

Quantitative treatment of coarsely binned low-resolution recordings in molecular absorption spectroscopy

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Received 18 October 2004; received in revised form 25 May 2005; accepted 14 June 2005

Abstract

Optical multichannel detectors like photodiode arrays or CCD cameras combined with grating spectrometers are commonly used as detection systems in quantitative absorption spectroscopy. As a trade-off to broad spectral coverage, banded spectral features are sometimes recorded with insufficient spectral resolution and/or insufficiently fine detector binning. This renders the true physical spectrum of recorded intensities changed by instrumental and spectrum specific artefacts thus impeding comparability between results from different set-ups. In this work, it is demonstrated that in the case of a “well-behaved” – i.e. free of ro-vibronic structure – absorption band like the iodine monoxide IO(4 ← 0) transition, these effects can easily change the apparent peak absorption by up to 50%. Also deviations from the strict linearity (Beer–Lambert’s law) between absorber concentration and apparent, i.e. pixelwise optical density occur. This can be critical in studies of chemical kinetics. It is shown that the observed non-linearity can cause errors of up to 50% in the determination of a second order rate coefficient for the IO self reaction. To overcome the problem, a consistent and rigorous integral approach for the treatment of intensity recordings is developed. Linearity between optical density and absorber concentration thereby is re-established. The method is validated using artificial test data as well as experimental data of the IO(4 ← 0) absorption transition, obtained in the context of I₂/O₃ photochemistry studies. The agreement is accurate to within ±2% (test data) and ±3% (experimental data) supporting the validity of the approach. Possible consequences for other spectroscopic work are indicated. © 2005 Elsevier B.V. All rights reserved.

Keywords: Optical multichannel analysis; Resolution; Binning; Undersampling; Absolute absorption cross-section; Chemical kinetics; Non-linearity; Beer–Lambert; Iodine monoxide (IO)

1. Introduction

Optical multichannel detectors such as photodiode arrays or CCD cameras combined with grating spectrometer are commonly used in many applications of quantitative spectroscopy. With such set-ups qualitative as well as absolute absorption cross-section spectra are determined. Absolute cross-sections of transient absorbers require studies of chemical kinetics using time resolved detection systems. In that context the advantage of multichannel systems with broad spectral coverage is the simultaneous coverage of as many absorbers as possible in one single experiment. Errors in the quantitative analysis caused by instabilities of the chemical system are completely avoided, if all relevant absorbers

can be monitored in one single experiment. As a trade-off, the spectral resolution, the linear dispersion, and the detector binning are often limited. This renders the true physical spectrum of recorded intensities changed by more or less serious instrumental and spectrum specific artefacts making the comparability of such spectra a critical issue in quantitative spectroscopy. As a consequence, absorption cross-section spectra and deduced quantities are likewise changed. Absolute cross-sections determined under different conditions are not comparable but are a function of the used set-up’s characteristics, which for the case of iodine monoxide is illustrated in Fig. 1. The same holds for rate constants determined from such observational data using pixelwise calculated optical densities (applying the Beer–Lambert law).

To overcome this problem, a consistent and rigorous approach for the treatment of intensity recordings is developed. It makes use of mathematical integration of intensities

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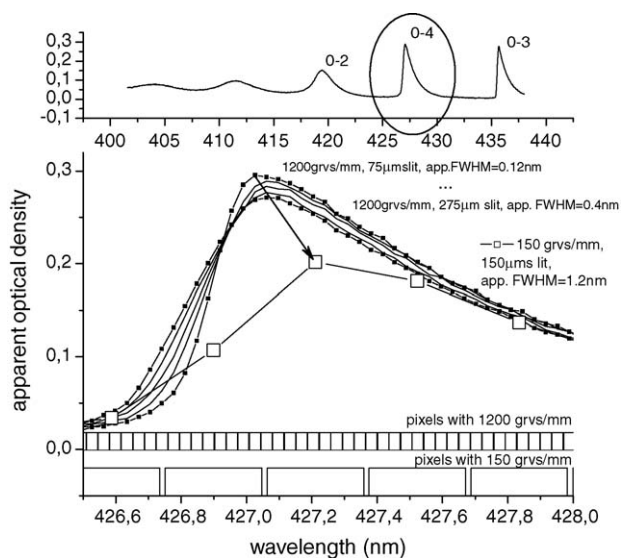


