ANALYSIS OF AN ^{18}O AND D ENHANCED FT-IBBCEAS WATER SPECTRUM: NEW ASSIGNMENTS FOR $HD^{18}O$, $HD^{16}O$, $D_2{}^{18}O$ AND $D_2{}^{16}O$ IN THE NEAR-INFRARED REGION (6000-7000 cm^{-1}).

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An experimental infrared spectrum[a] recorded using isotopically enriched water in the 6000-7000 cm^{-1} region with a spectral resolution of 0.02 cm^{-1} is analysed and assigned. The spectrum employs a combination of Fourier-transform (FT) spectroscopy and incoherent broad-band cavity-enhanced absorption spectroscopy (IBBCEAS) [b]. Application of FT-IBBCEAS to a sample mixture of 8.0 mbar of D_2O and 12.4 mbar of pure $H_2{}^{18}O$ in the optical cavity resulted in the observation of a large number of new absorption features in the spectrum, notably due to the rare $HD^{18}O$ isotope of water. This was possible due to the superior absorption sensitivity of FT-IBB-CEAS compared to other techniques previously employed in this region combined with the prescence of $D_2{}^{16}O$ in the sample. The assignment procedure is based on the use of known transition frequencies for $H_2{}^{16}O$ and $H_2{}^{18}O$, existing variational line lists for $HD^{16}O$ and $D_2{}^{16}O$ and newly calculated variational line lists for $HD^{18}O$ and $D_2{}^{18}O$, with a uniform intensity threshold applied. The main absorption comes from $HD^{16}O$ and $HD^{18}O$, for which there are few previous assignments in the region. The following new spectral features were identified. $D_2{}^{16}O$: 265 (all labelled); $D_2{}^{18}O$: 194 (all lower levels labelled); $HD^{16}O$: 213 (all labelled); $HD^{18}O$: 743 (all lower and 612 upper levels labelled). In all 3226 of the 4768 lines observed in the spectrum are assigned, resulting in a significant number of newly determined energy levels. The analysis demonstrates both the usefulness of this experimental approach for spectroscopic investigations of isotopic or dangerous samples, and the validity of the new variational line lists.

[a] J. Orphal, A. A. Ruth, Opt. Express 16 (2008) 19232-19243.
[b] A. A. Ruth, J. Orphal, S.E. Fiedler, Appl. Opt. 46 (2007) 3611-3616.