

The near-IR absorption spectrum of HD¹⁸O, HD¹⁶O, D₂¹⁸O and D₂¹⁶O using Fourier-transform incoherent broadband cavity enhanced absorption spectroscopy

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MOTIVATION & INTRODUCTION

Whilst the spectra of the primary isotopologue of water is well documented [1], there remain gaps in the knowledge of the less abundant water species [2, 3]. Although less significant than H₂¹⁶O, the understanding of these rare isotopologues remains important for both terrestrial and stellar atmospheric modelling as well as the completeness of spectroscopic databases. Isotopologue abundances are often used to trace atmospheric processes since isotopic variations can be caused by specific atmospheric drivers such as cometary and meteorite deposits at the top of the atmosphere. The trace water isotopologue HD¹⁸O, for instance, has been observed both in the Earth's atmosphere [4] and in the interstellar medium [5], where isotopic abundances vary significantly. Water isotopologue abundances also provide unique information on the atmospheric water cycle. Furthermore, data on isotopically substituted water is essential for the development of theoretical models and in particular helps to characterize effects due to the failure of the Born-Oppenheimer approximation which remains one of the major sources of uncertainty in spectroscopic calculations on water.

ABSORPTION SPECTRUM

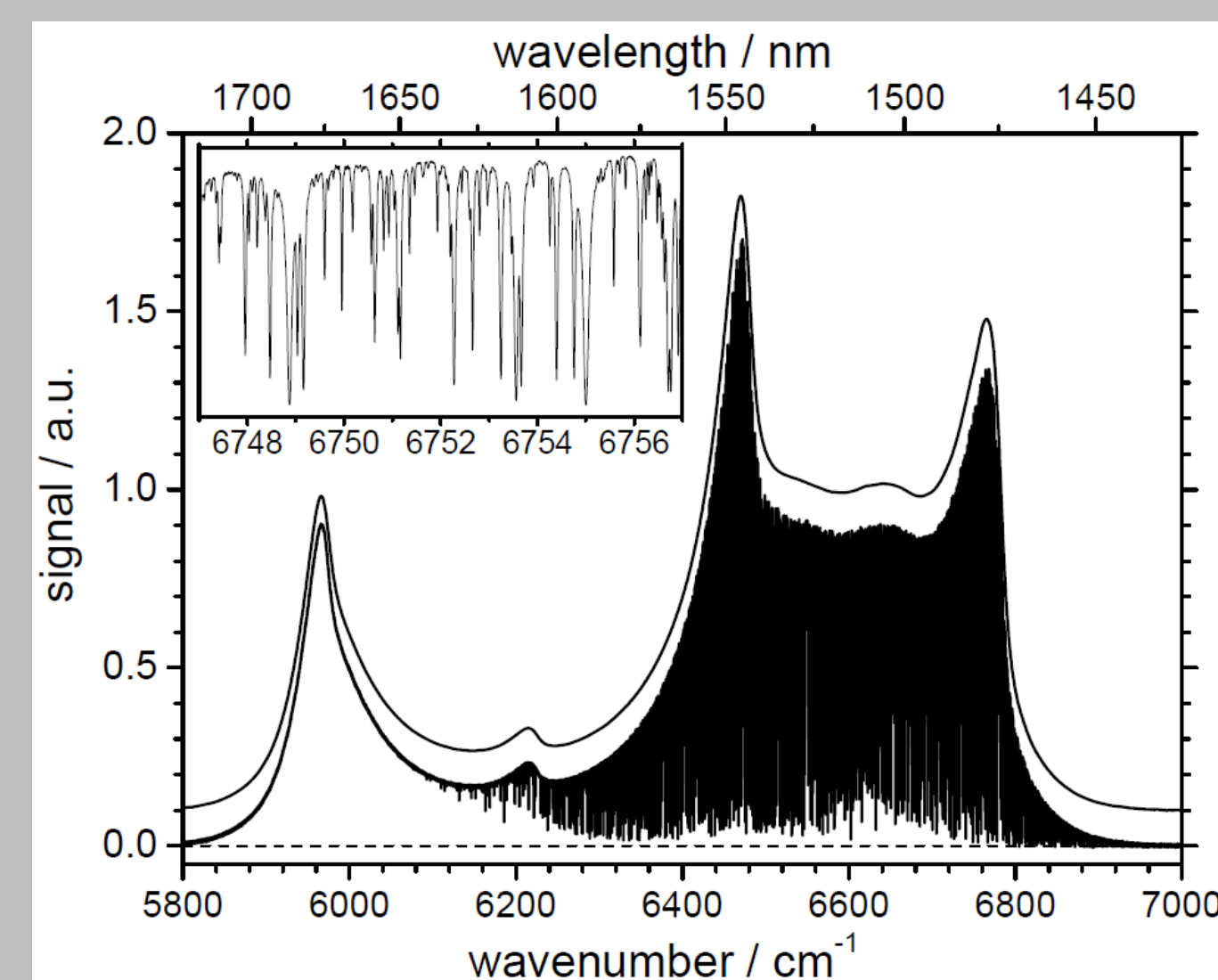


Figure 2: High-resolution spectrum of a mixture of 8.0 mbar of D₂O and 12.4 mbar of pure H₂¹⁸O in the optical cavity recorded with a spectral resolution of 0.02 cm⁻¹. The upper trace (shifted upwards for clarity) shows the spectrum of the empty cavity, the lower trace shows the spectrum obtained with the isotopic water mixture in the cavity. The recording time was 540 min. The inset shows the region from 6747 to 6757 cm⁻¹. More than 4700 absorption lines are observed in the 6000-7000 cm⁻¹ region, assignments are shown on the right.

