Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Nuclear Instruments and Methods in Physics Research B 213 (2004) 552–555
NIM B
Beam Interactions with Materials & Atoms
www.elsevier.com/locate/nimb

Anomalous Rayleigh scattering with dilute concentrations of elements of biological importance

Richard P. Hugtenburg [a,b], David A. Bradley [b,*]

[a] Queen Elizabeth Medical Centre, University Hospital Birmingham, Birmingham B15 2TH, UK
[b] School of Physics, University of Exeter, Stocker Road, Exeter EX4 4QL, UK

Abstract

The anomalous scattering factor (ASF) correction to the relativistic form-factor approximation for Rayleigh scattering is examined in support of its utilization in radiographic imaging. ASF corrected total cross-section data have been generated for a low resolution grid for the Monte Carlo code EGS4 for the biologically important elements, K, Ca, Mn, Fe, Cu and Zn. Points in the fixed energy grid used by EGS4 as well as 8 other points in the vicinity of the K-edge have been chosen to achieve an uncertainty in the ASF component of 20% according to the Thomas–Reiche–Kuhn sum rule and an energy resolution of 20 eV. Such data is useful for analysis of imaging with a quasi-monoenergetic source. Corrections to the sampled distribution of outgoing photons, due to ASF, are given and new total cross-section data including that of the photoelectric effect have been computed using the Slater exchange self-consistent potential with the Latter tail. A measurement of Rayleigh scattering in a dilute aqueous solution of manganese (II) was performed, this system enabling determination of the absolute cross-section, although background subtraction was necessary to remove K_β fluorescence and resonant Raman scattering occurring within several 100 eV of the edge. Measurements confirm the presence of below edge bound–bound structure and variation in the structure due to the ionic state that are not currently included in tabulations.

PACS: 32.80.Cy; 78.70.Ck; 87.64.Fb
Keywords: Rayleigh; Anomalous scattering; Trace elements

1. Introduction

Advances in X-ray technology, improvements in the associated atomic and molecular interaction theories and faster computers motivate the increased utilization of scattering processes in imaging and the incorporation of higher order corrections in radiation transport codes. This paper examines elastic Rayleigh scattering and its extension to higher orders of accuracy in transport codes. Rayleigh scatter is important in the energy range associated with high definition radiography (5–50 keV). The utilization of the Rayleigh scatter signal in an imaging context is supported by the possible exploitation of higher order phenomenon, such as anomalous dispersion behaviour occurring at inner atomic orbital energies.

S-matrix theory [1] is the most accurate means for calculating Rayleigh scatter cross-sections.

* Corresponding author.
E-mail addresses: richard.hugtenburg@uhb.nhs.uk (R.P. Hugtenburg), d.a.bradley@exeter.ac.uk (D.A. Bradley).

0168-583X/$ - see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0168-583X(03)01667-7

This method is computationally expensive and a lower order method (the use of form factors) can be substituted in certain circumstances. In the anomalous scattering correction to the form-factor construction [2,3], the atomic form factor is comprised of a further two angle independent components f' and f'', the real and imaginary anomalous scatter factors. Implied by this theorem is the inclusion of bound–bound transitions, occurring at discrete energies, E_{nm}, with oscillator strength, f_{nm}, otherwise f'' is proportional to the photoelectric cross-section, σ_{PE}, i.e.,

$$f''(E) = -\frac{\alpha E \sigma_{\mathrm{PE}}}{4\pi mc^2 r_0^2} - \frac{\pi}{2}\sum_{m,n} E_{nm} f_{nm}\,\delta(E - E_{nm}), \tag{1}$$

where α is the fine structure constant r_0 is the classical electron radius $e^2/mc^2 = 2.82 \times 10^{-15}$. f' is related to f'' by a dispersion relation. It is the rapid increase in the photoelectric cross-section at the edge which manifests as the well known scatter minima in the real component of the anomalous scattering factor (ASF).

The contribution to the Rayleigh scatter cross-section from bound–bound transitions is comprised of an infinite Rydberg series of maxima and minima approaching the edge [4]. This rich structure, if real, suggests the possibility of improved sensitivity to elemental composition and prevailing chemical state, the physical manifestation being a function of beam and detector resolution and non-zero line widths in the atomic system. In the case of the aqueous environment, influences such as the sharing of valence orbitals and the existence of dynamic chemical equilibria further complicate the issue. In terms of modelling these processes, information such as charge state may not be at hand, influencing achievable resolutions.

