Supporting Information of Mid-infrared cavity-enhanced two-photon absorption spectroscopy for selective detection of trace gases

Yu-Zhong Liu,[†] Meng-Yi Yu,[‡,¶] Yan-Dong Tan,[§] Jin Wang,[§] Cun-Feng Cheng,[*,‡,¶,§] Wei Jiang,[†,¶] and Shui-Ming Hu[*,¶,§]

[†]*School of Physical Sciences, University of Science and Technology of China, Hefei 230026, China*

[‡]*State Key Laboratory of Molecular Reaction Dynamics, University of Science and Technology of China, Hefei 230026, China*

[¶]*Hefei National Laboratory, University of Science and Technology of China, Hefei 230088, China*

[§]*Hefei National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China*

E-mail: cfcheng@ustc.edu.cn; smhu@ustc.edu.cn

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1. Two-photon absorption coefficient

The lowest-order transverse mode of a stable optical cavity, known as TEM_{00}, exhibits a Gaussian intensity profile characterized by a beam radius w. The on-axis intensity is expressed as $2P_{ic}/(\pi w^2)$, where P_{ic} represents the intra-cavity laser power. Assuming that gas molecules interact with the intra-cavity radiation in the TEM_{00} mode, the power absorbed by the molecules within the cavity due to TPA can be expressed as

$$P_{abs} = hc\nu R_{ss} N \pi w^2 L, \tag{S1}$$

where h is the Planck constant, c is the speed of light, N denotes the number density of molecules in the ground state, L is the cavity length, and R_{ss} is the steady-state absorption rate per molecule, which can be calculated using the density matrix method. In the weak absorption limit, neglecting the absorption loss in the intra-cavity laser power, the absorption coefficient α_2 induced by the two-photon transition can be written as

$$\alpha_2 = \frac{P_{abs}}{2LP_{ic}} = \frac{hc\nu R_{ss} N \pi w^2}{2P_{ic}}. \tag{S2}$$

It is important to note that α_2 is related to the beam waist, which is 0.7 mm in our experiment.

2. Cavity-enhanced two-photon absorption spectroscopy

When a laser is locked to a high-finesse cavity, the variation rate of the power inside the cavity is given by

$$\frac{dP_{ic}}{dt} = P_{in} - \beta P_{ic} - \gamma_1 P_{ic} - \gamma_2 P_{ic}^2, \tag{S3}$$

where P_{ic}, P_{in}, β, γ_1, and γ_2 are the intra-cavity laser power, injected laser power, empty cavity loss rate, single-photon absorption rate, and two-photon absorption rate, respectively. The empty cavity loss rate is given by $c(1-R)/L$, where R denotes the reflectivity of the cavity mirror. The SPA and TPA rates are equal to the corresponding absorption coefficients multiplied by the speed of light. In the context of gas absorption during the TPA process under off-resonance conditions ($\Delta\nu \gg \delta\nu_D$), where $\gamma_1 \ll \beta$, the contribution from SPA can be neglected. In the steady state, Equation S3 simplifies to:

$$\frac{dP_{ic}}{dt} = P_{in} - \beta P_{ic} - \gamma_2 P_{ic}^2 = 0. \tag{S4}$$

In the absence of absorption within the cavity, the injected laser power equals the cavity loss at steady state, leading to $P_{in} = \beta P_{ic,0}$, where $P_{ic,0}$ is the intra-cavity laser power without gas absorption. Consequently, the dimensionless TPA signal can be calculated as

$$S_{TPA} = \frac{\gamma_2}{\beta} P_{ic,0} = \frac{1 - P_{ic}/P_{ic,0}}{(P_{ic}/P_{ic,0})^2}. \tag{S5}$$

Experimental measurements yield the ratio between the intra-cavity laser powers with and without absorption as $\kappa = P_{ic}/P_{ic,0}$. Lehmann derived the TPA rate at resonance ($\Delta\nu_{02} = 0$) by neglecting the saturation effect under high sample pressure conditions.[1] When collisional effects dominate the system relaxation rate and the TPA linewidth is governed by homogeneous pressure broadening, the TPA rate γ_2° becomes independent of the sample gas pressure and can be written as

$$\gamma_2^\circ = \frac{A_{01} A_{12} a_p(J_0, J_1, J_2) f_0 x_a}{256\pi^4 h c^3 L k_B T_g \Delta\nu_{01}^2 \nu^4 b_p}, \tag{S6}$$

where A_{01} and A_{12} are the Einstein coefficients between the three levels, $a_p(J_0, J_1, J_2)$ is a dimensionless factor accounting for spatial degeneracy, f_0 represents the fraction of molecules in state 0, x_a is the mole fraction of the analyte in the sample gas, L is the cavity length, T_g is the gas temperature, $\Delta\nu_{01}$ is the detuning, ν is the center frequency, and b_p is the pressure broadening coefficient (half width at half maximum, HWHM).