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APPROACH

The experimental methodology combines the concept of absorption enhancement in an optically stable cavity over a broad spectral range (incoherent broadband cavity-enhanced absorption spectroscopy, IBBCEAS) with the high spectral resolution performance of Fourier-transform (FT) detection. The latter is required to resolve the fine structure of important atmospheric constituents and their isotopes in the near-infrared. The development of FT-IBBCEAS was to explore the potential of this technique for high-resolution molecular spectroscopy in the near-infrared region and to improve the sensitivity, selectivity and versatility of cavity-enhanced absorption spectroscopy while keeping the sample volume small.

The absorption spectrum of overtone bands of isotopically enriched water was measured between 5800 and 7000 cm⁻¹ [6] and analysed and assigned in the region 6000-7000 cm⁻¹ [7]. The quality of the spectra in this study is comparable to those obtained with Fourier Transform spectrometers employing standard multi-pass reflection cells, which generally require substantially larger sampling volumes.

ASSIGNMENTS

The assignment procedure is based on the use of known transition frequencies for H₂¹⁶O and H₂¹⁸O, existing variational line lists for HD¹⁶O and D₂¹⁶O, and newly calculated variational line lists for HD¹⁸O and D₂¹⁸O. The main absorption comes from HD¹⁶O and HD¹⁸O, for which there are few previous assignments in the region. A total of 4768 line were measured. Assignments to 743 new HD¹⁸O lines are presented.

