Fourier Transform NIR Incoherent Broadband Cavity-Enhanced Absorption Spectroscopy (FT-IBBCEAS) of HONO/DONO, HNO_3

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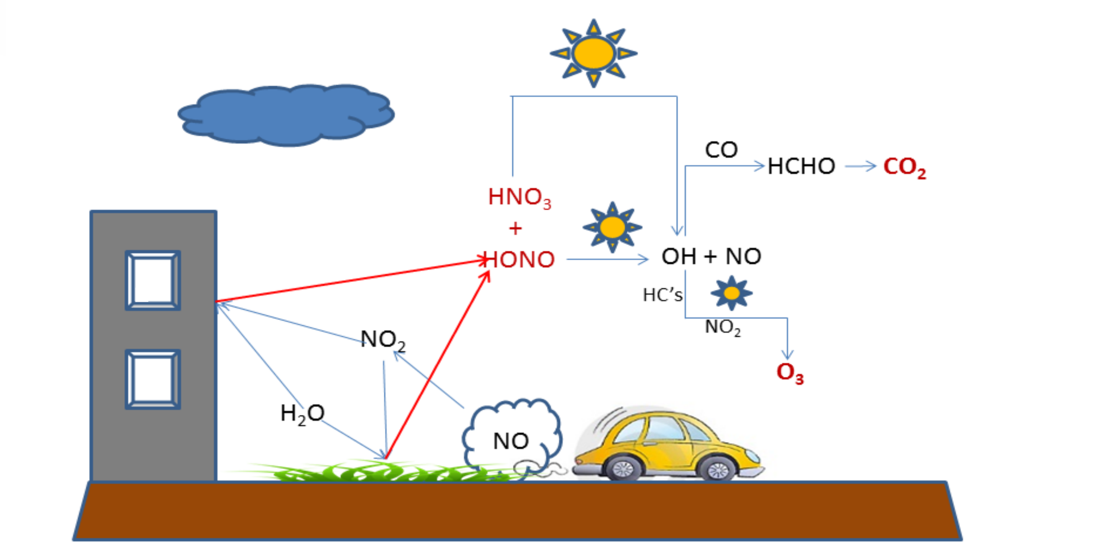
Motivation

a. Spectroscopy

E_v	HONO (cm^{-1})		DONO (cm^{-1})	
	cis	trans	cis	trans
ν_1	3426.1963(2)	3590.7704(1)	2533.5703(2)	2651.12844(7)
ν_2	1640.517(1)	1699.7602(1)	1625	1693.975(3)
ν_3	1261	1263.20705(4)	1008	1012.680(2)
ν_4	851.9431(3)	790.1171(3)	813.500(2)	736.266(1)
ν_5	609.224(2)	595.62003(3)	601	590.4(3)
ν_6	639.74320(6)	543.87971(7)	508.2(3)	416.1(3)
$\Delta E_{cis\text{-}trans}$	99±25		136±30	

High resolution Fourier transform spectra of DONO were first recorded by Halonen et al [1], who analysed the ν_3, ν_4, ν_5 and ν_6 fundamental bands of *trans* DONO and the ν_4 fundamental of *cis* DONO. However, no absorption band of DONO has been measured till date in the NIR region. Detailed studies of the ν_1 fundamental band of *trans* and *cis* DONO [2] between 2350 and 3000 cm^{-1} at 0.003 cm^{-1} resolution showed that unlike the ν_1 band of HONO, no strong perturbations exist for either isomer of DONO.

b. Atmospheric chemistry



HONO is a precursor of the most important oxidising agent in the troposphere, the hydroxyl (OH) radical. In polluted urban areas , this in turn leads to the formation of green house gases like O_3 and CO_2. The hydrolysis of NO_2 on heterogeneous surfaces is a well-known mechanism for formation of HONO, resulting in HNO_3 as a by-product. Simultaneous measurement of these species can thus help understand the production of the molecule and the reaction chemistry better.

