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The water vapour self-continuum by CRDS at room temperature in the 1.6 μm transparency window

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ABSTRACT

The water vapour self-continuum has been investigated by high sensitivity Cavity Ring Down Spectroscopy at room temperature in the 1.6 μm window. The real time pressure dependence of the continuum was investigated during pressure cycles up to 12 Torr for fifteen selected wavenumber values. The continuum absorption coefficient measured between 5875 and 6450 cm^{-1} shows a minimum value around 6300 cm^{-1} and ranges between 1×10^{-9} and 8×10^{-9} cm^{-1} for 8 Torr of water vapour. The continuum level is observed to deviate significantly from the expected quadratic dependence versus the pressure. This deviation is interpreted as due to a significant contribution of water adsorbed on the super mirrors to the cavity loss rate. The pressure dependence is well reproduced by a second order polynomial. We interpret the linear and quadratic terms as the adsorbed water and vapour water contribution, respectively.

The derived self-continuum cross sections, $C_s(T=296\ K)$, ranging between 3×10^{-25} and 3×10^{-24} $cm^2\ molecule^{-1}\ atm^{-1}$ are found in reasonable agreement with the last version of the MT_CKD 2.5 model but in disagreement with recent FTS measurements. The FTS cross section values are between one and two orders of magnitude higher than our values and mostly frequency independent over the investigated spectral region. The achieved baseline stability of the CRDS spectra (better than 1×10^{-10} cm^{-1}) level totally rules out water continuum absorption at the FTS level (1.2×10^{-7} cm^{-1} at 9 Torr) in the CRDS cell. In order to find the origin of such conflicting results, the differences and possible experimental biases in the two measurement methods are discussed.

1. Introduction

Water vapour absorption has a major role in radiative balance and feedback effects of climate change [1,2]. It represents more than 70% of the total atmospheric absorption at short wavelengths (<3 μm) in clear sky conditions and about 50% for cloudy conditions [2]. The water vapour spectrum shows regions of strong absorption, corresponding to the strong absorbing rotational and vibrational–rotational bands of the water monomer, and regions of weaker absorption between these bands, the so-called "transparency windows". These windows are particularly useful for remote sensing [3] as well as to determine surface [3] and cloud [4] properties. Unlike in the strong absorbing regions where contributions from the centres and intermediate wings of water vapour monomer lines dominate, in transparent windows in the infrared and near infrared, water vapour continuum absorption has a major contribution [5]. The definition of the water continuum is somewhat arbitrary as it corresponds to the difference between the measured ("true") absorption and that due to local lines calculated using a specified model [6,7]. In the atmosphere, the continuum decomposes into a dominant self-continuum component due to bimolecular interactions

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between water molecules and a foreign continuum due to interaction between water molecules and other species, mainly nitrogen or oxygen. The water self-continuum is expected to vary quadratically with the water number density and has a negative temperature dependence [5,8–11].

In spite of its importance, the origin of the water continuum is a matter of debate for several decades (see Ref. [12] for a recent review). For example the far-wing contributions were found to be the dominant source of the self-continuum in the 800–1150 cm^{-1} window [6,9,13] but the temperature dependence of the self-continuum cross-section obtained in Ref. [10] by cavity ring-down spectroscopy (CRDS) at 944 cm^{-1} is compatible with a water dimer model. Nevertheless due to large uncertainties on the different models (far-wing and dimer), the authors of Ref. [10] hesitate to conclude about the continuum origin in that transparency window. More recently, from extensive measurements by Fourier Transform Spectroscopy (FTS), Ptashnik et al. [5] suggested that in the near-infrared windows, at temperatures between 293 and 472 K, their results are more consistent with water dimer being the major contributor to the continuum.

The lack of reliable measurements in particular in the near infrared is a major limitation to test water vapour continuum interpretations and models. In particular, the MT_CKD model [14] which is a semi-empirical formulation of the continuum widely used in radiative transfer codes uses reliable experimental constraints in the microwave and infrared regions but lacks validation in the near infrared.

