IRS2012-467
International Radiation Symposium 2012
Dahlem Cube, Berlin, Germany, 06 – 10 August 2012
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The near-IR absorption spectrum of $HD^{18}O$, $HD^{16}O$, $D_2{}^{18}O$ and $D_2{}^{16}O$ using Fourier-transform incoherent broadband cavity enhanced absorption spectroscopy

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Using a combination of Fourier-transform (FT) spectroscopy and incoherent broad-band cavity-enhanced absorption spectroscopy (IBBCEAS) [1] very small optical densities can be measured with high spectral resolution over a wide spectral region (several hundred cm^{-1}) in a small sample volume. In the near infra-red these experimental features enable the detection of atmospheric trace constituents with high selectivity [2]. We applied FT-IBBCEAS to a sample mixture of 8.0 mbar of $D_2{}^{16}O$ and 12.4 mbar of pure $H_2{}^{18}O$ in the optical cavity. The spectral range covered was 5800 cm^{-1} to 7000 cm^{-1} at a resolution of 0.02 cm^{-1}. Even though the water isotope $H_2{}^{18}O$ has been studied before in this spectral region by different techniques with typical absorption path lengths of up to $\sim$100 m [3], the superior absorption sensitivity of FT-IBBCEAS in combination with D_2O being present in the cavity results in the observation of a large number of new absorption features in the spectrum which are notably due to the rare $HD^{18}O$ isotope of water. To analyse the spectrum line-lists for each of the six possible water isotopologues have been established using a uniform intensity threshold which gave a pool of 5547 candidate transitions. 3576 lines in the spectrum have assignments and 1971 lines are unaccounted for. The following spectral features were identified. $H_2{}^{18}O$: 346 assigned from 704 above threshold, $H_2{}^{16}O$: 304 from 566; $D_2{}^{16}O$: 233 from 295 (some of which are new); $D_2{}^{18}O$: 254 from 338 (all of these are new assignments). $HD^{16}O$: 1247+ from 1692; $HD^{18}O$: 1192+ from 1952, with $\sim$985 fully labelled, only 415 of these are listed in IUPAC (i.e. the upper state energy levels were already known) [4,5] (+: about 250 lines are blurred between $HD^{16}O$ and $HD^{18}O$).

The measurements demonstrate the usefulness of this experimental approach for spectroscopic investigations of isotopic or very dangerous samples, electric or plasma discharges or flames.

[1] A.A. Ruth, J. Orphal, S. E. Fiedler, "Cavity Enhanced Fourier Transform Absorption Spectroscopy using an Incoherent Broadband Light Source", Appl. Opt., **46** (2007) 3611-3616.

[2] J. Orphal, A. A. Ruth, "High-resolution Fourier-transform cavity-enhanced absorption spectroscopy in the near-infrared using an incoherent broad-band light source", Opt. Express, **16** (2008) 19232-19243.

[3] A.-W. Liu, O. Naumenko, K.-F. Song, B. Voronin, S.-M. Hu, "Fourier-transform absorption spectroscopy of $H_2^{18}O$ in the first hexade region", J. Mol. Spectrosc. **236** (2006) 127-133.

[4] IUPAC critical evaluation of the rotational-vibrational spectra of water vapor. Part I- Energy levels and transition wavenumbers for $H_2{}^{17}O$ and $H_2{}^{18}O$, J. Tennyson et al., JQSRT, **110** (2009) 573-596.

[5] IUPAC critical evaluation of the rotational-vibrational spectra of water vapor. Part I- Energy levels and transition wavenumbers for $HD^{16}O$, $HD^{17}O$ and $HD^{18}O$, J. Tennyson et al., JQSRT, **111** (2010) 2160-2184.