluorescent photons. The possibilities and limitations of in situ TEY XAS studies are highlighted.

**Keywords:** XAFS; EXAFS; SEXAFS; Total electron yield; In situ; Probing depth

## 1. Introduction

Ever since its development between the 1950s and the early 1970s, X-ray absorption fine-structure (XAFS) spectroscopy has been an important technique for fundamental studies of the morphology and electronic structure of heterogeneous catalysts [1–4]. Two modes of X-ray absorption spectroscopy, transmission and fluo-

rescence yield (FY) detection, have almost exclusively been applied to probe the structure of catalytically active materials. The former detection method determines the absorption coefficient directly as the logarithmic ratio between the intensity of the incoming X-ray beam and the fraction transmitted through the suitably thin and/or dilute sample. The latter makes use of the fact that the X-ray absorption edge spectrum is determined by the cross sections for photoionization of the atomic core levels, so that the number of characteristic fluorescent photons

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emitted in the decay of the X-ray induced core holes is proportional to the absorption coefficient. Both techniques are intrinsically bulk probes because the detected flux of X-ray photons penetrates matter typically by distances on the order of a few micrometers [5]. The lack of surface sensitivity is not a severe drawback if the catalytically active phase is dispersed enough to exhibit a sufficiently high fraction of reactive surface atoms. Transmission and FY XAFS spectroscopy have therefore predominantly been applied to catalysts with particle sizes well below 100 Å. Both techniques are unsuitable for studies of surface and near-surface processes in heterogeneous catalysts that are optically too dense, of low dispersion, or crystalline on a macroscopic scale. X-ray absorption studies of catalytic processes on the surface of these materials require an enhanced surface sensitivity. Detection of the total electron-yield (TEY) is the most straightforward method to approach this objective (for optically flat samples, such as single crystalline model catalysts, reflectivity measurements close to the critical angle for total reflection are a much more surface sensitive alternative).

In analogy to FY detection, TEY measurements rely on the proportionality between the X-ray absorption coefficient and the number of Auger electrons emitted during the core hole decay. The TEY experiment consists simply in measuring the total photoinduced ('drain') current from the sample while maintaining a moderate electric field (potential differences of 60–100 V are sufficient) over the sample using a biased counterelectrode. In the past, TEY detection has almost exclusively been applied *under vacuum conditions*, most commonly in studies of surface adsorbates, but also for investigations of thin films and of the near-surface properties of bulk samples. Surprisingly little attention was devoted to TEY measurements in *gaseous environments*, despite the fact that the collection of TEY data in a He-filled detector was described as long ago as 1979 [6]. Only over the last few years has gas-flow TEY detection (sometimes

also called 'conversion electron-yield' or CEY detection [7,8]) been adopted more routinely at synchrotron laboratories [9–14].

All gas-flow TEY studies reported in the literature have employed pure He as the detector gas. Experiments with catalytically relevant gases, moist environments and gas mixtures (including air) have not been reported. We have therefore carried out a programme of explorative work to assess whether such measurements are possible, and under which conditions the collected X-ray absorption information is reliable. From these studies, gas-flow TEY detection emerged as a versatile, simple and inexpensive method for the study of solid-state structures in reactive gas environments. The main aim of this paper is to attract the attention of researchers in the field of heterogeneous catalysis to this new in situ XAS technique, and to provide an entry point from which the current state-of-the-art is accessible to those who are not specialists in the field of XAFS. We will present spectra which cover a wide range of reaction conditions under which in situ TEY spectra have been successfully acquired. In their selection we have included several unusual cases where artificial distortions intrinsic to TEY detection are visible in the X-ray absorption spectrum. This particular selection was made because the underlying causes have so far remained unexplained in the literature [9] and, as with transmission and FY detection, knowledge of potentially complicating factors is an indispensable ingredient for meaningful interpretations of the acquired XAFS data. We will show that the distortions which are sometimes observed in TEY data are generally much less severe than those expected for FY- and transmission detection under comparable conditions. Gas-flow TEY detection thus opens up new possibilities for XAS investigations of a class of samples which was hitherto difficult, if not impossible, to study by other detection methods: namely specimens containing X-ray absorbers in high concentration and/or in an undispersed form.