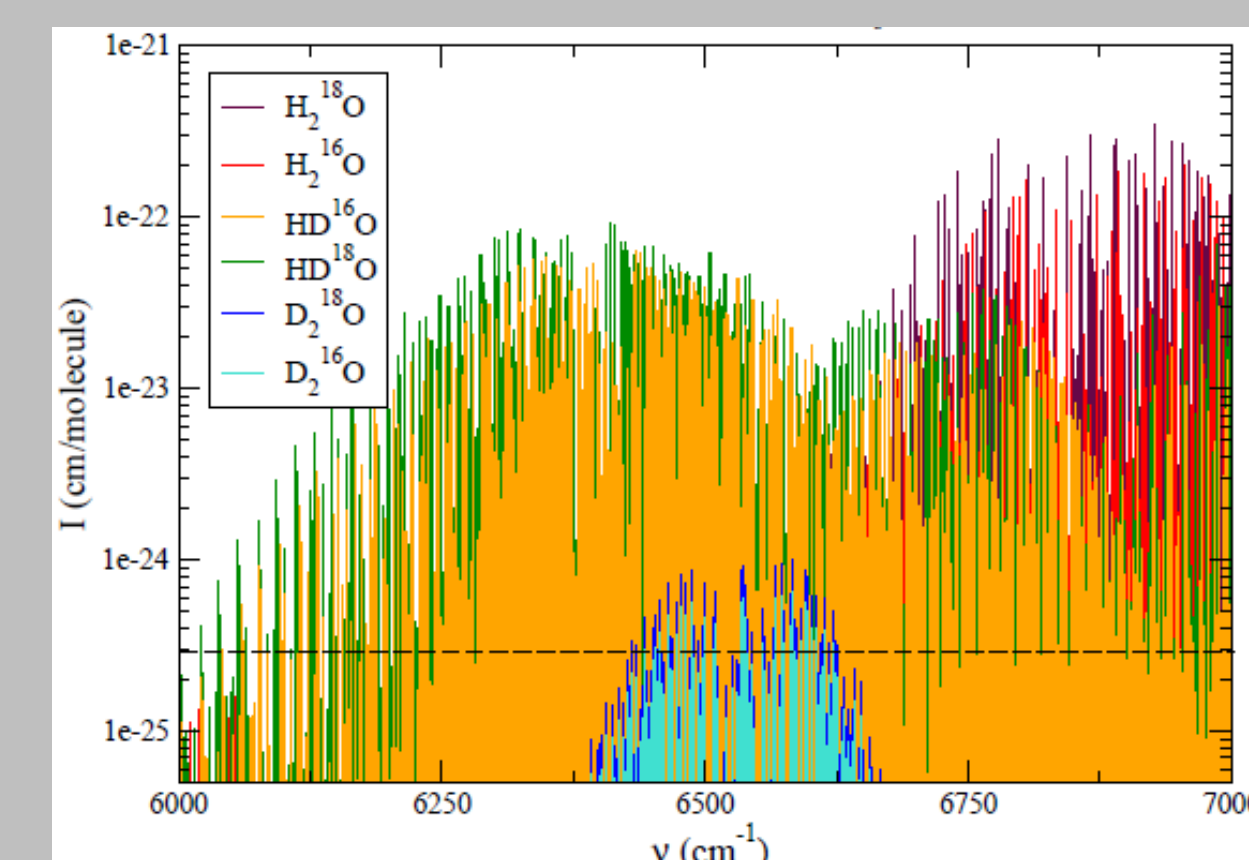


Figure 3: The combination of selected data sources for the six isotopologues of water in the 6000-7000 cm⁻¹ region. Intensities are scaled by the estimated experimental abundances given in Table 1. The dashed line indicates the intensity cut off.

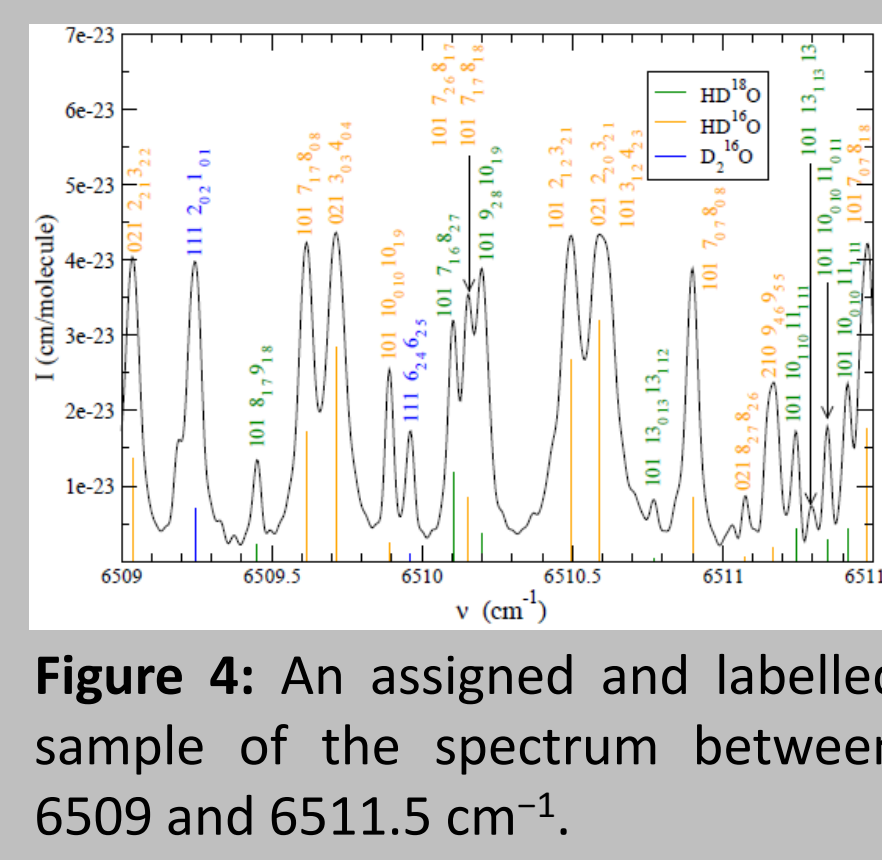


Figure 4: An assigned and labelled sample of the spectrum between 6509 and 6511.5 cm⁻¹.