Fig. 1. In the top graph, a section of the iodine monoxide absorption spectrum is shown, as obtained from intensity measurements recorded with a 1200 grooves mm^{-1} grating (\rightarrow 0.04 nm/pixel), 75 μm slit at effective FWHM of 0.12 nm. The IO(4 \leftarrow 0) absorption transition is indicated, which will be used as test spectrum throughout this work. The bottom graph shows the shape of this transition, as it is obtained under different spectroscopic conditions. Spectral width of pixels – i.e. size of bins – is indicated by the two different bar plots (top row: 1200 grooves mm^{-1} , 0.04 nm/pixel, bottom row: 150 grooves mm^{-1} , 0.32 nm/pixel). Clearly lower resolution as well as more coarse binning change the apparent shape and the height of the absorption spectrum.

across a suitable spectral interval, i.e. across a number of pixels of the multichannel detector. Pixelwise calculation of optical density is avoided. It re-establishes the strict linearity between absorber concentration and a deduced optical density, which is calculated relative to the peak of a given, a priori known, and higher resolved spectrum. Comparability of absolute cross-sections determined from different set-ups is thus achieved. Errors in rate coefficients are corrected.

1.1. Measurement of intensity spectra

To start with, the determining factors in the recording of intensity spectra are examined. On one hand the spectroscopic part is to be considered and on the other hand the detector part of the set-up. An atomic emission line shall be focussed into a spectrometer. The shape of the line, as it emerges from the spectrometer, describes the spectrometer's characteristic function, or shorter – but less accurately – the instrument's function. Neglecting technical imperfections it is characterised by linear dispersion and spectral resolution of the spectrometer. Linear dispersion is fully determined by knowledge of the spacing of the grating's grooves and the focal length of the spectrometer. Spectral resolution – loosely speaking – measures, how a monochromatic line is smeared out when imaged into the spectrometer's focal plane. It is determined by the number of grooves, which are *illuminated* (i.e. which contribute to the diffraction), by the selected

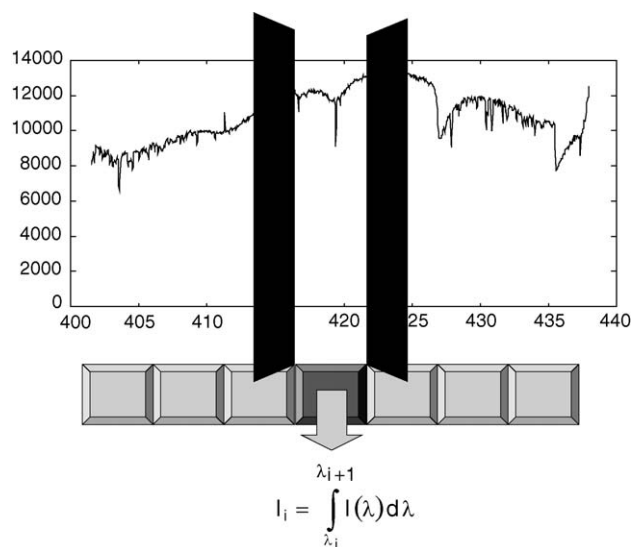


Fig. 2. The process of integrating intensities on a finite-sized semiconductor pixel is illustrated. The dark “blades” indicate the right and left borders of the pixel, in analogy to the blades of the slit in a single channel detector experiment. The intensity distribution incident on the pixel (indicated by the spectrum behind, depending on resolution and linear dispersion) is integrated within the limits of the pixel. This integrated intensity is the output signal of the pixel of the multichannel detector.

order of diffraction, and by the spectrometer's entrance slit width. The number of illuminated grooves depends on the filling of the spectrometer's field of view. This is usually not easily characterised impeding comparability of different experiments. The (rectangular) entrance slit, which is uniformly illuminated, is imaged by the spectrometer's optics to a rectangle in the focal plane. The augmentation of the spectrometer's optics determines the width of this image. Its edges are smeared out by diffraction.

The image – the characteristic function – is recorded by a multichannel detector placed in the focal plane of the spectrometer. Depending on the size, spacing, and number of detector pixels, the continuous spectrometer's slit function is converted to a discrete set of points. This process is often referred to as “sampling”. Strictly speaking, this is incorrect and misleading in the context of multichannel semiconductor detectors. Due to the finite pixel's width, the signal incident on the detector is not sampled but *spectrally integrated* or *binned* on the pixel (Fig. 2). Accordingly, the recording process should more accurately be referred to as *spectral binning*. The width of the spectral interval binned in a pixel will in the following be referred to as the spectral width of the pixel. It is determined by the geometric width of the pixel multiplied by linear dispersion (assuming a rectangular characteristic function of the pixel's sensitivity itself). As the blind spacing between pixels is usually small, it will be neglected here.

If the spectrometer's slit function (continuous valued in wavelength λ) is covered by a sufficient number of pixels so that its true shape is resembled closely, then the *spectral binning* is sufficiently fine. If this is not the case, the *binning* is too coarse (commonly: *undersampling*). Due to binning

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