## 2. Experimental

All experimental data were collected on stations 7.1, 8.1 and 9.2 at the synchrotron of the CCLRC Daresbury Laboratory (Warrington, UK) operating at an energy of 2 GeV with storage ring currents between 120 mA and 240 mA. Monochromatic beams (energy resolution approximately 1.4 eV–2 eV) were obtained with double Si(111) and Si(220) crystal monochromators with the crystals kept detuned at 50% of maximum reflectivity throughout each spectrum to suppress the transmission of higher harmonics. If not indicated otherwise, all spectra were collected at room temperature. The designs of the in situ TEY detectors used for this work have previously been published [15], except for a high-pressure (accessible range up to 80 atm) TEY cell which is described elsewhere [16,17].

## 3. Formation of the TEY and surface sensitivity of the gas-flow signal

The absorption of X-ray photons induces atomic core holes which decay in a cascade of radiationless and radiative transitions, leading to the emission of Auger electrons, secondary electrons (here defined as electrons with energy below 40 eV) and a comparatively small number of low-energy photoelectrons from the sample [8,9,18]. The formation of the TEY signal in a K-edge experiment is schematically illustrated in Fig. 1. Most kinetic energy is carried by the KLL Auger electrons, while LMM, MVV and other Auger electrons have energies which are approximately one (LMM), two (MVV, not shown in Fig. 1) or more (higher shells, also omitted from Fig. 1) orders of magnitude lower. In addition, fluorescent photons emitted in the radiative decay of the primary core holes can excite an additional contribution of energetic photoelectrons from less tightly bound core levels (the special role of these photoelectrons will be considered in Section 4 below). The KLL Auger electrons, which have the largest kinetic

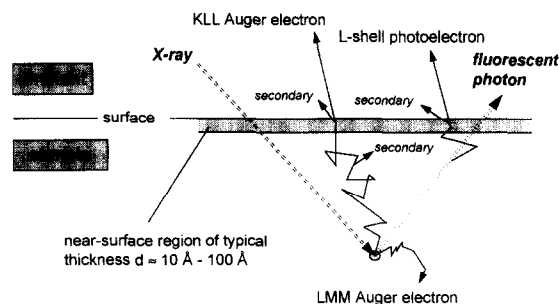


Fig. 1. Schematic illustration of the channels contributing to the TEY signal.

energy, travel the longest distance through the sample and thus dominate the depth information contained in the TEY [8,9,18]. The signal contributions due to secondary and higher order Auger decay events (LMM, MVV, etc.) are, for vacuum TEY detection, usually non-negligible [8,9]. For gas-flow detection they are insignificant, because charge multiplication in the ambient gas via impact ionization ('pair formation') weights the signal strongly towards the more energetic TEY contributions [8,18]. It should be noted that the average energy loss per pair formation event is almost independent of the energy of the impacting electron and varies little as a function of gas species [19]. Helium marks the upper end of the scale of pair formation losses (42.3 eV), while most other gases exhibit values in the range between 10 eV and 32 eV [19,20]. The insensitivity of the pair formation losses to both the gas species and the electron energy ensures a linear gas-flow TEY response to the X-ray absorption coefficient over a wide range of edge energies and gas compositions.

Energetic electrons created in the sample generate, through inelastic interactions, secondary electrons along their trajectories (Fig. 1). The low-energy secondary electrons escape only from a shallow region below the surface, the thickness of which being typically less than some 100 Å (note, however, that it can be significantly higher for some exceptional materials [21–23]). The magnitude of the secondary electron fraction in the TEY depends critically on the number of energetic electrons which