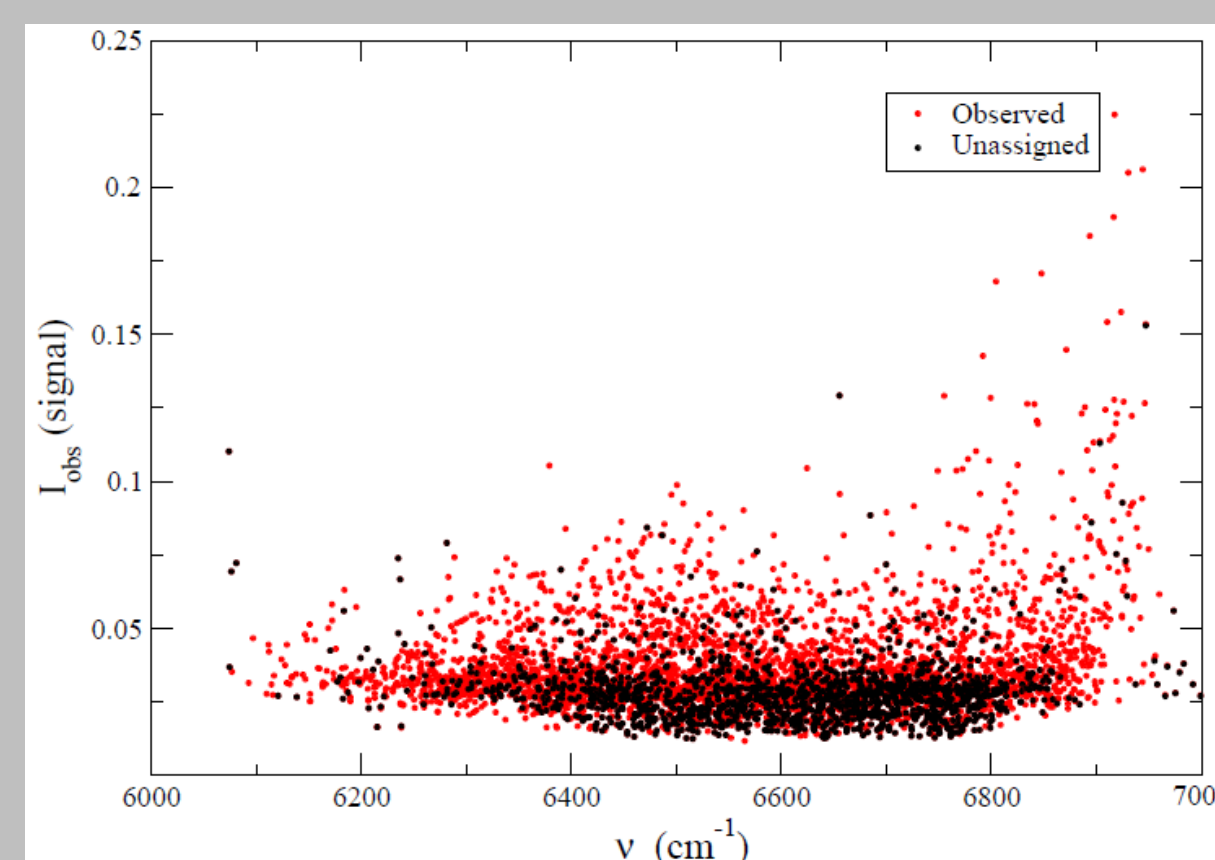


Figure 5: A comparison of all 3253 observed peaks and those 1512 remaining unassigned after the analysis. The majority of strong peaks in this region are now assigned.

