Far IR continuum absorption of H₂¹⁶O and H₂¹⁸O

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Water vapor is the main greenhouses gas and it is responsible for about 70% of solar radiation absorption by the Earth atmosphere. Water vapor absorption consists of resonance absorption (sum of water lines) and continuum absorption (smoothly varying with frequency). Even though continuum is several orders of magnitude weaker than absorption at the center of absorption lines, its integrated contribution to total atmospheric absorption is significant and exceeds contribution of other greenhouse gases, such as CO_2 and CH_4. Thus, appropriate calculation of radiation balance, modeling of global climate changes and atmosphere remote sensing require accounting of the water vapor continuum.

Nowadays the semi-empirical MTCKD model [1] is the standard model implemented in radiative transfer codes to describe the water absorption continuum. This model is a far wing model constrained on experimental data obtained in the IR frequency range mainly at room or elevated temperatures. Extrapolation of this model to other frequency ranges (including terahertz region) and atmospheric temperatures are hazardous and might deviate from new experimental data [2].

Appropriate description of water vapor continuum absorption requires development of physically based model. In spite of long history of theoretical and experimental investigation of the continuum, it remains poorly characterized and understood. Its nature is not fully settled yet. Nevertheless, it was established, that the continuum originates from non-ideality of water vapor and its magnitude is quadratic function of pressure (self continuum). There are several possible sources of continuum: intermediate wings of resonance lines, bound and quasi-bound water dimer absorption and collision induced absorption.

Our investigation of the continuum absorption in the frequency range of water molecule rotational band is motivated by: (i) filling the spectral gap on the continuum data, and (ii) determination of water dimer and intermediate wings contributions to the continuum.

The weakness of the continuum makes to use a spectrometer with a high sensitivity and a high stability. In the current study the continuum was measured using high resolution Fourier transform spectrometer IFS-125HR equipped with multipass gas absorption cell with total pathlength of 151 m, that allowed to distinguish weak continuum absorption even at few mbar of water vapor pressure. The measurements were performed at the AILES beamline of SOLEIL synchrotron. The high power and high stability of the synchrotron radiation allows increasing sensitivity of the spectrometer up to 15 times in comparison with standard laboratory sources. To cover the frequency range of the rotational band, the coherent (15-35 cm⁻¹) and standard (50-500 cm⁻¹) radiation modes of the synchrotron were used. In order to refine the magnitude and clarify the physical origin of the continuum, spectra of the two major water isotopologues, H₂¹⁶O and H₂¹⁸O, were considered. Recordings at several water vapor pressures were used to check the expected quadratic pressure dependence of the continuum.

The continuum was obtained by difference between experimental absorption α_{EXP} and modeled resonance absorption α_{WML}:

$$\alpha_C = \alpha_{EXP} - \alpha_{WML}.$$

Resonance absorption was modeled as sum of all significant lines of 7 most abundant water isotopologues:

$$\alpha_{WML}(\nu) = \sum_{j=1}^{7} \sum_{i} S_i^j \cdot \Phi(\nu),$$

where $\Phi(\nu)$ is Van Vleck - Weisskopf profile with commonly accepted wings cut off at 25 cm⁻¹ and line shape parameters (including line strength S_i, center frequency and collisional broadening coefficient) from HITRAN 2016 database [3].

The continuum cross-section was determined as

$$C(\nu,T) = \frac{\alpha_C(\nu) \cdot k_B T}{P^2}$$

where T is temperature, k_B - Boltzmann constant and P - water vapor pressure.

Water vapor absorption spectra in the frequency range of 15-35 cm⁻¹ were recorded at two pressures (11 and 16 mbar of natural water and 13 and 16 mbar of water sample enriched with O¹⁸). The coincidence of the continuum cross-sections corresponding to two pressures is a validation of the pressure squared dependence. Fig.1. compares our results to literature measurements [4-10] in the range up to 60 cm⁻¹ together with a calculated spectral function of (H₂¹⁶O)₂ dimer [11]. The experimental data show a good agreement with the frequency dependence of the function. The H₂¹⁸O continuum shows a similar spectrum in this range (Fig.2.). These facts confirm the dominating contribution of water dimer absorption to the observed continuum. It should be mentioned, that the MTCKD model does not account satisfactorily of the observed frequency dependence in this region (see Fig. 1).