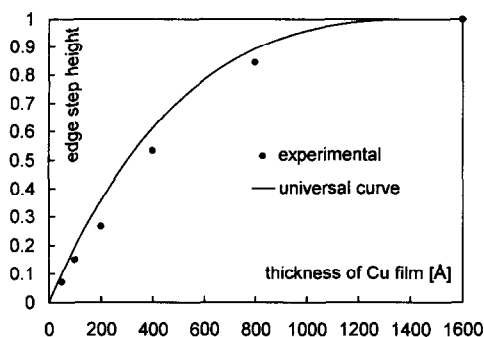


Fig. 2. He gas-flow signal attenuation function for the Cu K-edge TEY of metallic Cu (full line) calculated with the 'universal curve' derived in Ref. [18] compared to experimental signal attenuation results for Cu films deposited on quartz (data taken from [13]).

traverse the near-surface region [18,24–26]. The depth information carried by the secondary yield does therefore closely follow that carried by the energetic electrons escaping from the sample. However, because secondary electrons do not carry enough energy to undergo charge multiplication in the gas phase, they are not amplified under gas-flow conditions and can, in a good first approximation, be entirely neglected in treatments of the depth information carried by the TEY.

Because the depth information in the gas-flow TEY should simply be determined by the most energetic Auger electrons, attenuation functions for these electrons have recently been calculated for a wide range of materials (including compounds) as a function of energy. Fast Monte-Carlo algorithms [18,27] for the simulation of the electron trajectories yielded results that are in good agreement with available experimental TEY attenuation data for absorption edges in the keV range [18]. A simple analytical expression was derived which describes the depth information in the TEY signal solely in terms of the maximum Auger electron penetration range, a quantity which can be readily calculated for any electron energy if composition and mass density of the sample are known [18]. The resulting 'universal curve' achieves at least semi-quantitative agreement with all gas-flow TEY attenuation data reported in the literature.

A representative example is given in Fig. 2 for the case of Cu metal K-edge (8.98 keV) data.

#### 4. TEY contributions excited by fluorescent photons

If the absorber atoms are highly concentrated in the sample and characterized by a sufficiently high probability ( $> 30\%$ ) for fluorescent decay, then the information in the FY signal becomes visible in the TEY via excitation of energetic photoelectrons from the sample (cf. Fig. 1) and in the detector gas (provided the latter is sufficiently absorbing). Tabulations of relevant radiative and non-radiative decay rates and X-ray mass absorption coefficients are given in Refs. [28] and [5], respectively. The ensuing cross-coupling between the FY and the TEY channels is an unwanted effect because the FY signal from non-dilute samples carries inaccurate X-ray absorption information. These spectral distortions in FY spectra are commonly termed 'self-absorption' effects [29–31]. Their presence is most readily identified after normalization of the spectrum to the edge step height. When 'self-absorption' distortions are present, then the amplitude of pre-edge features appears enhanced, while all XAFS amplitudes in the post-edge region are artificially reduced. The dependence of the 'self-absorption' effect on experimental parameters is quite well understood so

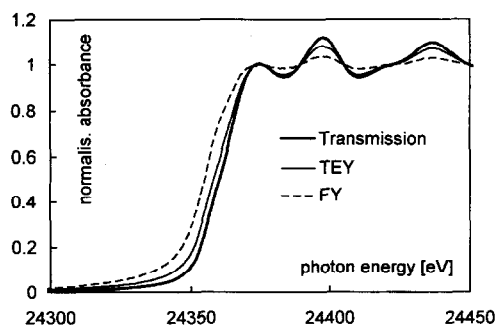


Fig. 3. Pd K-edge absorption spectra of a 125  $\mu\text{m}$  Pd foil measured via its FY and TEY compared to the transmission spectrum of a 8  $\mu\text{m}$  Pd foil.

that distortions in FY spectra can in principle be corrected for if the sample composition and the angles of X-ray incidence and fluorescence detection with respect to the sample during data collection are known [29,30]. However, an in-corrigeable side effect is that the counting statistics for the FY signal do also deteriorate so that the signal-to-noise ratio of the spectrum worsens considerably. A particularly drastic example for ‘self-adsorption’ distortions is given in Fig. 3, which compares an accurate K-edge spectrum of Pd metal to the FY- and TEY-spectra of an unsuitably thick Pd metal specimen. The characteristic ‘self-absorption’ distortions in the FY spectrum are immediately visible. Similar, albeit weaker, deviations from the transmission spectrum are also evident in the TEY data. This result is not unexpected because 82% of the Pd K-holes decay radiatively by emission of a fluorescent photon. As shown elsewhere, the TEY fraction due to fluorescence-excited L-shell photoelectrons can be calculated quite accurately, allowing the prediction (and correction) of the amplitude distortions in TEY spectra to within a few % accuracy.