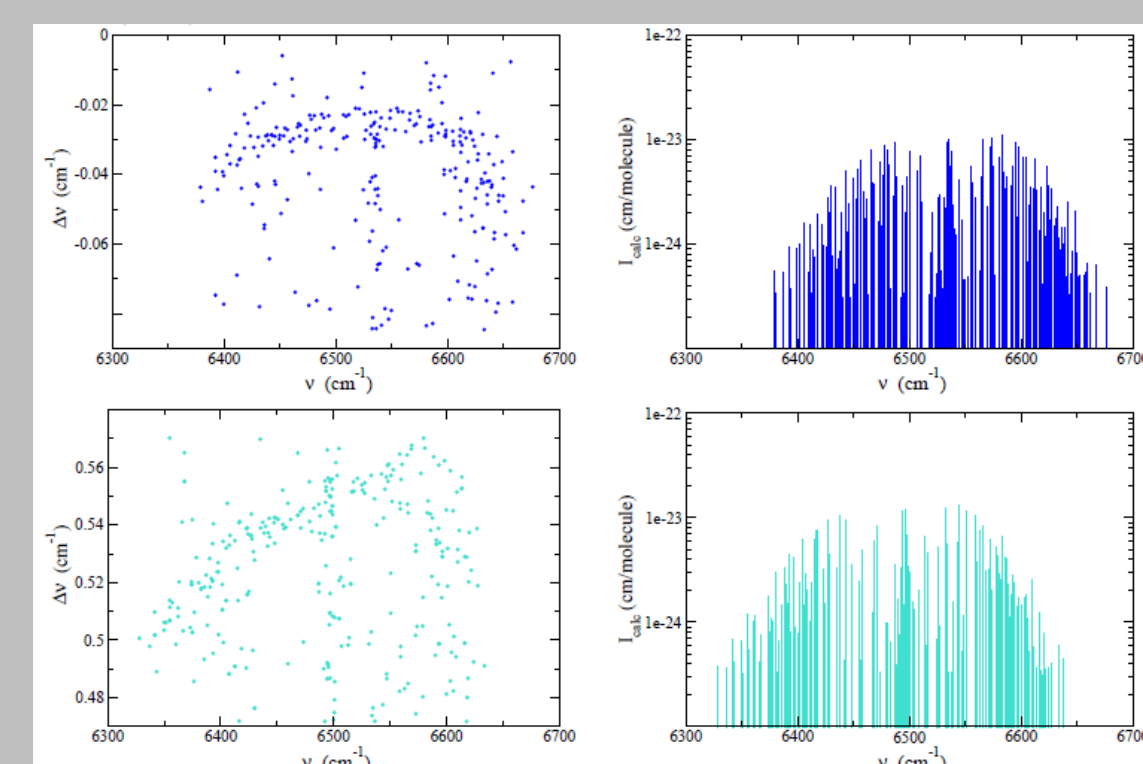


Figure 6a: Upper: Residuals of obs - calc line positions for D₂¹⁸O assignments (left) and the assigned features of D₂¹⁸O (right). Lower: Residuals of obs - calc line positions for D₂¹⁶O assignments (left) and the D₂¹⁶O assignments (right).

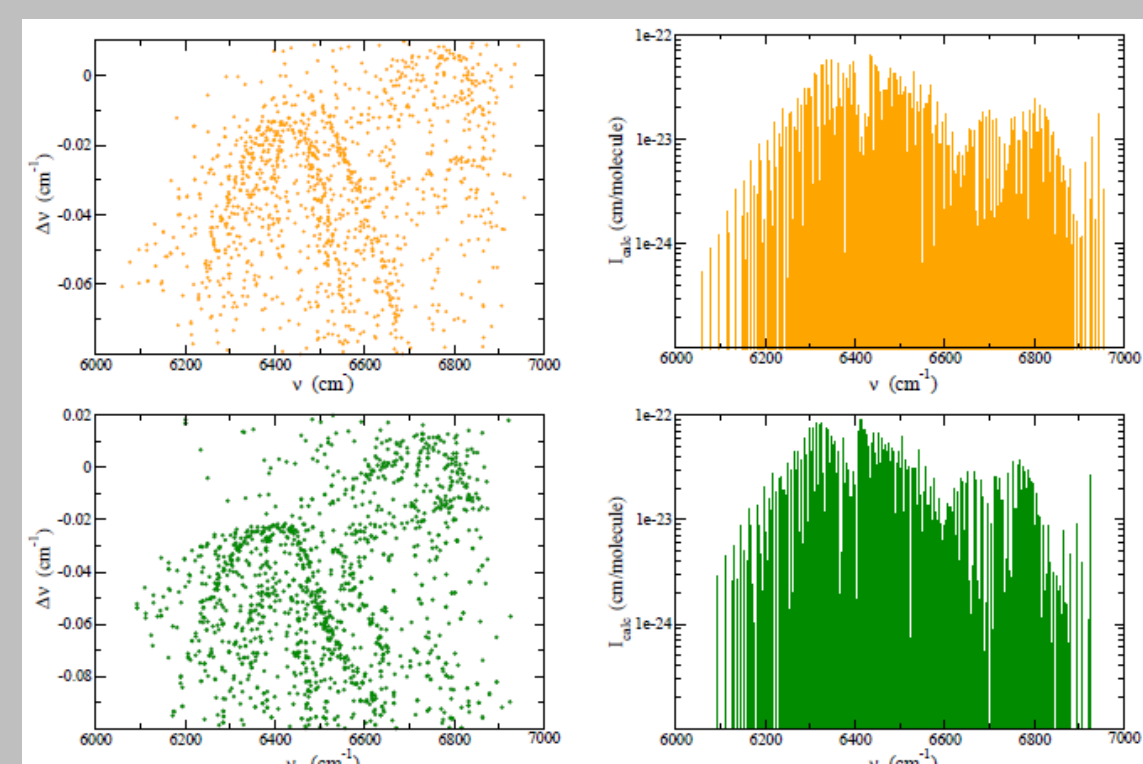


Figure 6b: Upper: Residuals of obs - calc line positions for HD¹⁶O assignments (left) and lines assigned (right). Lower: Residuals of obs - calc line positions for HD¹⁸O assignments (left) and lines assigned (right).

