

ARTICLE

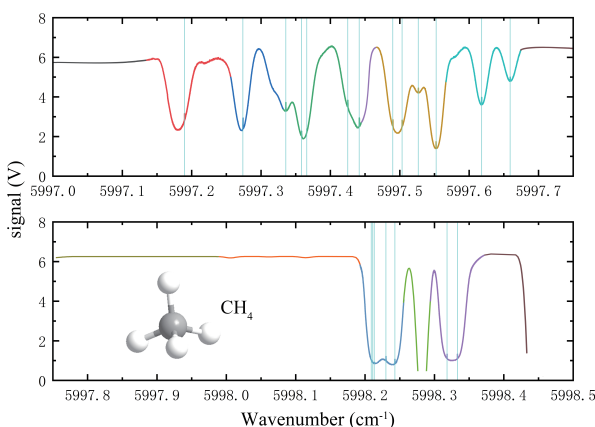
Saturated Absorption Spectroscopy of Methane around 1667 nm[†]Yuan Ding^a, Fanghui Cao^b, Jinke Li^a, Jin Wang^b, Anwen Liu^a, Yan Tan^{b*}, Shuiming Hu^a^a. State Key Laboratory of Molecular Reaction Dynamics, Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China^b. Hefei National Research Center of Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, China

(Dated: Received on July 10, 2024; Accepted on September 18, 2024)

Methane is the second most important greenhouse gas after carbon dioxide, and the reduction of methane emissions is a key focus in IPCC reports. At present, atmospheric methane is monitored through ground-based observations and satellite remote sensing that depend on spectral characteristics. However, the positions of the methane lines provided by the widely utilized HITRAN database lack the precision required for accurate retrievals. In this

work, we used cavity-enhanced absorption spectroscopy to record the absorption spectrum near the atmospheric detection window of methane at 1.66 μm . From the saturated absorption peaks (“Lamb dips”) observed on top of Doppler-broadened methane absorption lines, we determined the line positions with an absolute frequency accuracy of better than 2 MHz. The results also indicate the incompetence of the HITRAN database and theoretical models based on *ab initio* calculations of methane lines in this region.

Key words: Methane, Cavity ring-down spectroscopy, Doppler-free Lamb dips



I. INTRODUCTION

Methane is the second most important greenhouse gas after carbon dioxide, accounting for about 16% of the global radiative forcing of greenhouse gases [1]. Its atmospheric concentration has almost doubled since the industrial era. In 2023, the global average concentration of methane reached 1922.6 ppb, significantly exceeding the historical record of the past 650,000 years [2]. Given the relatively short atmospheric lifetime and low concentration of methane, rapid and accurate at-

mospheric methane monitoring is critical to addressing climate change [3, 4]. Accurate determination of the global methane mixing ratio is essential to understand the factors controlling methane emissions. Consequently, multiple satellite missions have been launched over the years, including the scanning imaging absorption SpectroMeter for atmospheric CHartographY (SCIAMACHY) [5], the greenhouse gases observing satellite (GOSAT) [6], methane remote sensing lidar mission (MERLIN) [7], and MethaneSAT which launched in 2024 [8, 9]. Active detection of atmospheric greenhouse gases requires precise positioning of laser probes [10]. The spectrum of methane is vital for the analysis and simulation of the Titan atmosphere, but the lack of reliable absorption coefficients in the near-infrared region remains a significant limitation. The near-infrared spectral region around 1.66 μm is chosen not only to mini-

[†] Part of Special Issue “In Memory of Prof. Xingxiao Ma on the occasion of his 90th Anniversary”.

* Author to whom correspondence should be addressed. E-mail: tanyan@ustc.edu.cn

mize the influence of atmospheric temperature variations and aerosol loading, but also to reduce cross-interference from other trace gases [11] such as CO₂ and H₂O. Therefore, this band is selected by most satellites.

Methane features four C_3 axes and a highly symmetrical spherical top structure. Its spectral complexity results from this high symmetry and strong vibrational-rotational coupling, which cause dense energy levels, overlapping lines, Doppler broadening from molecular motion, and pressure broadening from intermolecular collisions. Together, these factors lead to overlap of spectral lines in high-pressure environments or high-resolution spectral measurements, complicating spectral analysis [12]. The rotationally resolved spectrum of methane reaches up to 16180 cm⁻¹, but only the lower part of the icosad polyad (6800 cm⁻¹) is currently well assigned [13].