Figs. 4 and 5 illustrate two further cases of coupling between the FY and the TEY signal. In Fig. 4, several near-edge spectra of a Ni wafer covered by 220 Å of NiO are presented. The spectra were collected sequentially under

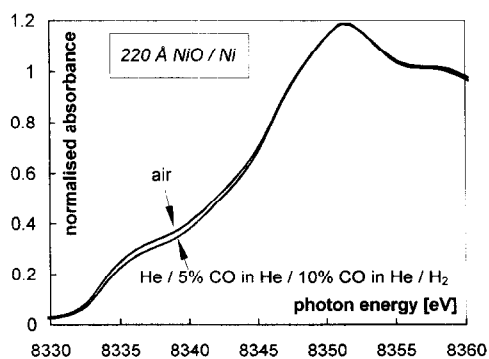


Fig. 4. Ni K near-edge spectra of a Ni wafer covered by 220 Å of NiO as a function of gas composition. The lower group of superimposed spectra represents data taken in 100% H<sub>2</sub>, 100% He, 5% CO in He and 10% CO in He. The somewhat offset, upper line corresponds to the X-ray absorption spectrum measured in air.

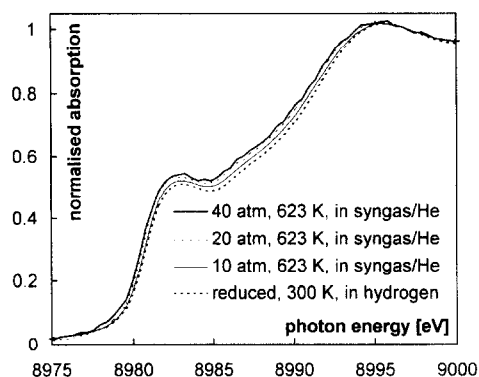


Fig. 5. Comparative near-edge spectra of a reduced Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> methanol synthesis catalyst as a function of gas composition, pressure and temperature. See caption in the inset of the figure for assignment of measurement conditions.

strictly identical conditions — with the exception of the detector gas composition. Only the spectrum collected in air exhibits a ‘self-adsorption’ distortion, while the spectra collected in H<sub>2</sub>, He and CO/He mixtures are indistinguishable. The reason for the deviation between the TEY response in air and the other gases is the higher absorption coefficient for the Ni K-fluorescence in air [5]. Similarly, Fig. 5 contains Cu K-edge absorption spectra of a commercial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> methanol synthesis catalyst [11] as a function of gas composition, temperature and pressure. The dotted spectrum was taken at room temperature in 100% H<sub>2</sub> after reduction of the catalyst at 250°C. The other three spectra were collected under *methanol synthesis conditions* in a gas mixture containing 1% CO, 1% CO<sub>2</sub>, 8% H<sub>2</sub> and 90% He at 250°C and at 10 atm, 20 atm and 40 atm total pressure. Closer inspection of the spectra reveals that a small, but significant ‘self-absorption’ distortion develops with increasing pressure which is caused by fluorescence-induced ionization events in the gas phase. The small spectral changes observed as a function of synthesis gas pressure are therefore not an indication for genuine changes of the catalyst, which remains entirely in a metallic state under synthesis conditions.

## 5. Possibilities and limitations

The spectra in Figs. 4 and 5 illustrate a wide range of in situ conditions compatible with TEY detection and of direct relevance to catalytic studies. In addition to the gas compositions referred to in these figures we have also performed measurements in He-based mixtures containing  $N_2O$ ,  $CO_2$  and alkanes, as well as in moist environments such as a methanol saturated stream of He (Fig. 6). Given the variety of gas compositions investigated, it appears unlikely that there are gas environments which are entirely unsuitable to TEY detection. In moist gas environments the possibility exists that condensation occurs in the vicinity of the TEY detection electrodes. We observed repeatedly that moisture from a methanol saturated atmosphere at room temperature caused a fluctuating DC current between sample and biased collector which was approximately two orders of magnitude larger ( $10^{-7}$  A) than typical TEY sample currents. This short-circuit current disappeared entirely upon heating the detector to temperatures above the evaporation point of the condensate.

