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Journal of Quantitative Spectroscopy & Radiative Transfer 96 (2005) 205–239

Journal of Quantitative Spectroscopy & Radiative Transfer

www.elsevier.com/locate/jqsrt

Semi-empirical calculation of air-broadened half-widths and air pressure-induced frequency shifts of water-vapor absorption lines

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Received 27 August 2004; received in revised form 30 November 2004; accepted 30 November 2004

Abstract

This paper describes a semi-empirical calculation of the air-broadened half-widths and the air pressure-induced frequency shifts for the $H_2^{16}O$ isotopologue. This semi-empirical calculation is based on fits of several recent high-quality measurements and theoretical calculations to the first-order terms in the expansion of the complex Robert–Bonamy (CRB) equations, which yields a second- and first-order polynomial function of the differences in the upper- and lower-state vibrational quantum numbers for the half-width and line shift, respectively. The aim of this work was to obtain a complete set of air-broadened half-widths and air pressure-induced frequency shifts for transitions of $H_2^{16}O$ present in the *HITRAN* database from microwave to the visible in order to supplement the observed and calculated values. For around 700 sets of rotational quantum numbers ($J'K'_aK'_c \leftarrow J''K''_aK''_c$), semi-empirical coefficients describing the vibrational dependence of the air-broadened half-widths and the air pressure-induced frequency shifts have been obtained directly from the fit of experimental and/or theoretical data. The accuracy of the parameters deduced from this calculation is estimated to be between 5% and 10% for the air-broadened half-widths and between 0.001 and 0.01 $cm^{-1}\,atm^{-1}$ for the air pressure-induced frequency shifts. For sets of rotational quantum numbers for which either none or insufficient experimental/

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0022-4073/$ - see front matter
doi:10.1016/j.jqsrt.2004.11.018

theoretical data were available to deduce a vibrational dependence, further approximations have been used to obtain a complete set of semi-empirical coefficients.

Keywords: Water-vapor absorption; Air-broadened half-width; Air pressure-induced line shift; Line shape

1. Introduction

Interpretation of atmospheric spectra requires high-precision line parameters describing line positions, intensities, pressure-broadened half-widths, and line shifts of gases present in the terrestrial atmosphere. Of these gases, water vapor is one of the most important greenhouse gases in the terrestrial atmosphere. Due to its relatively strong dipole moment, it is a major atmospheric absorber of infrared radiation with over 60,000 significant transitions ranging from the microwave region to the visible, of which about half are for the principal isotopologue $H_2^{16}O$. Accurate line parameters of water vapor are needed for remote sensing of this molecule, but also for their impact on other molecules since water-vapor transitions are often present in the channels used to detect and quantify other trace species.

Among the fundamental spectral parameters needed for terrestrial atmospheric radiative models (used to model natural radiative processes and to interpret remote-sensing data), there remain many deficiencies for the air-broadened half-widths, γ_{air}, and the air pressure-induced line shifts, δ_{air}. The goal of this work is to give a complete set of semi-empirical coefficients in order to calculate the γ_{air} and δ_{air} parameters of any rovibrational transition of the $H_2^{16}O$ isotopologue in order to update these parameters for the 2004 edition of the *HITRAN* database [1]. For the other isotopologues of water vapor, the number of references for the air-broadened half-widths and especially for the air pressure-induced frequency shifts is currently too small to determine the vibrational dependence of γ_{air} and δ_{air}.

Advances in the spectroscopy of water vapor and its key role in atmospheric and astrophysical studies have recently been reviewed [2]. The air-broadened half-widths for water vapor show a greater dynamic range and variability of values compared with other molecular absorbers in the atmosphere. The spectral line parameters used for remote-sensing simulations are usually obtained from the *HITRAN* database [1]. Because the preliminary positions, intensities, and assignment of the new *HITRAN* edition [1] were available, we used this version in order to set up a complete set of transitions for $H_2^{16}O$, for which we generated air-broadened half-widths and air pressure-induced frequency shifts. In the previous *HITRAN* [3], the γ_{air} parameters for the $H_2^{16}O$ isotopologue were selected from an assortment of about 300 measurements [4–7] and 2500 theoretical calculations [8] that are independent of the vibrational transition as well as a small number of vibrationally dependent measurements [6,7]. For other transitions, the γ_{air} parameters were estimated using scaled average values as a function of the rotational quantum number J [9]. Theoretical progress in the complex Robert–Bonamy theory (CRB) [10] to include the imaginary terms in the calculation of pressure-broadened half-widths [11] led to the prediction of vibrational dependence of the half-width, which is now confirmed by measurement [12]. Gamache and Hartmann [12] have demonstrated that the vibrational dependence can easily be modeled by a simple function. This dependence is shown in Fig. 1,