Atomic and molecular spectroscopy has long been used as a frequency reference, and emerging applications require more precise reference lines. For example, methane and acetylene near-infrared provide optical frequency references for fiber optic communications [14, 15]. The application value of methane's 1.65 μm spectrum necessitates higher precision in the parameters of the spectral line. The $2\nu_3$ band of CH₄ is located at 1.65 μm , and many transitions in the P and R branches have been extensively measured. Since the release of the GOSAT methane line list [6, 16], several studies have been carried out on methane spectra in the 1.67 μm region. Campargue *et al.* [17, 18] recorded methane spectra at liquid nitrogen and room temperature using differential absorption spectroscopy. Based on these spectra, they provided an empirical list of methane lines (WKLMC) [19] that covers the range of 5852–6183 cm⁻¹. Compared to the GOSAT-2009 line list, this dataset contains more entries and improves sensitivity by orders of magnitude. This list has also been incorporated into the HITRAN2012 database [20, 21] and serves as the main source of most spectral data in this wavelength range. Subsequently, the HITRAN database updated some spectral line parameters in 2016 based on the work of Nikitin *et al.* [6, 22]. Line shape parameters for methane in the $2\nu_3$ band were investigated by Nikitin *et al.* using data from the TANSO-FTS instrument on GOSAT. The theoretical spectroscopic database Theo-ReTS uses *ab initio* potential and dipole moment surfaces from extensive variational calculations [23]. Yang *et al.* [24] provided a list of methane

spectral lines in the 6075.3–6078 cm⁻¹ region, with most line positions more accurate than previous studies. This improvement is primarily due to the precise spectral line positions obtained by recording high-resolution saturated absorption (Lamb-dip) spectra.

Compared to the R and P branches, the Q branch has denser lines and related work is relatively sparse with lower precision. Due to the complexity involved in the high congestion and severe overlap of most of the methane Q branch lines, measurements and analysis of the profiles of the Q branch lines are very limited. Zolot *et al.* [14] extensively measured individual transitions in the Q branch at 1.6 μm using Fourier transform spectroscopy (FTS). However, this work was limited by the spectral resolution and the number of measurable absorption lines. Ishibashi *et al.* [25] studied the R(0) and Q(1) lines of methane near 1.66 μm using the saturated absorption line of ¹³C₂H₂ at 1.54 μm as a frequency reference, and achieved an accuracy of about 6 MHz. In this work, we use the cavity-enhanced absorption spectroscopy (CEAS) method to perform saturated absorption spectroscopy measurements on rotational transitions in the Q branch of the 00001 $\rightarrow$ A1 vibrational band of methane near 5998 cm⁻¹ (1667 nm).

II. EXPERIMENTS

The configuration of the experimental setup is shown in FIG. 1. The light source was a tunable external cavity diode laser (ECDL, TOPTICA DL PRO). The laser frequency was phase-modulated by an electro-optic modulator (EOM) and locked to an optical cavity with the Pound-Drever-Hall (PDH) method. The optical cavity consisted of a pair of high-reflective mirrors (HR, $R \simeq 0.99997$) with a distance of 76 cm. The cavity was enclosed in a vacuum chamber, with its temperature controlled by a feedback servo system. Two platinum thermal sensors were affixed to the optical cavity wall to monitor the cavity temperature, which was recorded at 296 K with a drift of less than 50 mK over the spectrum. Cavity-enhanced absorption spectroscopy (CEAS) was performed by scanning the cavity length and recording the light intensity transmitted from the cavity. A piezoelectric transducer (PZT) was connected to one of the high-reflective mirrors (HR), allowing the cavity length to be modified by altering the voltage applied to the PZT. Given that the probe laser frequency was precisely locked to the cavity, any adjustment in

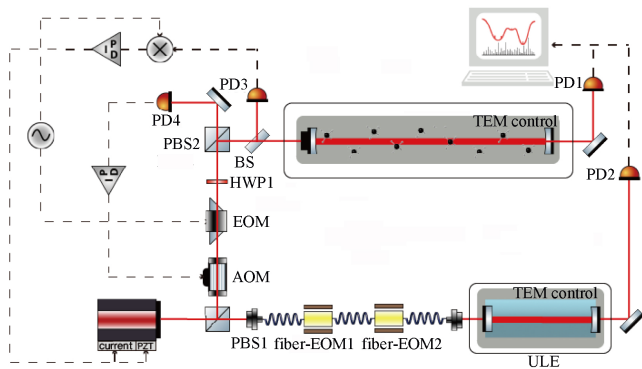


FIG. 1 Experimental setup for CEAS. AOM: acousto-optic modulator, EOM: electro-optic modulators, HWP: half-wave plates, PBS: polarizing beam splitter, BS: beam splitter, PD: photodetector, ULE: ultra-low-expansion glass cavity.

the cavity length resulted in a corresponding change in the laser frequency. Typically, a continuous scan of about 0.13 cm^{-1} could be accomplished by scanning the PZT from 0 to 100 V. To enhance the sensitivity of the CEAS measurement, the laser power was regulated using a feedback loop that manages the signal directed to an acousto-optic modulator (AOM). With the servo loop engaged, the laser power variation could be minimized to less than 1%. A sample spectrum measured using a methane sample gas with a partial pressure of 2 Pa is presented in FIG. 2, showing several narrow saturated absorption peaks (Lamb dips) on top of overlapped Doppler-broadened absorption lines.

