Detection of Ambient Formaldehyde by Incoherent Broadband Cavity Enhanced Absorption Spectroscopy

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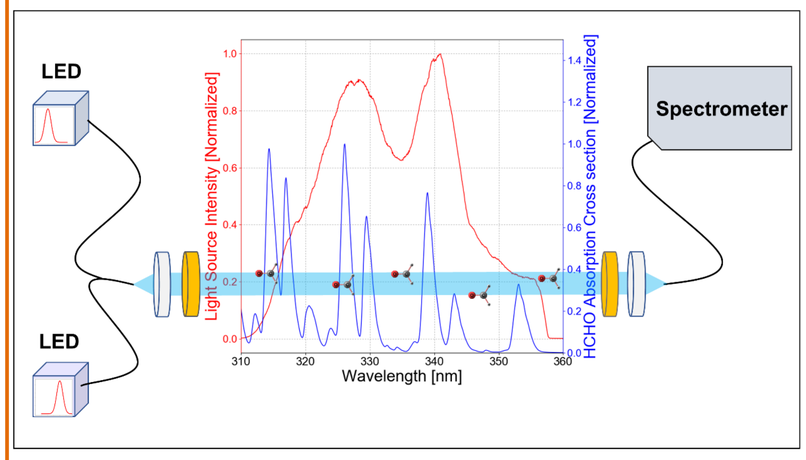
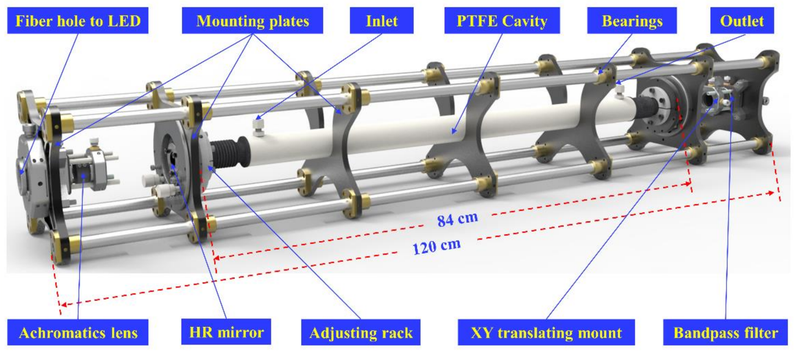
Abstract

A new LED-based IBBCEAS was developed herein to measure HCHO in ambient air. Two LEDs (325 and 340 nm) coupled by a Y-type fiber bundle were used as an IBBCEAS light source, which provided both high light intensity and a wide spectral fitting range. The instrument was successfully deployed for the first time in a field campaign and delivered results that correlated well with those of a commercial wet-chemical instrument based on Hantzsch fluorimetry (R2 = 0.769). The combined light source based on Y-type fiber bundle overcomes the difficulty of measuring ambient HCHO via IBBCEAS in near-ultraviolet range, which may extend IBBCEAS technology to measure other atmospheric trace gases with high precision.

Instrumental setup



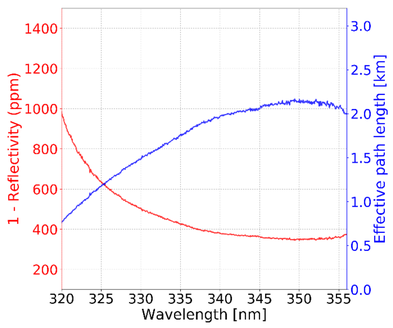
The optical layout of the IBBCEAS system consists of a light source module, an optical cavity module, and a spectrometer. Using two LEDs coupled by a Y-type fiber bundle as the light source is the core of the whole system.



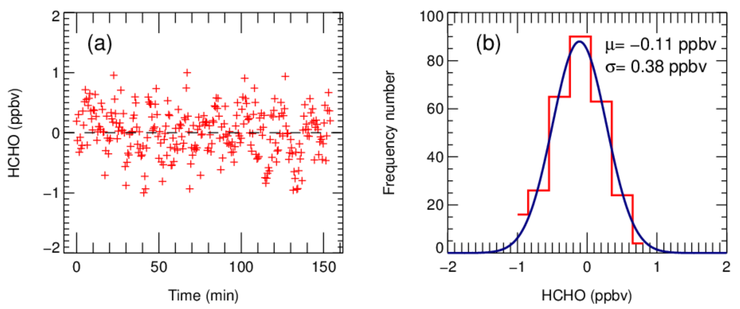
The entire cavity module adopts the cage structure design to enhance the system stability; this design is more convenient for replacing parts and adjusting the optical path, which can improve system reproducibility.

Instrumental performance

Overview



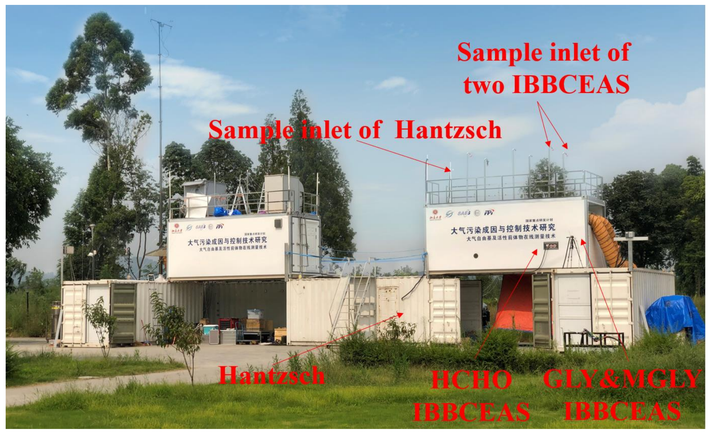
The reflectivity of the two cavity mirrors used herein was 0.99965 (1–reflectivity = 350 ppm loss) at 350 nm, which corresponded with an effective optical path length of 2.15 km within a 0.84 m cavity.