In the 50-500 cm⁻¹ range, H₂¹⁶O and H₂¹⁸O continuum spectra were recorded for a number of pressures between 2 and 6 mbar. The very good quadratic pressure dependence of the measured continuum was obtained. The continuum absorption corresponding to H₂¹⁶O and H₂¹⁸O molecules are similar in shape and

magnitude. Non-smooth frequency dependence of the $H_2^{16}O$ and $H_2^{18}O$ continua is observed between retrievals performed in nearby micro-windows (Fig.3). Inadequate modern line shape modeling in the range of intermediate wing (detuning of 5-10 cm^{-1} from line center) is believed to be responsible of the obtained fluctuations. We believe that investigation of isotopic dependence of the continuum could help to determine contribution of intermediate wings of resonance lines.
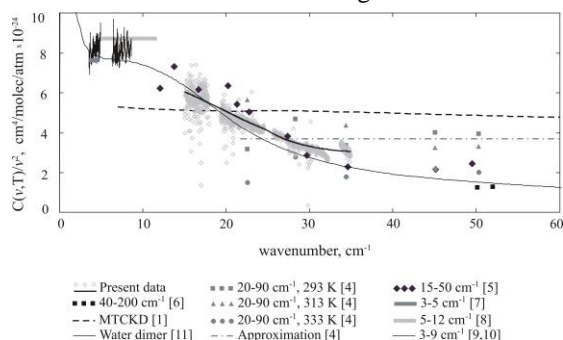

Fig. 1. Calculated water dimer spectral function [11], water vapor ($H_2^{16}O$) self-continuum cross-section normalized by frequency squared: obtained data, results of previous measurements.
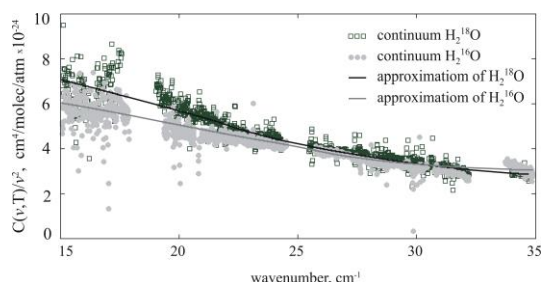
Fig. 2. Water vapor ($H_2^{16}O$ and $H_2^{18}O$) self-continuum cross-section normalized by frequency squared.

The new data on $H_2^{16}O$ continuum are in a good agreement with results of our previous measurements in the range of 40-200 cm^{-1} [6] and with results obtained by Burch in the range of 350-800 cm^{-1} [5]. New data filled the 200-350 cm^{-1} "gap" where the continuum was not measured before (Fig.3). The data confirmed that the widely used in atmospheric applications MT-CKD model [1] overestimates the continuum amplitude by about 30% in the whole range of the rotational band of H_2O (Fig.3).
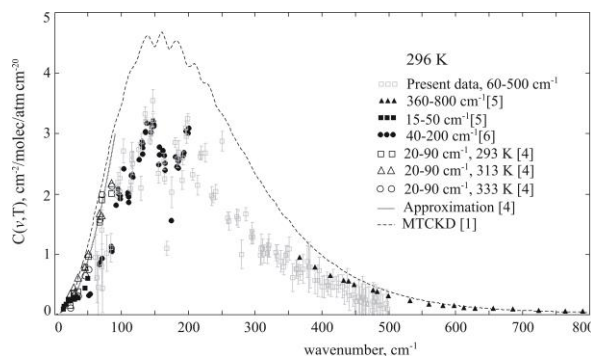
Fig. 3. Comparison of our data on the continuum with results of previous experimental studies [4-6] and MTCKD model [1].

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