A beam from the probe laser was coupled into a 10-cm-long Fabry-Pérot interferometer made of ultra-low-expansion (ULE) glass for frequency calibration. A dual-stage fiber electro-optic modulator was used to create several sidebands, each separated by a predetermined frequency of 99.77355 MHz, precisely 1/15th of the free spectral range of the ULE cavity. The transmission signal from the ULE cavity was recorded during the laser scan, as shown in the example in FIG. 2 (blue curve in (b)), and the peaks induced by the carrier and the sidebands were used to calibrate the laser frequency. In the area between neighboring peaks, a cubic spline interpolation technique was used to map PZT voltages to laser frequencies. The absolute frequency of a longitudinal mode of the ULE cavity has been calibrated by an optical frequency comb (OFC). The OFC is synthesized by an Er:fiber oscillator with its repetition frequency ($f_r \approx 184 \text{ MHz}$) and carrier offset frequency ($f_0 \approx 20 \text{ MHz}$) referenced to a local active hydrogen maser (VCH-1003M). The accuracy of OFC combs is better

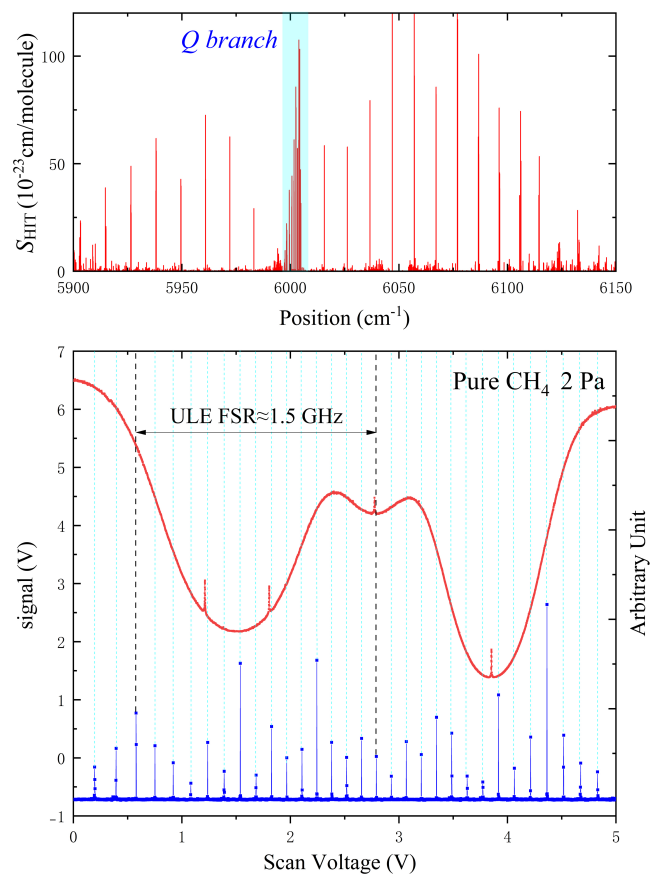


FIG. 2 (a) Overview of the $2\nu_3$ band spectrum of CH_4 around 6000 cm^{-1} , sourced from the HITRAN database. The light-blue shading marks the Q branch analyzed in this study. (b) The measured CEAS spectrum (red line) around 5997.47 cm^{-1} and the transmission spectrum (blue line) of the ULE etalon utilized for frequency calibration. The ULE's free spectral range is 1496.603 MHz , with side-band peaks generated by two EOMs separated by 99.77355 MHz .

than 1×10^{-12} (0.19 kHz at $1.57 \text{ }\mu\text{m}$). The drift of the ULE mode frequency has been measured to be less than 0.24 MHz/day . The calibration uncertainty of the laser frequency is estimated to be 0.2 MHz , mainly from the nonlinearity of the PZT which the cubic spline interpolation cannot fully correct.

III. RESULTS AND DISCUSSION

A. Line positions and the uncertainty budget

In CEAS analysis, the connection between cavity transmission and the molecular absorption coefficient $\alpha(\nu)$ can be expressed as:

$$\frac{I(\nu)}{I_0(\nu)} = \exp\left(-\frac{\alpha(\nu)L}{1-R}\right) \quad (1)$$