Pressure dependence

In the low-pressure limit, the line profile results from the convolution of Lorentzian pressure broadening and Gaussian transit-time broadening.[2] The overall HWHM can be approximated as $\Gamma \approx \sqrt{\Gamma_t^2 + (b_p p_g)^2}$, where Γ_t is the transit time broadening and p_g is the sample gas pressure. Therefore, we can express the TPA rate as

$$\gamma_2 = \frac{b_p p_g}{\Gamma} \gamma_2^\circ \tag{S7}$$

At low pressures, the TPA rate γ_2 depends not only on the mole fraction of the target molecule but also on the total sample pressure. TPA signals from a CO_2 sample with a 4.92% $^{13}C/C$ ratio were measured at six different pressures, all under the same laser power injected into the cavity. In Figure 3C, the red line shows a fit of the TPA data according to Equation S8 below. The fit optimized two parameters: the pressure-independent TPA signal S_{TPA}° and Γ_t/b_p.

$$S_{TPA} = \frac{p_g}{\sqrt{(\frac{\Gamma_t}{b_p})^2 + p_g^2}} S_{TPA}^\circ \tag{S8}$$

The pressure-independent TPA signal for the sample containing 4.92% $^{13}C/C$ is determined to be 0.0826(6) at an injection laser power of 17 mW. The value of Γ_t/b_p is found to be 4.5(2) Pa.

Saturation effect

Saturation of the two-photon transition reduces γ_2 by a factor of $1/(1+G^2)$, where G is the two-photon saturation parameter defined as $G = I/I_{sat}$. In our experiments, the saturation intensity for TPA is approximately 26 kW/cm^2, resulting in a G value of about 0.03.[1] Note that the intra-cavity laser power adjusts according to changes in the TPA rate when measuring samples containing different concentrations of $^{13}CO_2$ while maintaining the same input laser power P_{in}. To eliminate systematic deviations caused by optical saturation, all measured TPA signals are corrected to their unsaturated values using $S_{TPA,US} = (1+G^2)S_{TPA}$ in this work. TPA signals from the sample with 4.92% ^{13}C/C were measured at 20 Pa under six different injected laser powers. In Figure 3B, a linear fit confirms that the saturation-corrected TPA signal is proportional to the input laser power in our experimental system.

3. Experimental setup

The optical layout of the experimental setup is presented in Figure S1. The mid-infrared light source is a homemade OPO laser with a configuration similar to that described in our previous studies.[3,4] An external cavity diode laser (ECDL, Precilasers) operating at 1064 nm, with a linewidth of 10 kHz over an integration time of 100 μs, was used as the pump seed. This seed laser was amplified using a Yb-doped fiber amplifier, delivering up to 10 W of output power for pumping the OPO. The power of the idler output of the OPO, ranging from hundreds of milliwatts to over 1 W across the wavelength range of 2.6 to 4.3 μm, was achieved by selecting different poling periods of the periodically poled lithium niobate (PPLN) crystal and adjusting its temperature. For measurements of the two-photon absorption, MIR light at a wavelength of 2778 nm was coupled into an optical cavity with a length of 75 cm. This cavity comprises two plano-concave mirrors, each with a radius of curvature of 1 m (Layertec Gmbh Inc.). The reflectivity at 2778 nm was measured to be

