

Electronic Supplementary Information

**Fast molecular fingerprinting with coherent, rapidly tunable dual-comb spectrometer near 3  $\mu\text{m}$**

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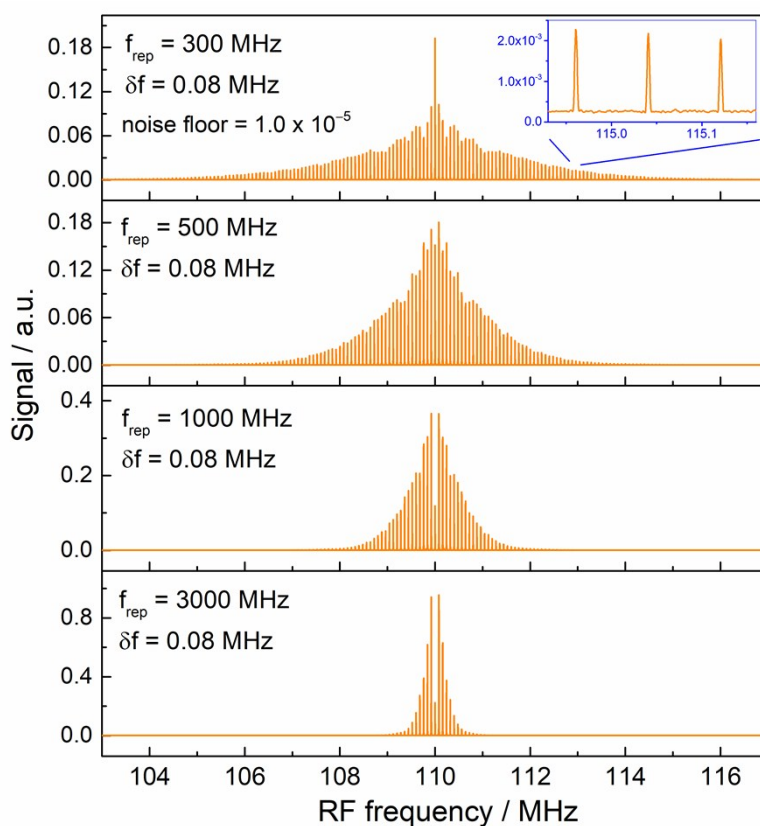
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Part A shows comb-mode-resolved spectra with different pulse repetition frequencies, Part B presents how to obtain the molecular transmittance spectrum by employing comb-mode-resolved spectroscopy, and Part C shows dual-comb molecular spectra at different spectral regions. ESI includes 5 figures.

### A. Comb-mode-resolved spectra with different pulse repetition frequencies

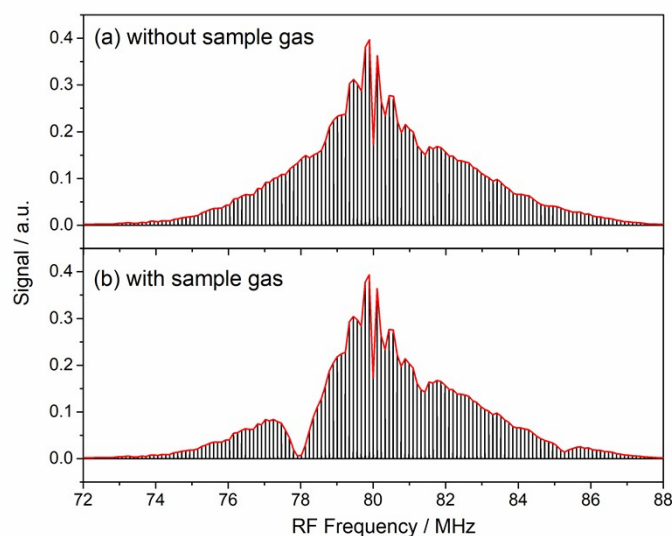
The mid-infrared dual comb spectrometer was built relying on electro-optic intensity modulators (EOIMs) and difference frequency generation (DFG). The EOIMs were driven by the 30 ps electrical pulse generators (EPGs) to generate 30 ps optical pulsed lasers based on a single cw fiber laser. The pulse repetition frequencies, which correspond to the comb-mode spacings ( $f_{\text{rep}}$  and  $f_{\text{rep}} - \delta f$ ), can be easily tuned from a few hundred MHz to a few GHz by adjusting the repetition frequency of EPGs. In order to record entire dual-comb spectrum, one of the combs was center frequency shifted (+80 MHz or +110 MHz) by an acousto-optic frequency shifter (AOFS). To perform the dual-comb spectroscopy, two combs were spatially overlapped and detected with a photovoltaic HgCdTe (MCT) detector, then digitized and Fourier-transformed by a data-acquisition board. Figure S1 shows the down-converted dual-comb spectra with different pulse repetition frequencies in the RF domain. The tunable range of pulse repetition frequencies is 80–4000 MHz ( $2.6 \times 10^{-3}$ – $0.13 \text{ cm}^{-1}$ ), which is limited by the EPGs and RF electronic components. Additionally, the quality of a dual-comb spectrometer can be evaluated using figure of merit<sup>1</sup>, which is defined as the product of the SNR (average SNR of comb lines), normalized by the square root of the acquisition time, and the number of resolved frequency elements ( $\text{SNR} \cdot \text{M} \cdot \text{s}^{-1/2}$ ). For our system, the figure of merit was  $\sim 2.21 \times 10^6 \text{ s}^{-1/2}$ .