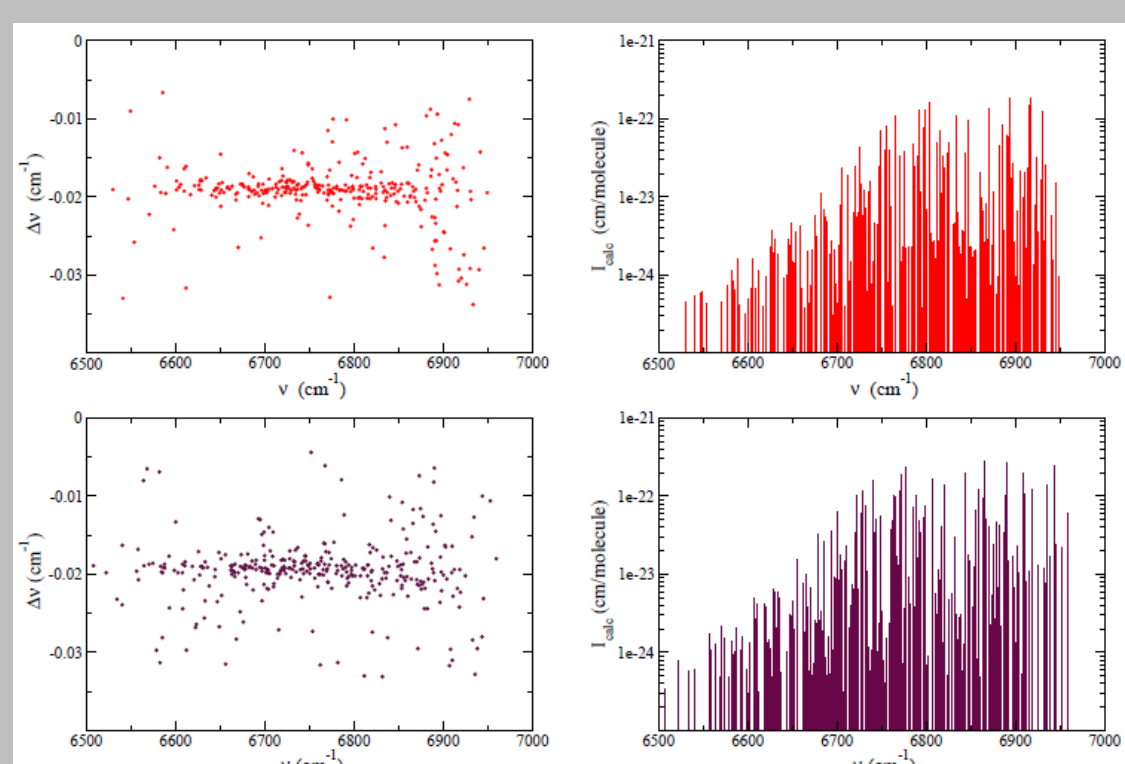


Figure 6c: Upper: Residuals of obs - HITRAN line positions for H₂¹⁶O (left) and the assigned H₂¹⁶O features (right). Lower: Residuals of observed - MARVEL line positions for H₂¹⁸O (left) and the assigned H₂¹⁸O features (right).

EXPERIMENTAL SETUP

Specifications of instrument used at LISA (Paris) [8]:
Lamp: super quiet Xe arc lamp (Hamamatsu, 75W)
Cavity length: $d = 90$ cm
Mirror reflectivity: ca. 0.9974 (1450 – 1700 nm)
FT-Spectrometer: Bruker HR125
Resolution of measurements: 0.02 cm⁻¹