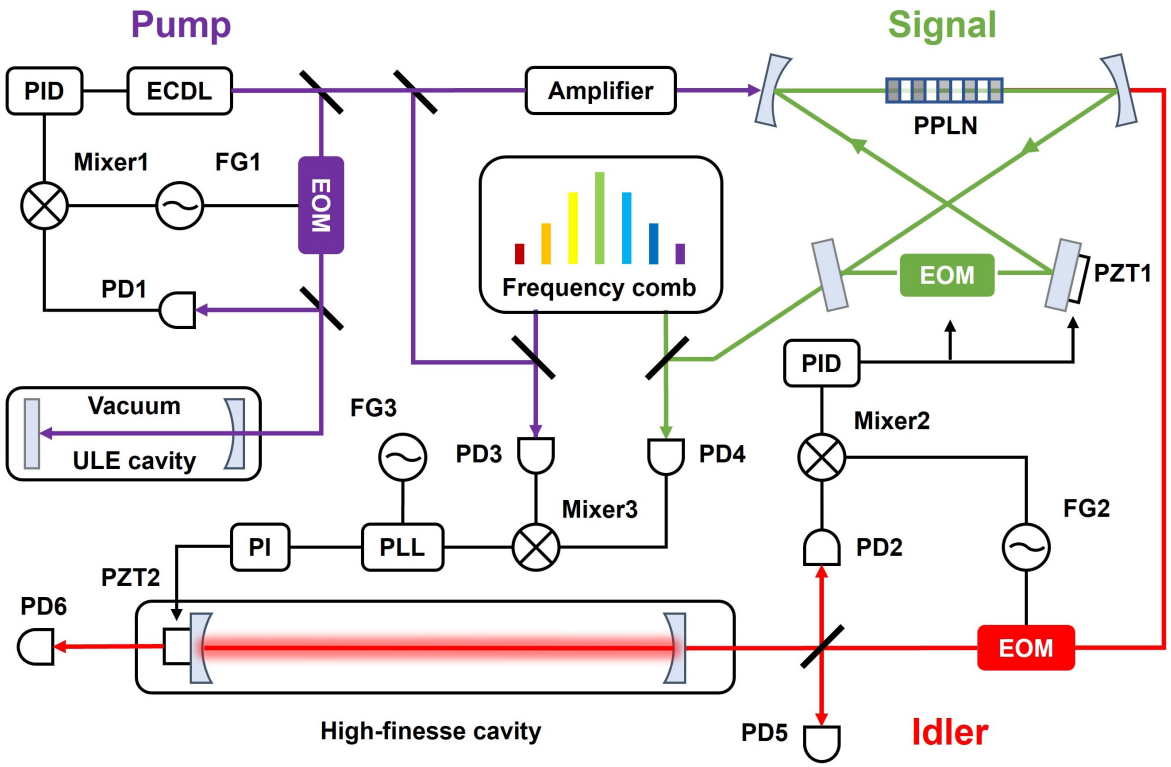

Figure S1: Detailed schematic of the experimental setup. ECDL: external cavity diode laser, EOM: electro-optical modulator, ULE: ultra-low expansion glass cavity, PPLN: periodically poled lithium niobate, PZT: piezoelectric ceramic transducer, PID: proportion-integration-differentiation, PI: proportion-integration, PLL: phase lock loop.

99.967% using the ring-down method. The cavity's free spectral range is approximately 200 MHz, and the beam waist radius at the focal point is about 0.654 mm. The optical cavity is enclosed within an aluminum vacuum chamber with a volume of approximately 7.5 liters. To minimize cavity length variations, the chamber is thermally stabilized using a feedback servo, achieving temperature stability better than 10 mK at 300 K.

In the experiment, A three-step locking scheme was implemented to ensure precise frequency control: (i) The OPO pump laser was locked to an ultra-low expansion (ULE) cavity using the Pound-Drever-Hall (PDH) technique to suppress frequency fluctuations. (ii) The idler output of the OPO was coupled into the high-finesse cavity for TPA measurements. The idler laser frequency was locked to the cavity using another PDH servo, with the fast and slow feedback signals applied to an electro-optical modulator (EOM) placed inside the OPO cavity and a piezoelectric transducer (PZT) attached to one OPO cavity mirror, respectively. (iii) A near-infrared (NIR) optical frequency comb ($f_{rep} \approx 200$ MHz) referenced to a local active hydrogen maser (VCH-1003M) was used to calibrate the OPO's pump and signal laser frequencies. The beat notes between the pump and signal lasers and the frequency comb were recorded, and the difference between the two beat notes was further compared to a preset radio frequency (RF) signal. This difference was processed through a phase-locking circuit, and the feedback signal was applied to the PZT of the high-finesse cavity to control its length. By linking the cavity length to the frequency difference between the pump and signal lasers (equivalent to the idler frequency), precise frequency scans of the idler laser were achieved by adjusting the RF source frequency.

Fig. S2 shows the transmittance spectrum of a blank sample with an intra-cavity laser power of 5.6 W, indicating an RMS noise level of about 2×10^{-4}. Such a noise level is equivalent to a detection limit of about 7×10^{-8} $\mathrm{cm^{-1}Hz^{-1/2}}$. As shown in Equation 1 of the main manuscript, the dimensionless TPA signal amplitude is derived from the transmittance of the cavity. Note that the transmitted light intensity noise increases as the square root of the light intensity. Therefore, the signal-to-noise ratio of the transmittance (and also for the

TPA signal) is expected to grow with the laser power.

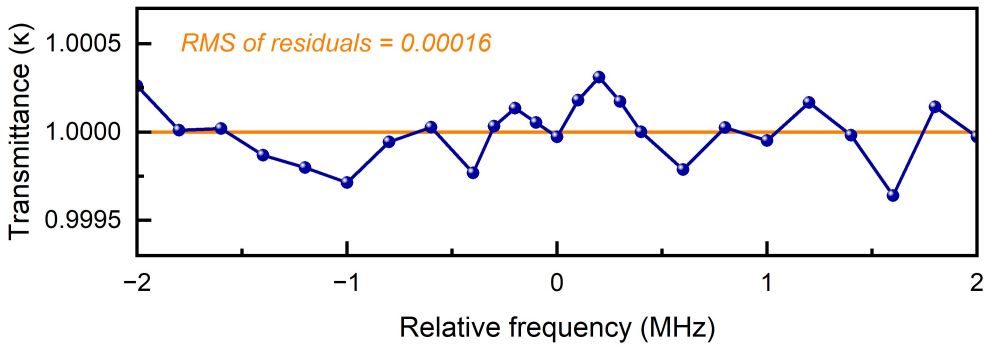

Figure S2: Noise level of the CEAS measurement.

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