The work summarised in Section 3 shows that the depth probed by TEY detection is a strong function of absorption edge energy, sample composition and density. The probing depth varies between a few 10 Å at sub-keV energies

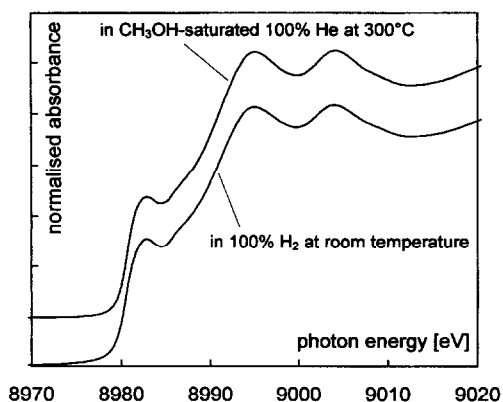


Fig. 6. Near-edge spectra of pure, dispersed Cu in  $H_2$  and in a methanol-saturated He atmosphere at  $300^\circ C$ .

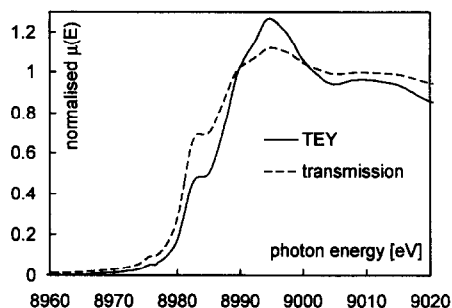


Fig. 7. Comparison between a transmission spectrum of CuO which is severely distorted by 'thickness' effects and the TEY spectrum of the same sample.

and several 1000 Å for X-ray energies above 10 keV. Gas-flow TEY detection is therefore best categorized as a bulk probe with enhanced near-surface sensitivity. For gas-solid reactions which involve changes in the subsurface region of the sample, the TEY technique could yield information on the structural changes in the near-surface region. An alternative way to obtain true surface information by gas-flow TEY detection is to study thin and ultrathin films of X-ray absorbers adsorbed on a support containing different atomic species — in analogy to traditional SEXAFS experiments [32–34].

Its near-surface sensitivity makes the TEY technique much less susceptible, albeit not entirely immune (vide supra), to spectral distortions, due to the 'self-absorption' and 'thickness' effects, than FY and transmission detection of data from non-dispersed, concentrated and/or macroscopically heterogeneous samples [35]. All spectra in Figs. 4–6 could not have been acquired by FY or transmission detection without destroying the integrity of the original samples by grinding or milling, and dilution in a matrix (usually boron nitride) to achieve the required low absorber concentrations. Moreover, even if transmission and FY samples are carefully prepared, the successful collection of accurate data is not guaranteed. This is illustrated for a particularly severe case in Fig. 7 which contains the near-edge transmission spectrum of CuO (99.9% pure, JM Chemicals, UK) which had been carefully ground in a mortar

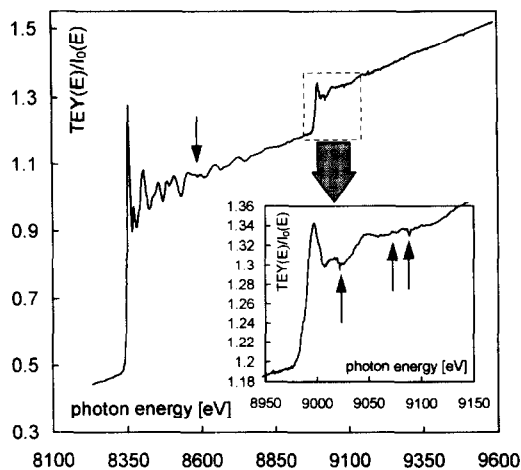


Fig. 8. Raw TEY data for the calcined precursor to an unsupported Cu/Ni catalyst containing 95 at% Ni and 5 at% Cu.