Indeed, the measurement of weak broadband absorption signals is particularly challenging. As the continuum absorption retrieval depends on the difference of the light intensities transmitted through the absorption cell in absence and in presence of water vapour, a very high stability of the baseline during the entire measurement period is mandatory. In particular, it is necessary to ensure that the alignment of the spectrometer and the optical properties of the absorption cell are not affected by the injection of water vapour.

Compared to FTS which requires longer acquisition times, laser techniques have the advantage of providing real time measurements at a chosen wavelength. In this context, Cavity Ring Down Spectroscopy (CRDS) is a highly sensitive technique particularly suitable for such studies. To our knowledge, up to now the CRDS technique was applied only a few times to the characterization of water vapour continuum in the mid- and near infrared. Aldener et al. [15] determined an upper limit of $(9.2 \pm 0.2) \times 10^{-27}$ cm^2 $molecule^{-1}$ at 11 500 cm^{-1} for the water vapour continuum absorption using a pulsed-CRDS set-up based on a dye laser. The CRDS technique was also used with continuous lasers (CW-CRDS): Cormier and co-workers [10,16] reported measurements at three wavenumbers of the 10 μm transparency window around 940 cm^{-1} while Reichert et al. [17] reported self-continuum cross section at 278 and 296 K for two spectral points of an absorption band (10 611.6 and 10 685.2 cm^{-1}).

The aim of the present contribution is to report the results of our CW-CRDS investigation of the self-water continuum at room temperature for a selected set of spectral points in the 1.6 μm transparency window. The very weak continuum level in the 1.6 μm window explains why room temperature measurements of the absorption cross-section of the continuum in this window are very limited. Up to very recently, the only room temperature measurement available in this window was that reported by Bicknell et al. [18] using a calorimetric–interferometric method. These authors reported a value of 2.1×10^{-24} cm^2 $molecule^{-1}$ atm^{-1} for the total (self and foreign) water continuum cross section at 6150 cm^{-1}. This value is nine times larger than the continuum cross section calculated by the MT_CKD model. Very recently, Ptashnik et al. [19] reported an even larger value of $3.5 \pm 2 \times 10^{-23}$ cm^2 $molecule^{-1}$ atm^{-1} by FTS combined with a long multipass cell leading to a two orders of magnitude disagreement with the MT_CKD value. Nevertheless the lack of sensitivity of these FTS measurements leads to high uncertainties on the data especially near room temperature where maximum water pressures are limited by saturation.

The principles of the CRDS technique, the different factors contributing to the intensity loss rate in the CRDS experiment and the data acquisition are presented in Section 2. Section 3 is devoted to the continuum retrieval by subtraction of the monomer local lines contribution. In Section 4, we show from the pressure dependence of the CRDS spectra that the absorption of water adsorbed on the surface of the high reflectivity mirrors contribute to the measured continuum. The data treatment (Section 5) leads to estimated values of the gas phase continuum which are discussed in Section 6.

2. CRDS measurements

2.1. Principles and definitions

A CRDS spectrum is obtained from the wavelength dependence of the lifetime of photons trapped in a high finesse cavity formed by two high reflectivity mirrors constituting the CRDS cell [20]. When a laser emission is in frequency resonance with one of the longitudinal CRDS cavity modes, a constructive interference occurs, leading to a transmitted intensity through the cavity. When this transmitted intensity reaches a certain threshold, the injection of photons in the cavity is stopped and the exponential cavity photon's depletion time – or ring-down time $\tau(\nu)$ (in s) – is measured with a photodiode.

The loss rate, $LR(\nu)$ (in cm^{-1}), at a given wavenumber value, ν, is deduced from the measured cavity ring-down time:

$$LR(\nu) = \frac{1}{c\tau(\nu)} \tag{1}$$

where c is the speed of light neglecting the refractive index of the gas, very close to 1.

The ring-down time of the evacuated cavity, τ_0, depends on the very weak transmittivity, T, of the high reflectivity mirrors and additional losses, L, including the absorption by the dielectric coating layers and scattering