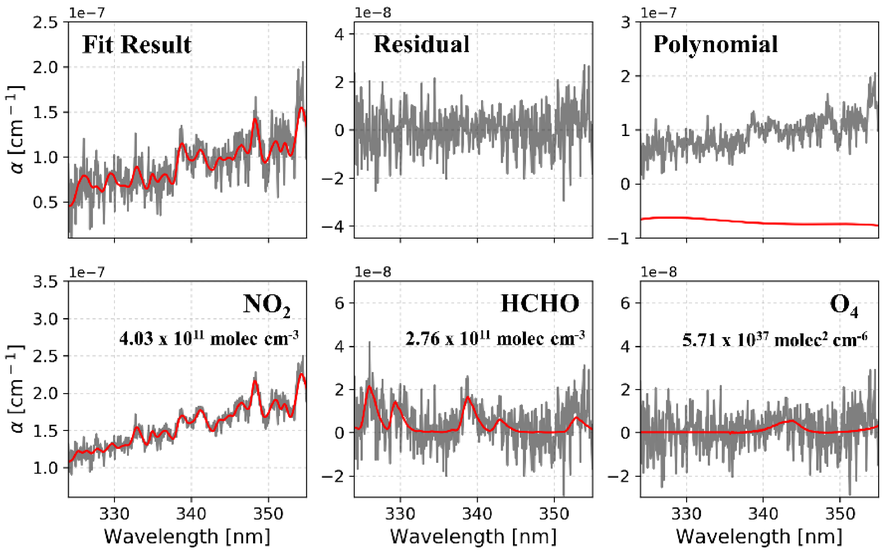
At an integration time of 30 s, the measurement precision (1σ) for HCHO was 380 parts per trillion volume (pptv) and the corresponding uncertainty was 8.3%.

Field Application

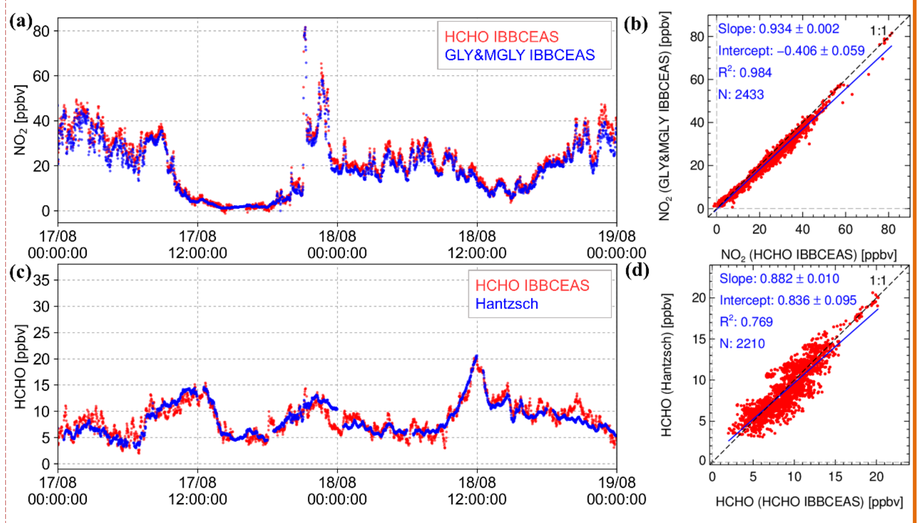
Our IBBCEAS system has been deployed in two campaigns which were held in Szechwan and Shanghai, respectively.



Measurement site in the Szechwan Basin and laboratory containers where the HCHO IBBCEAS, GLY&MGLY IBBCEAS, and Hantzsch instruments were deployed.



An example of spectral fitting for one spectrum (60 s average) measured during a field campaign on 15 August 2019 at 08:59. The red line represents the fitted spectrum, and the black line is the fitted result plus the residual. Corresponding NO2 and HCHO concentrations is 16.4 ppbv and 11.2 ppbv, respectively.



Partial data from the field campaign in the Szechwan Basin. (a) Time series of NO2 concentrations measured by HCHO IBBCEAS and GLY&MGLY IBBCEAS. (b) Correlation plot for NO2 measurements by two IBBCEAS. (c) Time series of NO2 concentrations measured by HCHO IBBCEAS and Hantzsch instrument. (d) Correlation plot for HCHO measurements.

Outlook

- When LED power and mirror reflectivity still limit HCHO IBBCEAS performance, improving the mechanical stability of the IBBCEAS system could be a good option. To reduce system noise, reducing degrees of freedom can improve the system optical stability and optimizing sampling gas paths can improve sampling flow stability.
- Coupling two LEDs as a light source can be extended to detect other trace gases (e.g. glyoxal and HONO) in ambient air by IBBCEAS in the ultraviolet and visible spectra.

Reference

Liu, J., Li, X., Yang, Y., Wang, H., Kuang, C., Zhu, Y., Chen, M., Hu, J., Zeng, L., and Zhang, Y.: Sensitive Detection of Ambient Formaldehyde by Incoherent Broadband Cavity Enhanced Absorption Spectroscopy, Anal Chem, 10.1021/acs.analchem.9b04821, 2020.

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