The current work looks at the accurate evaluation of Rayleigh scatter in support of imaging methods dependent on the utilization of near-edge maxima observed in the photoelectric absorption cross-section such as dual-energy absorption methods and X-ray fluorescence (XRF). The implementation of anomalous Rayleigh scatter in a Monte Carlo code enables the magnitudes of various radiation components to be determined in realistic circumstances. In particular Rayleigh and Compton scatter signals in the direction of the scatter minimum associated with a polarized source, are a complex function of detector collimation, the degree of polarization of the source and multiple scatter in the sample. An extension to the Monte Carlo code, EGS4 [5], incorporating ASF corrections, has been implemented for the following six elements of biological importance in the range $Z = 24$–30, potassium, calcium, manganese, iron, copper and zinc. The Monte Carlo code can be used to compare scatter signals in fluorescent and transmission imaging modes in moderately thick (several mm) planar targets. The availability of codes, such as RTAB [6] allow a specific potential to be used for the determination of Rayleigh and photoeffect cross-sections and form factors, suggesting the incorporation of self-consistent cross-sectional data in Monte Carlo calculations.

Near-edge Rayleigh scattering intensities have been measured for the element manganese in solution using a synchrotron radiation source at an energy resolution that is sufficient to enable qualitative comparison with the anomalous scatter features discussed in this paper.

2. Methods

2.1. Experimental details

Measurements of Rayleigh scatter were performed on station 16.5 at the Synchrotron Radiation Source (SRS), Daresbury Laboratories. In this work, known concentrations of aqueous manganese were irradiated with monoenergetic X-rays in the range 6.52–6.57 keV. A Si monochromator crystal was used in the 220 orientation achieving eV energy discrimination. A multi-element hyper-pure Ge detector was positioned at an orthogonal angle to the beam in the plane of polarization, the typical detector arrangement used to minimize scatter contributions in XRF with polarized X-rays. The large ($\approx$10°) acceptance angle of the detector coupled with a 5% beam component polarized out of the plane and good focusing capabilities on this station meant that Rayleigh scatter was a significant effect. Energy

windowing was employed with the aim of separating Rayleigh and K_α fluorescence contributions.

In practical terms K_β contributions cannot be distinguished from the Rayleigh scatter signal, amounting to 4% of the total fluorescent signal for manganese, contributing a further 15% to the background above edge. The K_α signal is used to identify and eliminate the K_β and resonant Raman scattering contributions based on the assumption that the branching ratios are independent of energy over the short energy range of the experiment.

In order to minimize competition with changes in transmission across the K-edge, evident in the Rayleigh signal, it is necessary to employ a thin target. A 1 mm thick target containing 1000 ppm (1 mg/ml) manganese (II) in solution was used in this experiment this being 4.5% of the mean-free-path length between manganese photoelectric interactions above the K-edge.

2.2. Computational methods

The introduction of anomalous scatter into a transport code demands an unusually fine energy graduation. The RTAB database [6] provides data and codes for generating total and differential Rayleigh scattering cross-sections within the framework of a specific atomic orbital model. The program FFTAB, included in the RTAB distribution, was used to generate a table of cross-sections for the elements in this study. FFTAB enables the specification of a tolerable error in interpolation between energy points based on the evaluation of the Thomas–Reiche–Kuhn (TRK) sum rule, which states that an integral over all energies of the imaginary scattering amplitude should equal the number of electrons. The code will determine new points in order to reach a target tolerance defined in relative and absolute terms.

The Monte Carlo code, EGS4, implements Rayleigh scatter using the relativistic form-factor tabulation of Hubbell and Øverbø [7]. EGS4 uses the same energy grid for photoelectric absorption and coherent scattering. The grid is based on 9 fixed values per decade as well as extra points associated with edge discontinuities. The implementation of anomalous scattering corrections examined in this paper extends upon this philosophy and 8 extra points have been added to the grid that are associated with the rapidly varying Rayleigh cross-sections in the vicinity of an edge, achieving an overall error of 20% for the elements in question according to the TRK sum rule. Since photoelectric effect data has also been generated from the Slater exchange potential model in the process of evaluating the dispersion integral to obtain ASFs, it is interesting to retain these in preference to the default EGS4 data. The percentage changes in the total Rayleigh cross-section due to ASF corrections are shown in Fig. 1.

The user-code XRFCOMP, developed initially for X-ray tube based XRF studies [8], has been recently updated to include anomalous scattering corrections and provides a general purpose tool to assess multiple scatter effects for polarized sources in thick planar slabs. XRFCOMP utilizes LSCAT, a low-energy scattering expansion to EGS4, which has been recently extend to include detailed relaxation processes in a multi-element environment used in this study [9]. The user-code is available from the first author on request.

3. Experimental results

Measurements of near-edge Rayleigh scatter for a dilute (1 mg/ml) solution of manganese (II)

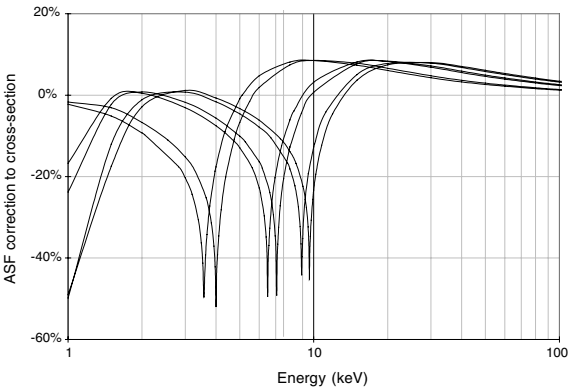

Fig. 1. Percentage changes due to the anomalous scattering corrections of relativistic Rayleigh scattering cross-sections for (in order of increasing Z and K-edge energy as indicated by the ASF minima) K, Ca, Mn, Fe, Cu and Zn calculated for neutral atoms using the Slater exchange potential with a Latter tail.