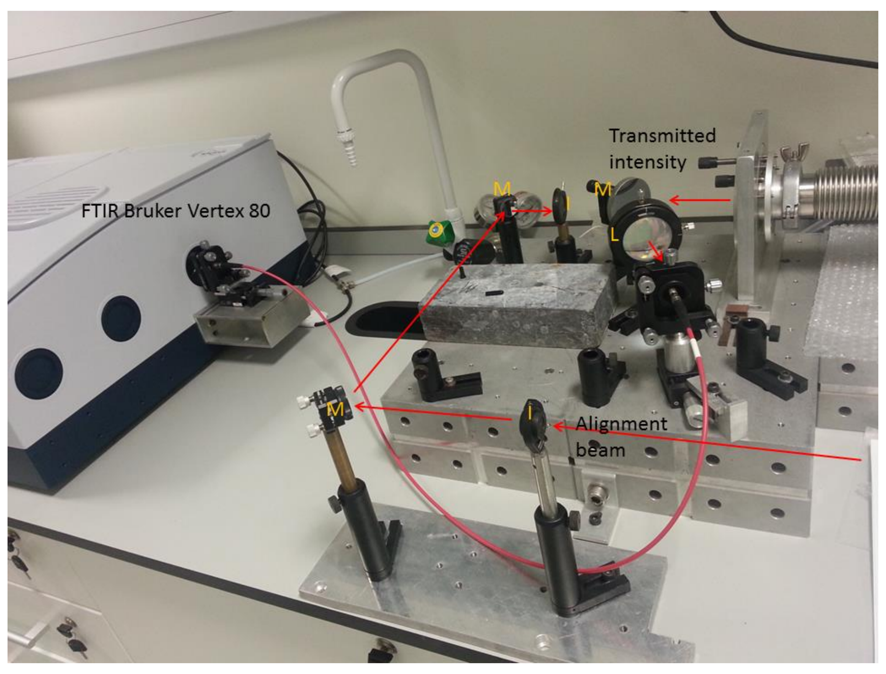
Experimental Setup

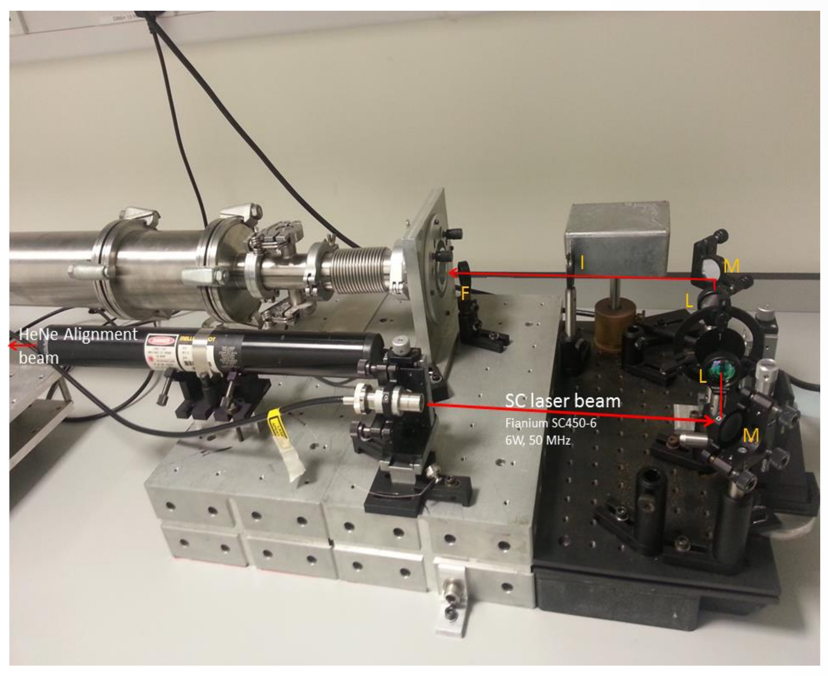
FTIBBCEAS [3, 4]

- Measures the Fourier transform of the transmitted light intensity through a stable optical cavity (length , d = 6.44 m) consisting of high reflectance mirrors
- All spectra were recorded at a resolution of 0.08 cm^{-1} between 5500 and 8000 cm^{-1}
- NIR→ Less spectral congestion, vibrational overtones' detection
- The transmission signal strength is measured with and without the absorber of interest present inside the cavity ($I(\lambda)$ and $I_0(\lambda)$ respectively). From the ratio of the wavelength-dependent transmitted intensities, the reflectivity of the mirrors $R(\lambda)$ and the sample path length per pass d inside the cavity, the sample's extinction coefficient $\varepsilon(\lambda)$ is calculated as

$$\varepsilon(\lambda) \approx \frac{1}{d}\left(\frac{I_0(\lambda)}{I(\lambda)} - 1\right)\left(1 - R(\lambda)\right) = \frac{N}{V}\sigma(\lambda) = \frac{P}{kT}\sigma(\lambda)$$

