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The effect of spectroscopic parameter inaccuracies on ground-based millimeter wave remote sensing of the atmosphere

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ABSTRACT

A sensitivity study was performed to assess the impact that uncertainties in the spectroscopic parameters of atmospheric species have on the retrieval of gas concentrations using the 265–280 GHz region of the electromagnetic spectrum. Errors in the retrieval of O_3, N_2O, HNO_3, and ClO from spectra measured by ground-based radiometers were investigated. The goal of the study was to identify the spectroscopic parameters of these target species, and other interfering species, available in the JPL and HITRAN 2008 catalogues, which contribute the largest error to retrieved atmospheric concentration profiles in order to provide recommendations for new laboratory measurements. The parameters investigated were the line position, line strength, broadening coefficients and their temperature dependence, and pressure shift. Uncertainties in the air broadening coefficients of gases tend to contribute the largest error to retrieved atmospheric concentration profiles. For O_3 and N_2O, gases with relatively strong spectral signatures, the retrieval is sensitive to uncertainties in the parameters of the main spectral line that is observed. For HNO_3, the uncertainties in many closely spaced HNO_3 lines can cause large errors in the retrieved profile, and for ClO, the error in the profile is dominated by uncertainties in nearby, stronger O_3 lines. Fourteen spectroscopic parameters are identified, for which updated measurements would have the most impact on the accuracy of ground-based remote sensing of the target species at 265–280 GHz.

1. Introduction

Millimeter wave spectroscopy is a powerful tool for studying the composition of the stratosphere and mesosphere. The fine frequency resolution in measured spectra and the low Doppler broadening in the atmosphere, relative to pressure broadening, enable the retrieval of altitude profiles of atmospheric composition using spectra obtained with ground-based instruments. The sensitive receivers employed for microwave and millimeter wave observations have enabled the ground-based measurement of trace gases with weak spectral lines such as chlorine monoxide (ClO) [1], which plays a large role in polar ozone (O_3) chemistry [2].

The retrieval of gas concentrations from measured atmospheric spectra requires some a priori information on the observation system and the atmosphere. Part of this information is the spectroscopic parameters of atmospheric gases, which are generally taken from spectroscopic line catalogues. Along with the pressure and temperature of the local environment, these parameters are used to calculate the distribution, in frequency, of the

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energy emitted from molecules during a transition to a lower rotational state, commonly known as a spectral line. The motivation for the work here was to quantify the systematic errors that will be present in the retrieved volume mixing ratio (VMR) profiles of trace gases due to uncertainties in the spectral parameters from existing catalogues, and also to identify those uncertainties, which have the largest impact on VMR retrievals in the 265–280 GHz region to provide recommendations for new lab measurements.

This study was performed specifically for the ground-based millimeter wave remote sensor, SPÉIR [3], an instrument designed at the University of Toronto for trace gas measurements in the Arctic atmosphere. SPÉIR is designed to operate in the 265–280 GHz frequency range and measure emitted radiation from rotational transitions of O_3, ClO, nitric acid (HNO_3), and nitrous oxide (N_2O): referred to here as the target species. SPÉIR is designed for operations at the high-Arctic Polar Environment Atmospheric Research Laboratory (PEARL), located in Eureka, Nunavut, Canada (80.05 °N, 86.42 °W, 610 m ASL) [4]. The 265–280 GHz spectral region has been utilized for several ground-based instruments, including the Millimetre-wave Radiometer 2 (MIRA 2) [5] and the Radiometer for Atmospheric Measurements At Summit (RAMAS) [6], as well as those used for the first observation of enhanced lower stratospheric ClO in the Antarctic [7] and the first published measurements of the diurnal and secular variation of stratospheric ClO [8,9].

Error estimates for retrievals using measurements in this frequency range have often included a contribution from spectroscopic parameter uncertainty, but it is unclear to what extent a given spectroscopic parameter of a molecular transition contributes to the error in a retrieved VMR profile. A study performed for the satellite-borne European Space Agency candidate Millimetre-wave Acquisitions for Stratosphere/Troposphere Exchange Research (MASTER) [10] thoroughly characterizes all available spectroscopic parameters that affect trace gas retrievals using that instrument's five spectral bands between 294.0 and 626.5 GHz. To our knowledge, no studies to date provide a detailed examination of the currently available spectroscopic parameters for all trace gases that affect ground-based remote sensing within the 265–280 GHz range. The aim of this paper is to provide such a study, using existing catalogues, for ground-based instruments that utilize the 265–280 GHz range.