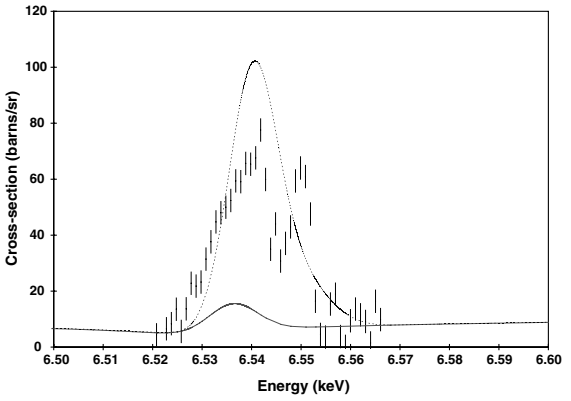

Fig. 2. Theoretical bound–bound resonance structure in near-edge Rayleigh scatter for neutral Mn (—) and Mn^{2+} (- - -) and measurements (statistical error indicated) from a solution of 1 mg/ml manganese sulphate.

sulphate are shown in Fig. 2. The energy calibration is accurate to within 5 eV. The measurement is compared with the ASF model near edge determined for neutral and twice ionized manganese using data generated from the RTAB database and codes and smoothed to a resolution of 5 eV. Discrepancies with the measurement in a dilute system suggest complex effects, in particular the 1s to 5p and 1s to 6p dipole resonances are resolved separately although broadening in excess of the 0.44 eV bandwidth of the synchrotron is evident, being probably due to the influence of the aqueous environment.

These results demonstrate that, at the resolution of the experiment, variation in the cross-section due to ionic state is measurable. These details may not be known in a radiographic analysis and lower resolution data, such as presented in this study, is desirable where improvements in low resolution background subtraction is sought, such as in XRF and dual-energy absorptiometry methods with quasi-monoenergetic sources.

4. Conclusion

The anomalous Rayleigh scatter correction to the form-factor method offers a practical and accurate description of Rayleigh scatter for forward scattering with intermediate Z elements such as may be exploited for contrast enhancement or calibration via scatter signal in dual energy and fluorescence imaging modes. The detection of anomalous Rayleigh features in a dilute (1 mg/ml) solution of manganese (II), in particular the confirmation of below edge bound–bound resonance structure, and evidence of changes in the structure as a function of the ionic state further supports the use of the approximation in an imaging context.

A further step toward the use of anomalous scatter in radiographic techniques is its incorporation in a Monte Carlo code. Substitution of the total Rayleigh cross-section data for ASF corrected data is considered as a means to reflect the energy dependence of the anomalous scatter factor terms. Tables were generated of adjusted cross-sections for the grid of fixed energy points traditionally used by the code EGS4 as well as those calculated at a set of judicious energies to obtain an overall uncertainty in Rayleigh scatter amplitude of 20% and an energy resolution of 20 eV. The latter is satisfactory for studies where information about the ionization state or valence occupation of an element under consideration is not known. The data has been computed using the Slater exchange potential and Latter tail throughout, enabling the generation and use of new photoelectric data.

References

[1] L. Kissel, R.H. Pratt, S.C. Roy, Phys. Rev. A 22 (1980) 1970.
[2] L. Kissel, B. Zhou, S.C. Roy, S.K. Sen Gupta, R.H. Pratt, Acta Cryst. A 51 (1995) 271.
[3] D.A. Bradley, S.C. Roy, L. Kissel, R.H. Pratt, Radiat. Phys. Chem. 56 (1999) 175.
[4] J.P.J. Carney, R.H. Pratt, L. Kissel, S.C. Roy, S.K. Sen Gupta, Phys. Rev. A 61 (2000) 052714.
[5] W.R. Nelson, H. Hirayama, D.W.O. Rogers, Rep. SLAC-265, Stanford Linear Accelerator Center, California, 1985.
[6] L. Kissel, Radiat. Phys. Chem. 59 (2000) 185.
[7] J.H. Hubbell, I. Øverbø, J. Phys. Chem. Ref. Data 9 (1979) 69.
[8] R.P. Hugtenburg, J.R. Turner, D.M. Mannering, B.A. Robinson, Appl. Radiat. Isot. 49 (1998) 673.
[9] Y. Namito, H. Hirayama, Nucl. Instr. and Meth. A 423 (1999) 238.