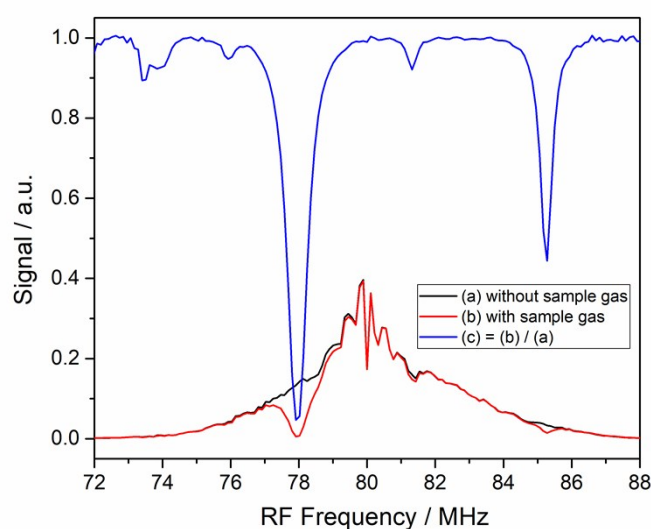
**Figure S1.** Comb-mode-resolved RF spectra with different pulse repetition frequencies. Data recording time of each spectrum is 52.429 ms at a sampling rate of 500 MS/s.

## B. Molecular spectral measurements using comb-mode-resolved spectroscopy

To perform the quantitative molecular absorption spectroscopy, we recorded the dual-comb spectra of a cell with and without gas sample, as shown in Fig. S2. With the dual-comb spectroscopy, each comb line provides one spectral sampling point (indicated as red curve in Fig. S2.). For dual-comb setup using dispersive configuration, the amplitude of molecular transmission spectrum was obtained from the spectrum with gas sample divided by the spectrum without gas sample, as shown in Fig. S3. The transmittance intensity spectrum,  $T(\nu)$ , is the square of the amplitude spectrum and the absorbance spectrum is equal to  $-\ln[T(\nu)]$ .