- The mirror reflectivity is determined by filling the chamber with a known concentration of CO_2 (pressure P= 6 mbar), and estimating the extinction coefficient based on the absorption cross-section of the sample at a particular wavelength.





Experimental setup: M-Mirror, L-lens, I-Iris, F- Filter. For measurements in the region of interest, a longpass filter centred at 1100nm (Thorlabs, FEL1100) was introduced between the laser and the cavity.

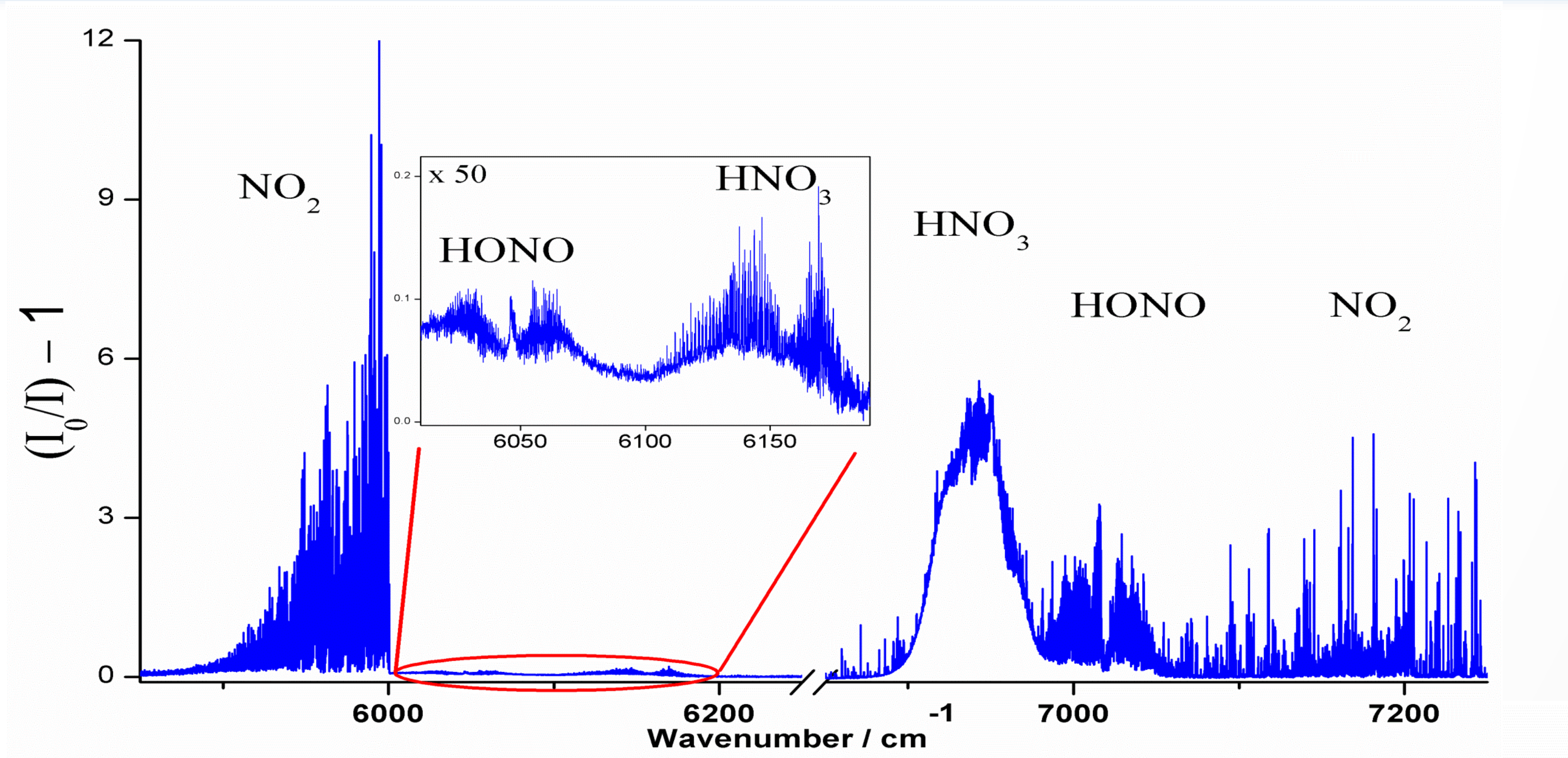
Results

Simultaneous detection of HNO_3/HONO/NO_2 in the NIR

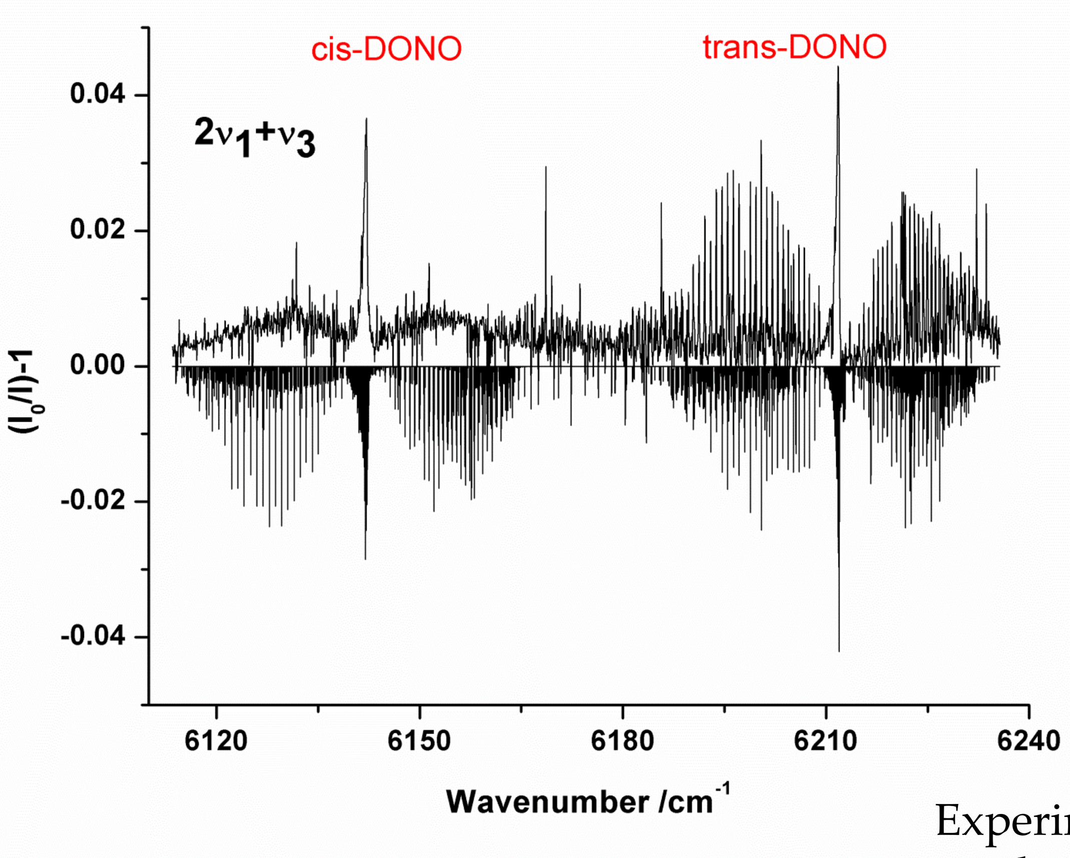
- Several rotationally resolved overtone bands of HONO, HNO_3 and NO_2 were detected simultaneously across the NIR spectral range, demonstrating the potential of FTIBBCEAS to detect multiple trace gases simultaneously through their known line positions.