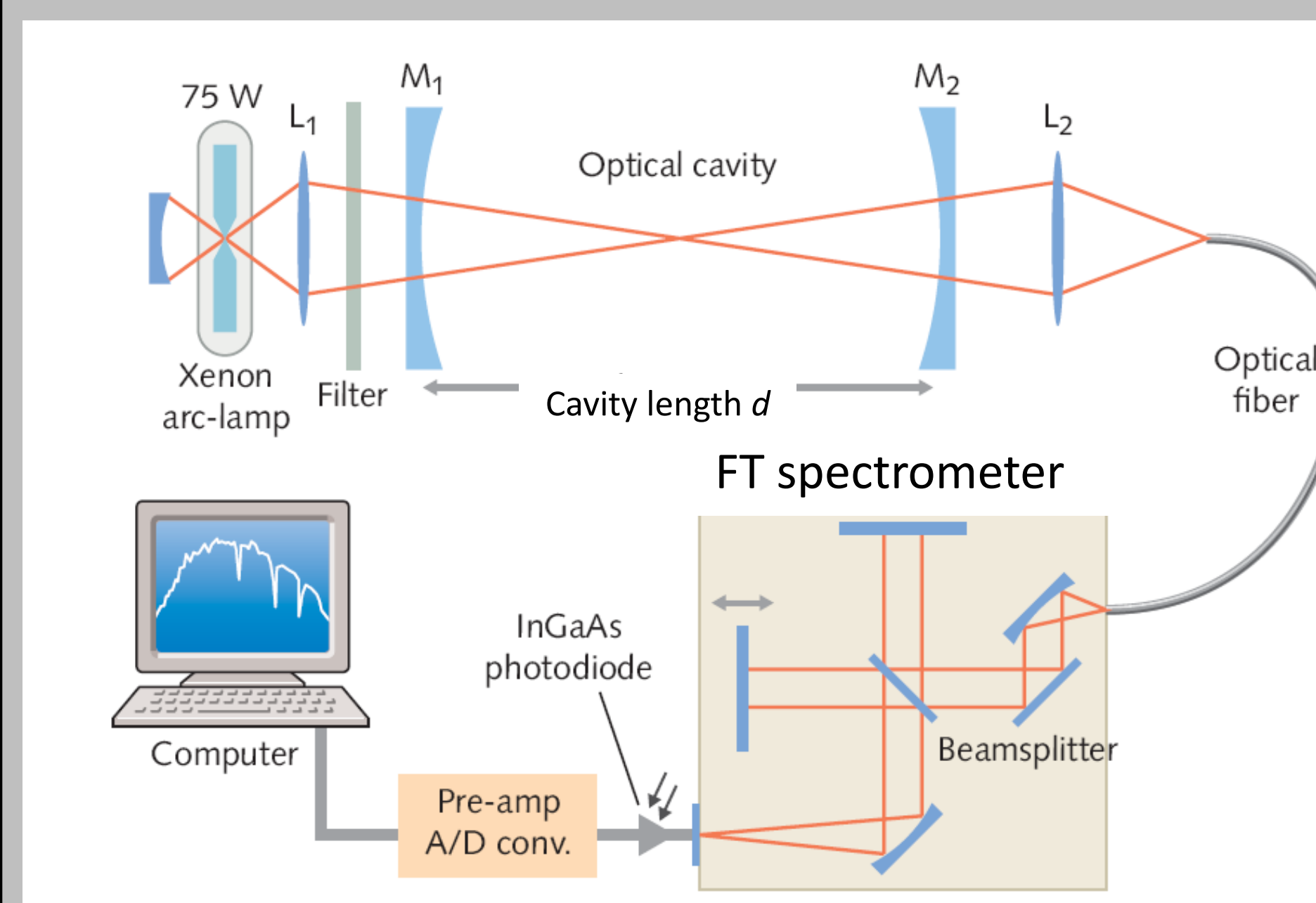


Figure 1a: Schematic of FT-IBBCEAS instrument at LISA and UCC.

Specifications of instrument at UCC (**Figure 1b**):
Lamp: super quiet Xe arc lamp (Hamam., 75W)
Cavity length: $d = 165$ cm
Mirror reflectivity: ca. 0.9997 (800 – 1200 nm)
FT-Spectrometer: Bruker Vertex 80
Resolution of instrument: 0.09 cm⁻¹