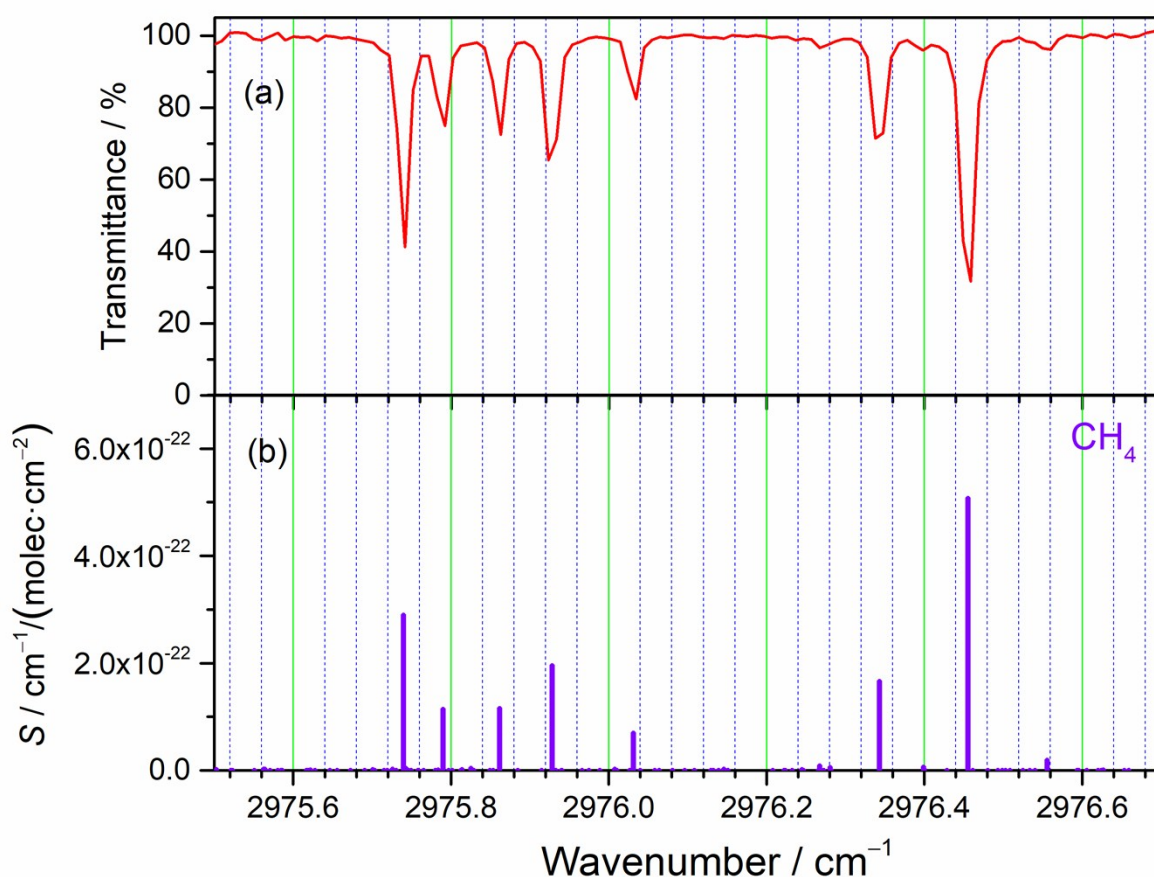
**Figure S2.** Comb-mode-resolved spectra in RF domain. The red curves indicate the amplitude of each comb line peak. Here, the experimental conditions are same as Fig. 2.



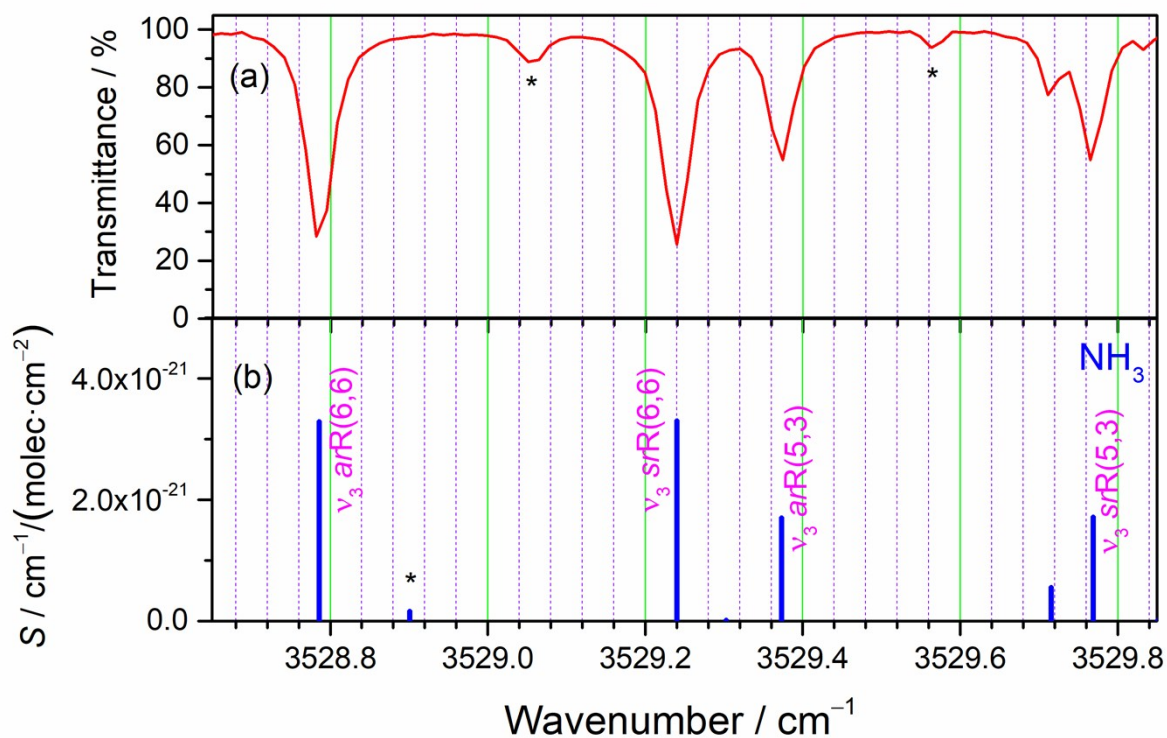
**Figure S3.** Dual-comb amplitude spectra. The amplitude signal of molecular transmission is equal to the sample spectrum divided by the background spectrum (without gas sample).