- **Estimated particle densities**

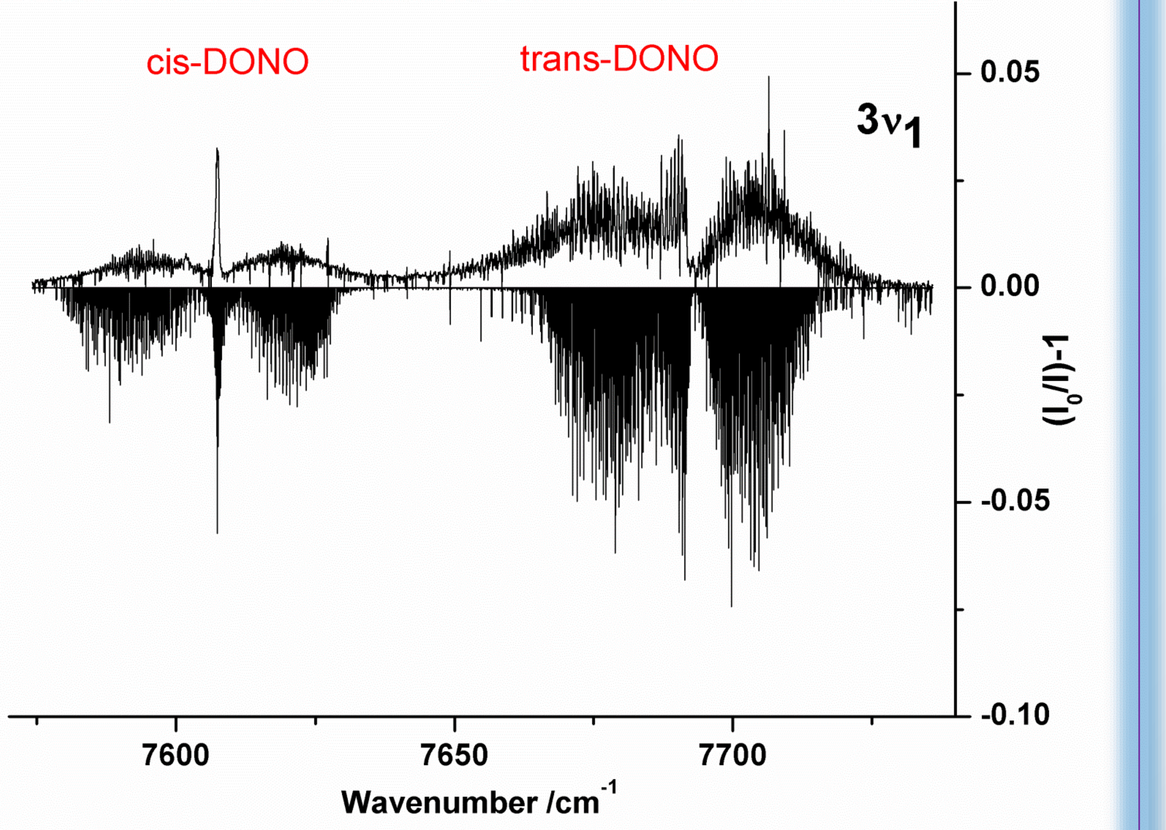
  n_{HONO}≈2.42×10^9 molecule cm^{-3}
  n_{NO2}≈2.7×10^{16} molecule cm^{-3}
  n_{HNO3}≈1.6×10^{13} molecule cm^{-3}



The NIR spectra of DONO



	$2\nu_1+\nu_3$ (cm^{-1})		$3\nu_1$ (cm^{-1})	
	cis	*trans*	*cis*	*trans*
E_v	6142.55(1)	6212.029(5)	7607.55(2)	7692.496(8)
A	2.3532(5)	2.9770(3)	2.3539(6)	2.9559(4)
B	0.4216(1)	0.3961(4)	0.4229(1)	0.4037 (5)
C	0.3635(1)	0.3302(4)	0.3601(1)	0.3204 (5)
D_k	-1.3(1)E-5	5.2(6)E-5	-9.2(7)E-5	4.8(3)E-5
D_{jk}	6.1(11)E-6	-5.9(30)E-7	-4.5 (2)E-5	-7.6(15)E-7
D_j	-1.3(1)E-6	3.9(4)E-7	1.5(2)E-7	5.1(5)E-7



Experimental (top) and simulated [5] (bottom) spectra at 300 K, 0.08 cm^{-1} resolution, and the table of spectroscopic constants obtained from PGOPHER fit.

References

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