and dispersed in boron nitride to achieve an edge step height of  $\Delta\mu(E_0) \cdot x = 0.5$ . The distorted transmission spectrum shows that the heterogeneity of the diluted sample was still large enough to result in a strong ‘thickness’ effect (Fig. 7). We encountered similar problems with samples of NiO, Cu<sub>2</sub>O and pure transition metal powders. TEY detection circumvents these problems readily, as the pure sample is simply placed on the conducting sample support. Indications for small ‘self-absorption’ distortions, as observed in the TEY spectra of the metallic samples in Figs. 3–5, have so far not been

identified in any TEY spectrum of a compound. Note also that conductivity of the sample is not essential for TEY measurements because charge neutrality can be maintained by the secondary gas phase charges excited by energetic electrons. Thus, we have measured the TEY spectra of macroscopically thick coatings of insulators such as Cr<sub>2</sub>O<sub>3</sub> without any charging problems. Likewise, we measured the TEY signal from the front surface of a 0.5 cm thick sample of pure ZnO supported on a Ta foil.

A remarkable feature of gas-flow TEY detection is the high signal-to-noise quality of the spectra which is routinely achieved when care is taken to shield detector and connections to the signal preamplifier from environmental electromagnetic noise. The most common problem is electromagnetic interference from resistive heaters in the in situ cell. Their effect is seen particularly in the spectra of Fig. 5 which were acquired at elevated pressures. In the absence of electromagnetic noise, data collection times with a stepper motor driven monochromator are of the order of 30 min or less if the absorber concentration in the sample is higher than approximately 20 at%–30 at%.

Generally, for X-ray fluxes of the order of  $10^{11}$  photons/s the noise level in the data is limited by spectrometer- or detector circuit

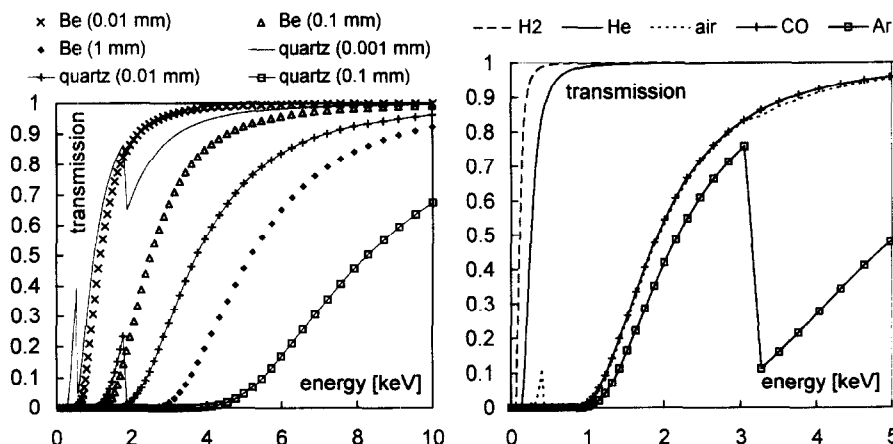


Fig. 9. Left diagram: transmission of Be (0.01 mm, 0.1 mm, 1 mm) and quartz (0.1  $\mu$ m, 1  $\mu$ m, 10  $\mu$ m) as a function of photon energy. Right diagram: transmission of a pathlength of 1 cm filled with H<sub>2</sub>, He, air, CO and Ar as a function of photon energy. Absorption coefficients taken from Ref. [5].

noise, but not by the counting statistics. However, the signal quality deteriorates rapidly when the concentration of the element of interest decreases below 5 at%–10 at%, especially when the absorption edge of the minor component ‘rides’ on the absorption edge spectrum of the major sample constituent. This is illustrated in Fig. 8 which contains raw TEY data for the calcined precursor of an unsupported Cu/Ni alloy steam reforming catalyst containing 95 at% Ni and 5 at% Cu. The strong background absorption due to the Ni K-edge on the pre-edge region of the Cu K-edge amplifies all spectrometer noise considerably. Particularly pronounced are Bragg diffraction glitches (indicated by black arrows) in the monochromator transmission function, which are sustainably small relative to the intensity of the Ni XAFS features, but large compared to the small Cu edge step (see inset of Fig. 8). However, even when a second absorption edge is absent from the pre-edge region of a small edge of interest, the background signal due to ionization events in loosely bound orbitals of the sample can be substantial. For small concentrations of absorbers, FY detection is the preferred detection mode because of its better counting statistics [36].