### C. Dual-comb spectra at different spectral regions

For the tunable MIR dual-comb spectrometer, the center wavelength of MIR combs could be simply changed by tuning the wavelength of either the signal comb or the pump laser with suitable poling period of PPLN crystal for the difference frequency generation (DFG). For each DFG system, there were two 5% MgO-doped multi-channel PPLNs with the same size and were manufactured by HC photonics. The poling periods at each channel of the two PPLNs were 19.5, 19.8, 20.1, 20.4, 20.7, 21.0, 21.3  $\mu\text{m}$  and 20.6, 20.9, 21.2, 21.5, 21.8, 22.1, 22.4, 22.7, 23.0, 23.3  $\mu\text{m}$ , and the both sides of the PPLNs were optical polished and AR coated for the pump, signal and idler wavelengths. All PPLN crystals were held in an oven which were also manufactured by HC photonics. The temperature of the PPLN crystal in an oven could be maintained and controlled from 15 to 85  $^{\circ}\text{C}$ . With this many poling periods and the widely temperature controllable range, the wavenumber of the idler beam could be tuned from 2818 to 3360  $\text{nm}$  (2976–3548  $\text{cm}^{-1}$ ). The dual-comb molecular spectra near 3.36 and 2.83  $\mu\text{m}$  are shown in Figs. S4 and S5, respectively.



**Figure S4.** (a) A dual-comb transmittance spectrum near 3.36  $\mu\text{m}$ . The comb-mode spacing ( $f_{\text{rep}}$ ) is 303 MHz and the  $\delta f$  is 0.33 MHz. The data recording time is 671 ms at a sampling rate of 500 MS/s. Here, a 32.5-m multi-pass cell was filled with a gas mixture of  $\text{CH}_4/\text{N}_2$  (1/48, 43.2 Torr, 295 K). (b) The corresponding transition lines of  $\text{CH}_4$  taken from HITRAN database.<sup>2</sup>



**Figure S5.** (a) A dual-comb transmittance spectrum near 2.83  $\mu\text{m}$ . The comb-mode spacing ( $f_{\text{rep}}$ ) is 404 MHz and the  $\delta f$  is 0.25 MHz. The data recording time is 671 ms at a sampling rate of 500 MS/s. Here, a 32.5-m multi-pass cell was filled with a gas mixture of  $\text{NH}_3/\text{N}_2$  (1/333, 103.3 Torr, 295 K). (b) The corresponding transition lines of  $\text{NH}_3$  taken from HITRAN database.<sup>2</sup> The marked weak lines (\*) indicate obvious discrepancies between the observed spectrum and HITRAN database that might be caused by either no assignments<sup>3</sup> or rotational perturbations.

## References

- (1) N. R. Newbury, I. Coddington, and W. C. Swann, *Opt. Express*, 2010, **18**, 7929–7945.
- (2) The HITRAN Database, <http://hitran.org/>.
- (3) N. Maaroufi, N. Dridi, A. Farji, F. K. Tchana, X. Landsheere and H. Aroui, *J. Quant. Spectrosc. Radiat. Transfer*, 2019, **227**, 94–105.