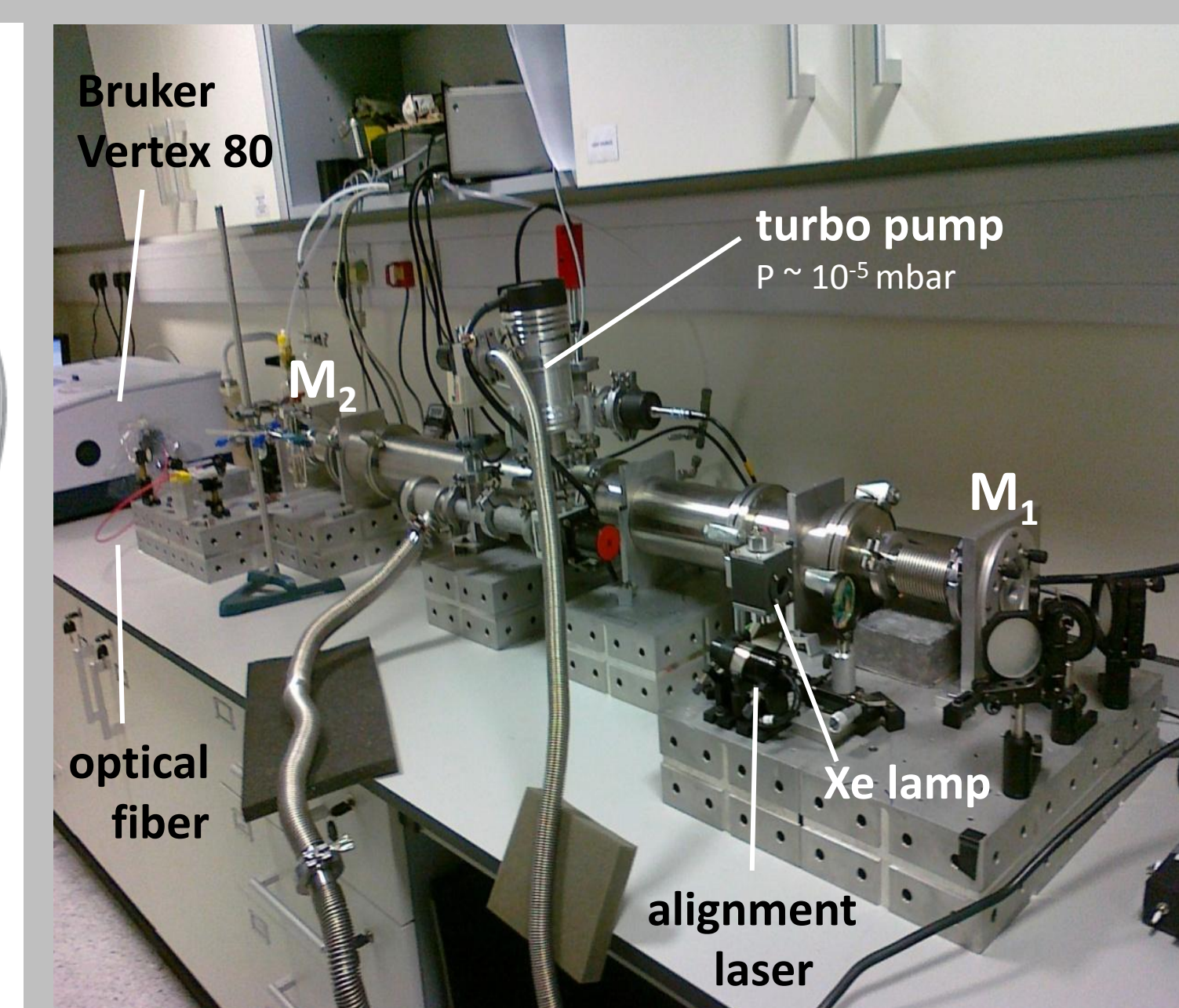


Figure 1b: Photograph of FT-IBBCEAS instrument at UCC

RESULT OVERVIEW

Isotopologue	Abundance	
	experimental	natural
HD ¹⁸ O	0.290	6.23 x 10 ⁻⁷
H ₂ ¹⁸ O	0.225	1.99 x 10 ⁻³
HD ¹⁶ O	0.186	3.11 x 10 ⁻⁴
D ₂ ¹⁶ O	0.145	0.977
D ₂ ¹⁸ O	0.093	4.90 x 10 ⁻¹¹
D ₂ ¹⁶ O	0.060	2.42 x 10 ⁻⁸

Table 1: Experimental and natural abundances for the six water isotopologues present in the gas mixture in **Figure 2**. The experimental abundances are estimated statistically.

Isotopologue	Assigned	New	Labelled
HD ¹⁸ O	1206	743	1075
HD ¹⁶ O	1272	213	1272
D ₂ ¹⁸ O	273	194	273
D ₂ ¹⁶ O	265	265	265

Table 2: A summary of assignments made for each isotopologue. The number of new assignments and labellings are also noted.

Isotopologue	Upper Levels	CD Confirmed	New
HD ¹⁸ O	411	288	131
HD ¹⁶ O	424	297	52
D ₂ ¹⁸ O	136	93	136
D ₂ ¹⁶ O	134	89	134
Total	1105	767	453

Table 3: A summary of upper energy levels observed for each isotopologue. The number of new levels and the number confirmed by combination differences (CD) are noted.

SUMMARY

A broad band **cavity-enhanced absorption method** using an incoherent light sources and Fourier Transform detection scheme has been developed for the measurement of high resolution absorption spectra of relevant atmospheric trace constituents in the near IR. The approach has been successfully applied to **isotopically enriched water** between 5800 and 7000 cm⁻¹ in the laboratory. The analysis has made large numbers of new assignments to five water isotopologues, many of which are previously unobserved. Many energy levels are also observed for the first time and an effort has been made to provide the standardised labels for the new assignments and energy levels where possible. In all 3253 of the observed 4768 line have been assigned representing the vast majority of strong features in the spectrum. Future work will focus on other spectral regions and different target compounds.

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