Finally, the spectral region accessible by in situ TEY XAS is limited only at lower energies, mostly by the transmission of the X-ray window materials and the lengths of the gas paths which the incident X-ray beam has to traverse to reach the sample. How such design choices determine the performance of the cell is illustrated in Fig. 9. In the left diagram, the transmission characteristics of two window materials used in our own work are compared as a function of material thickness. It is seen that quartz window thicknesses well below 0.01 mm and Be windows below 0.1 mm thickness are required to allow experiments with even moderately ( $E \approx 1\text{--}2$  keV) soft X-ray energies. Similarly, assuming a pressure of 1 atm and a gas path between window and sample of 1 cm, CO, Ar, and air would all be too absorbing to permit measurements at absorption edges below 1.5 keV. Con-

siderable dilution of these gases with He or severe shortening of the gas path between window and sample to well below 1 mm would be necessary to achieve a good gas transmission. These considerations demonstrate how difficult the construction of an in situ TEY XAS cell for measurements in the soft and ultra-soft X-ray region would be. However, the development of such equipment is nevertheless desirable because it would permit the study of adsorbed low- $Z$  atoms under reaction conditions. The FY setup developed at Brookhaven over the last decade has been a first step in this direction [37–39]. In the meantime, the practical low-energy limit to the application of gas-flow detection is mainly determined by the availability of XAFS beamlines to which an in situ gas-flow TEY cell can be attached: in most cases, this limit is close to photon energies in the range between 2 keV and 4 keV.

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### References

- [1] R.A. van Nordstrand, *Adv. Catal.* 12 (1960) 149.
- [2] J. Evans, in: *Catalysis*, Vol. 8, The Royal Society of Chemistry, Cambridge, 1989, p. 1.
- [3] R. Prins and D.C. Koningsberger, in: D.C. Koningsberger and R. Prins (Eds.), *X-Ray Absorption. Principles, Applications, Techniques of EXAFS, SEXAFS and XANES* (Chemical Analysis), Vol. 92, Wiley, New York, Chichester, Brisbane, Toronto, Singapore, 1988, p. 321.
- [4] P. Johnston and P.B. Wells, *Radiat. Phys. Chem.* 45 (1995) 393.
- [5] B.L. Henke, E.M. Gullikson and J.C. Davis, *At. Data Nucl. Data Tables* 54 (1993) 181.
- [6] N.J. Shevchik and D.A. Fischer, *Rev. Sci. Instrum.* 50 (1979) 577.
- [7] C.E. Bouldin, R.A. Forman and M.I. Bell, *Phys. Rev. B* 35 (1987) 1429.



