Journal of Quantitative Spectroscopy & Radiative Transfer 94 (2005) 225–254

Journal of Quantitative Spectroscopy & Radiative Transfer

www.elsevier.com/locate/jqsrt

Wavelength modulation absorption spectrometry from optically saturated collision-broadened transitions

Florian M. Schmidt[a], Aleksandra Foltynowicz[a], Jörgen Gustafsson[b], Ove Axner[a,*]

[a]*Department of Physics, Umeå University, SE-901 87 Umeå, Sweden*
[b]*Department of Chemistry and Biomedical Sciences, University of Kalmar, SE-39182 Kalmar, Sweden*

Received 18 June 2004; received in revised form 3 September 2004; accepted 8 September 2004

Abstract

A theoretical investigation of the influence of optical saturation on wavelength modulation absorption spectrometry (WMAS) signals from collision-broadened transitions is presented. Expressions are derived for the *n*th Fourier coefficient of the analytical detector signal, and thereby also for the *n*th harmonic signal from a WMAS instrumentation (i.e. the *nf*-WMAS signal), from a wavelength modulated collision-broadened transition exposed to optical saturation. The flux- (or irradiance-) and modulation-amplitude dependences of the *nf*-WMAS signal on resonance are scrutinized in detail. It is shown that the *n*th Fourier coefficient of the wavelength modulated analytical detector signal from an optically saturated collision-broadened transition can be written as a product of a flux-dependent (ϕ) bleaching function, given by $(1+\phi/\phi_{sat})^{-1}$ and identical to that appearing for ordinary, unmodulated absorption spectrometry (AS), and a flux-, detuning-, and modulation-amplitude-dependent wavelength modulated peak-normalized saturation-broadened Lorentzian lineshape function, specific for the WMAS technique. It is found that the *nf*-WMAS signal on resonance decreases faster than an ordinary AS signal as a function of laser flux when smaller-than-optimum modulation amplitudes are used, but slower when larger-than-optimum modulation amplitudes are used. When optimum (or close-to-optimum) modulation amplitudes are being used, on the

*Corresponding author. Tel.: +46 90 786 6754; fax: +46 90 786 6673.
E-mail address: ove.axner@physics.umu.se (O. Axner).

doi:10.1016/j.jqsrt.2004.09.010

other hand, the flux dependence of the WMAS signal resembles to a large degree that of ordinary AS. The conditions for when WMAS from collision-broadened transitions has the same flux dependence as ordinary AS are identified.

Keywords: Wavelength modulation; Diode laser; Absorption spectrometry; WMS; WMAS; Optical saturation; Bleaching

1. Introduction

Wavelength modulation absorption spectrometry (WMAS), often also referred to as tunable diode laser absorption spectrometry (TDLAS) in the literature, is a diode laser-based technique for sensitive detection of atomic and molecular species in gas phase [1–6]. The technique has been used for many types of applications, e.g. environmental monitoring, remote sensing, and spectrochemical applications, under a variety of conditions [7–9]. The powerfulness of the WMAS technique stems from its capability to reduce the influence of $1/f$ noise (the modulation shifts the detection to high frequencies where the $1/f$ noise is small) [5]. The reduction of noise is in practice achieved by modulating the wavelength of the diode laser at a given frequency, f, whereas detection is performed at a harmonic thereof, i.e. at a frequency nf, where n is an integer, most often 2, although also 4 and 6 can be used [3,10–13]. The detection of the selected harmonics is most often carried out by the use of a lock-in amplifier [14,15].

The modulation and detection scheme used in the WMAS technique causes the signal output to have shapes and strengths that differ from the ordinary Lorentzian, Gaussian, or Voigt line profiles that appear in ordinary, unmodulated absorption spectrometric (AS) techniques under various conditions. It has been shown that the WMAS output, detected at the nth harmonic, often referred to as the nf-WMAS signal, is given by the nth Fourier coefficient of the detector signal [10,16]. Whenever an analyte is detected, the nth Fourier coefficient of the detector signal is, in turn, dominated by the nth Fourier coefficient of the wavelength modulated lineshape function for the transition used for detection of the analyte [10,16]. Analytical expressions for the nth Fourier coefficients of wavelength modulated lineshape functions as well as detector signals from absorption profiles with Lorentzian [10,17], Gaussian [10,18], and Voigt [10] form have therefore previously been given in the literature.

However, all these expressions have been derived under the condition that the laser light is not significantly affecting the population of the levels between which the transition takes place (i.e. that the light acts as a weak probe of the population).When strong diode lasers are used for detection of species with large transition dipole moments (so-called strong transitions), and especially under focused conditions, as for example when double modulation techniques are being used [13,19], the population of the levels might be affected by the laser light, primarily by the effect of optical saturation. Since optical saturation affects both the strength and shape of an absorption profile, and the WMAS signals depend on both of these, the previously derived expressions for the various lineshape functions are no longer directly applicable. The present paper therefore presents a derivation of the nth Fourier coefficient of the analytical detector