Journal of Quantitative Spectroscopy & Radiative Transfer 108 (2007) 256–276

Journal of Quantitative Spectroscopy & Radiative Transfer

www.elsevier.com/locate/jqsrt

Laboratory measurements of dry air atmospheric absorption with a millimeter wave cavity ringdown spectrometer

Andrey I. Meshkov, Frank C. De Lucia*

Department of Physics, The Ohio State University, Columbus, OH 43210, USA

Received 2 January 2007; received in revised form 17 April 2007; accepted 20 April 2007

Abstract

Fast scan submillimeter spectroscopy (FASSST) cavity ring down spectroscopy has been used to measure the dry air continuum, and separately its individual component parts, at ~6000 frequencies in the spectral region between 170 and 260 GHz. These measurements have been made at pressures that range from 0 to 3 atmospheres and in the temperature range between 230 and 320 K. For several of the components these are the first measurements made at or near atmospheric conditions. These measurements contain all of the information necessary to parameterize the observed absorptions in terms of the fundamental line and continuum interactions without the need to import external parameters. The inversion of this analysis makes possible the calculation of atmospheric absorption with meaningful uncertainties over this spectral region for temperatures and pressures of atmospheric interest.

Keywords: Atmospheric; Millimeter wave; Absorption; Dry air; Continuum; Nitrogen; Oxygen; Microwave absorption

1. Introduction

Propagation of microwave, millimeter-wave, and submillimeter-wave radiation in the earth's atmosphere has been a subject of interest and controversy for many years. While the propagation near the peaks of the molecular absorption lines appears to be in good agreement with predictions based on the results of high-resolution spectroscopy (the line frequencies, half-widths, and intensities), the window regions between these lines have significant excess absorption above that predicted by a straightforward model based on high-resolution spectroscopy. This excess absorption is usually attributed to a continuum, which is sub-divided into a dry air continuum and a moist air continuum according to whether or not water is included. There have been a wide variety of explanations for this behavior including contributions from dimers and polymers [1], collision-induced absorption, lineshape effects associated with lines nearby in frequency, and lineshape effects associated with the far wings of very strong lines in the THz region.

Accordingly, there has been considerable laboratory work directed at these issues as well as their physical underpinnings. These have included fundamental studies of the shapes of collision-broadened lines near

*Corresponding author. Tel.: +1 614 688 4774; fax: +1 614 292 7557.
E-mail address: fcd@mps.ohio-state.edu (F.C. De Lucia).

0022-4073/$ - see front matter
doi:10.1016/j.jqsrt.2007.04.001

atmospheric pressure [2], microwave studies of the absorptions in compressed oxygen [3,4], and continuum measurements at high pressure in nitrogen and other gases [5].

These results have been collected together in propagation models, the most well known being the several millimeter wave propagation models and their modifications by Liebe [6–8] and their review by Rosenkranz [9]. More recently, these issues have become of interest and importance to submillimeter radio astronomers as they seek to identify and use the best sites for their telescopes [10]. Finally, they play a fundamental role in the deconvolution of atmospheric remote sensing data [11].

For the dry air continuum work described here, the experimental challenges have involved the fact the absorptions are small over the relatively short paths available in the laboratory and the potential for minor contaminations to provide absorptions comparable to that of the dry air itself.

1.1. The physics

Atmospheric absorption in this spectral region is determined by a number of physical phenomena, many of which are interrelated and indeed some of which are even difficult to separate philosophically, for example, the relation between the far wings of spectral lines and 'continua' effects.

This paper specifically addresses what is often referred to as the 'dry air continuum.' Remarkably, in spite of its importance to propagation there exist no laboratory measurements of this continuum or its underlying phenomena at or near atmospheric conditions in the millimeter spectral region. This is due in large part to their relative weakness under laboratory conditions.

'Dry air' is ordinarily considered to be a mix of 79% nitrogen and 21% oxygen. Nitrogen and oxygen are similar homonuclear molecules, but with two important differences. First, unlike most molecules, oxygen is in a $^3\Sigma$ rather than $^1\Sigma$ electronic ground state and as a result has a line spectrum due to its magnetic dipole moment [12]. While magnetic dipole interactions are several orders of magnitude weaker than electric dipole interactions, the abundance of oxygen in the atmosphere makes these lines important. For example, they lead to the well-known atmospheric absorptions near 60 and 119 GHz. Additionally, this magnetic dipole moment leads to a so-called Debye absorption [2,8,13–15].

Secondly, the molecular quadrupole moment of oxygen is much smaller than that of nitrogen, making it a less important, and often ignored [8], collision partner. Because collision-induced absorption (CIA) is proportional to pressure squared, one experimental approach to overcoming its relative weakness has been to make measurements at high pressure. This has been done for the major contributor, nitrogen [5,16–19]. However, for oxygen and 'dry air' mixtures, the line contributions (which at atmospheric pressures are orders of magnitude greater) complicate this approach significantly [3,20,21].

1.2. Parameterization

To make the results of atmospheric models accessible to the user communities, data from a variety of sources that describe these phenomena are typically collected together in a parameterized model. The inputs to these models typically include collected spectroscopic parameters (line positions and strengths, pressure broadening and line mixing parameters, CIA from gases and gas mixtures, etc.). The most successful and widely used are those due to Liebe [6–8], with interpretations and commentary by Rosenkranz [9] and more recently Pardo et al. [10].

For the contribution of the CIA to atmospheric absorption, most have adopted a parameterization for dry air equivalent to

$$\alpha_{\mathrm{Dry}} = C(T)P^2\nu^2 = C_0P^2\nu^2\theta^n \tag{1}$$

with

$$\theta = \frac{T}{300\,\mathrm{K}} \tag{2}$$

and the $C(T)$ being temperature-dependent constants, C_0 being a temperature independent constant, P being the pressure, and ν being the frequency.