- [8] S.L.M. Schroeder, G.D. Moggridge, R.M. Ormerod, T. Rayment and R.M. Lambert, *Surf. Sci. Lett.* 324 (1995) L371; *Surf. Sci. Lett.* 329 (1995) L612.
- [9] A. Erbil, C.S. Cargill, III, R. Frahm and R.F. Boehme, *Phys. Rev. B* 37 (1988) 2450.
- [10] W.T. Elam, J.P. Kirkland, R.A. Neiser and P.D. Wolf, *Phys. Rev. B* 38 (1988) 26.
- [11] G.D. Moggridge, T. Rayment, R.M. Ormerod, M.A. Morris and R.M. Lambert, *Nature* 358 (1992) 658.
- [12] K.M. Kemner, Z. Wang, R.A. Mayanovic and B.A. Bunker, *Nucl. Instrum. Methods B* 71 (1992) 345.
- [13] T. Girardeau, J. Mimault, M. Jaouen, P. Chartier and G. Tourillon, *Phys. Rev. B* 46 (1992) 7144.
- [14] J. Pant and T.M. Hayes, *Rev. Sci. Instrum.* 65 (1994) 3389.
- [15] G.D. Moggridge, S.L.M. Schroeder, R.M. Lambert and T. Rayment, *Nucl. Instrum. Methods B* 97 (1995) 28.
- [16] S.L.M. Schroeder, G.D. Moggridge, R.M. Lambert and T. Rayment, in preparation.
- [17] S.L.M. Schroeder, Ph.D. thesis, University of Cambridge (1996).
- [18] S.L.M. Schroeder, *Solid State Commun.* 98 (1996) 405.
- [19] B. Sitar, G.I. Merson, V.A. Chechin and Y.A. Budagov, *Ionization Measurements in High Energy Physics (Springer Tracts in Modern Physics)*, Vol. 124, Springer-Verlag, Berlin, 1993.
- [20] K. Kleinknecht, *Detectors for Particle Radiation*, Cambridge University Press, Cambridge, London, New York, 1986.
- [21] S. Hanany, P.S. Shaw, Y. Liu, A. Santangelo, P. Kaaret and R. Novick, *Phys. Rev. B* 48 (1993) 701.
- [22] B.L. Henke, J.P. Knauer and K. Premaratne, *J. Appl. Phys.* 52 (1981) 1509.
- [23] H. Seiler, *Z. Angew. Phys.* 22 (1967) 249.
- [24] D.C. Joy, *Monte Carlo Modelling for Electron Microscopy and Microanalysis (Oxford Series in Optical & Imaging Sciences)*, Vol. 9, Oxford University Press, New York, 1995.
- [25] S. Luo and D.C. Joy, *Scanning Microsc.* 4 (1990) 127.
- [26] D.C. Joy, *J. Microsc. Oxford* 147 (1987) 51.
- [27] R. Browning, T.Z. Li, B. Chui, J. Ye, R.F.W. Pease, Z. Czyzewski and D.C. Joy, *J. Appl. Phys.* 76 (1994) 2016.
- [28] M.O. Krause, *J. Phys. Chem. Ref. Data* 8 (1979) 307.
- [29] L. Tröger, D. Arvanitis, K. Baberschke, H. Michaelis, U. Grimm and E. Zschech, *Phys. Rev. B* 46 (1992) 3283.
- [30] J. Goulon, C. Goulon-Ginet, R. Cortes and J.M. Dubois, *J. Phys. Paris* 43 (1982) 539.
- [31] T.M. Hayes and J.B. Boyce, *Solid State Phys.* 37 (1982) 173.
- [32] P.H. Citrin, *Surf. Sci.* 299–300 (1994) 199.
- [33] J. Haase and A.M. Bradshaw, in: R.Z. Bachrach (Ed.), *Synchrotron Radiation Research: Advances in Surface and Interface Science*, Vol. 2, Issues and Technology, Plenum Press, New York, 1992, p. 55.
- [34] J. Stöhr, in: D.C. Koningsberger and R. Prins (Eds.), *X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*, Wiley, New York, Chichester, 1988, p. 443.
- [35] S.M. Heald, in: D.C. Koningsberger and R. Prins (Eds.), *X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS and XANES*, Wiley, New York, Chichester, Brisbane, Toronto, Singapore, 1988, p. 87.
- [36] J. Jaklevic, J.A. Kirby, M.P. Klein, A.S. Robertson, G.S. Brown and P. Eisenberger, *Solid State Commun.* 23 (1977) 679.
- [37] J.L. Gland, in: R. Vanselow and R. Howe (eds.), *Chemistry and Physics of Solid Surfaces VII (Springer Series in Surface Sciences 10)*, Springer Verlag, Berlin, Heidelberg, New York, 1988, p. 221.
- [38] J.G. Chen, B.D. DeVries, J.T. Lewandowsky and R.B. Hall, *Catal. Lett.* 23 (1994) 25.
- [39] S.M. Davis, G. Meitzner, D.A. Fischer and J.L. Gland, *J. Catal.* 142 (1993) 368.