The layout of the paper is as follows: Section 2 describes the radiative transfer through the atmosphere, and the forward and inversion models that are used to retrieve information about atmospheric gas concentrations and to characterize the errors. Section 3 outlines the setup that was used for the forward and inverse modeling, particularly the catalogued spectroscopic parameters. Section 4 shows the results, discusses the errors in retrieved atmospheric gas concentrations due to inaccuracies in spectroscopic parameters, and makes recommendations for additional spectroscopic data that would offer the most benefit to ground-based remote sensing in the 265–280 GHz frequency region. Section 5 provides concluding remarks.

2. Radiative transfer and optimal estimation

This section explains the basic principles of the transfer of electromagnetic energy through the atmosphere, and how atmospheric spectra are used to retrieve VMR profiles of atmospheric gases.

2.1. Radiative transfer through the atmosphere

The intensity, I, of atmospheric radiation at a known frequency, ν, is given by Schwarzschild's equation under local thermodynamic equilibrium:

$$I = I_0 e^{-\tau(l)} + \int_0^l B(T(l))\alpha(l)e^{-\tau(l)}\,dl, \tag{1}$$

where I_0 is a background source term (usually the cosmic microwave background in the case of ground-based atmospheric emission measurements), l is the path length through the atmosphere, τ is the optical depth, T is the temperature, B is the blackbody function, and α is the absorption coefficient. The absorption coefficient must be calculated in order to solve Eq. (1) and involves summing contributions from individual spectral lines and also from non-resonant terms of water vapour, oxygen, nitrogen, and carbon dioxide, known as continua absorption. The subject of continua is not discussed further in this work but details can be found in e.g., [11–13]. The atmosphere contains a mixture of gases and the absorption coefficient is calculated by summing over all species: $\alpha = \Sigma_{\text{species}}\alpha_{\text{species}}$. The absorption coefficient for a particular molecular species is defined by three quantities: the line strength S, the line shape $f(\nu,\nu_0)$, and the number of molecules per unit volume n:

$$\alpha_{\text{species}} = nS_{ij}(T)f(\nu,\nu_0). \tag{2}$$

The centre-frequency (position), ν_0, of a spectral line and the line strength are parameters that are included in spectroscopic line catalogues. In the microwave/millimeter wave region of the electromagnetic spectrum a good approximation of line shapes due to pressure broadening is given by the Van Vleck–Weisskopf profile [14]**:**

$$f_{vw}(\upsilon,\upsilon_0) = \left(\frac{\nu}{\nu_0}\right)^2 \frac{\gamma_L}{\pi}\left[\frac{1}{(\nu-\nu_0-\delta\nu_0)^2+{\gamma_L}^2}+\frac{1}{(\nu+\nu_0-\delta\nu_0)^2+{\gamma_L}^2}\right], \tag{3}$$

where $\delta\nu_0$ is the shift in the position of the line centre due to air pressure (herein pshift). γ_L is the Lorentz half-width at half-maximum (HWHM) given by [15]

$$\gamma_L(p,p_s) = \gamma_{\text{air}}\,(p-p_s)\left(\frac{T_0}{T}\right)^{n_{\text{air}}} + \gamma_{\text{self}}(p_s)\left(\frac{T_0}{T}\right)^{n_{\text{self}}}, \tag{4}$$

where p is the pressure of the air sample, p_s is the partial pressure of the species in question, T_0 is a known reference temperature, γ_{air} and n_{air} are the air-broadening parameter and its temperature dependence, respectively, and γ_{self} and n_{self} are the self-broadening parameter and its temperature dependence, respectively. All of these parameters besides temperature and pressure are found in spectroscopic line catalogues. The right-hand side of Eq. (4) is composed of two parts: broadening caused by foreign, or air, molecules (left), and self-broadening (right).