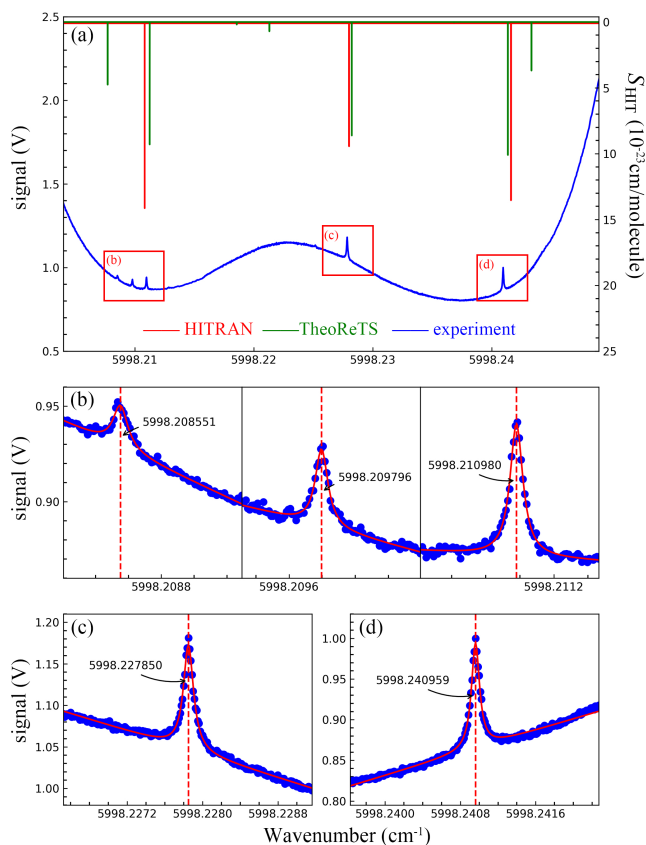


FIG. 3 (a) Example of CEAS-saturation spectra for the Q lines at the sample pressures respectively, along with the residuals (lower panels) retrieved with a Lorentzian profile. Line centers and intensities according to the HITRAN database [26] and TheoReTS calculations [23] are represented in red and green lines. (b, c, d) Partial enlargement of (a).

where I and I_0 denote the light intensities with and without the presence of the sample, respectively, R is the reflectivity of the high-reflective mirrors, L is the cavity length, and c is the speed of light. The identified Lamb dips were modeled using Lorentzian profile. Given that the saturated absorption lines are quite narrow, with the standard fitting range for each line being approximately 0.001 cm^{-1} , a linear baseline was utilized for the fitting process. A segment of the spectrum between 5998.20 cm^{-1} and 5998.25 cm^{-1} is shown in FIG. 3(b–d), with blue dots depicting the experimental measurements and the red line showing the fitted curve. It is observable that the simulated spectra closely match the experimental data, and the magnitude of the fitting residuals is similar to the level of experimental noise.

Calibration of the frequency is a significant contributor to the uncertainties observed in this study. The ULE cavity employed during the experiment was main-

tained at a stable temperature. Its frequency was tracked using the OFC, revealing a drift rate of approximately 10 kHz per hour. Daily frequency correction procedures were applied during the experiment to ensure an accuracy better than 0.2 MHz. Implementing two fiber-EOMs to produce sidebands in the reference optical path greatly enhanced the peak density for calibration purposes. Each mode interval of the ULE cavity was uniformly partitioned into 15 segments, with sidebands spaced 99.773548 MHz apart. The RF source's uncertainty and the daily variation in the ULE cavity's FSR were both significantly below 1 kHz, making them negligible for this study. The main contributor to the uncertainty was the interpolation process that mapped PZT voltages to laser frequencies, resulting in an uncertainty of approximately 0.2–1.9 MHz. The nonlinearity in the PZT frequency scan was assessed by scanning the PZT in both forward and reverse directions, with the central frequency deviation remaining below 0.2 MHz.

We examined how different fitting models could affect our results. Specifically, we were concerned about the baselines used during fitting, as the Lamb dips are superimposed on the Doppler-broadened absorption line. We used two different baselines to fit the spectrum: (1) a linear baseline; (2) a Voigt profile as the baseline. The discrepancy in peak centers between the two methods was found to be approximately 1 kHz, which is well within the calibration uncertainty. This suggests that the baseline choice does not significantly affect the results given the current precision.

Additional sources of uncertainties consist of the pressure shift and power shift. According to our earlier research [27, 28], these factors each contribute less than 0.01 MHz. Therefore, the overall uncertainties for most line positions given in this work are in the range of 0.3–2.0 MHz ($0.00001\text{--}0.00007\text{ cm}^{-1}$), and the uncertainty budget is summarized in Table I.

B. Comparison to databases

We analyzed the spectral region associated with the Q branch of the $00001 \rightarrow A1$ vibrational transition of methane within the $5996\text{--}6000\text{ cm}^{-1}$ interval. Table II summarizes the lines observed in this region, together with the rotational assignments and the line centers from the HITRAN [26] database and the TheoReTS calculation.

Most lines around 6000 cm^{-1} given in the current HITRAN database are from the $2\nu_3$ band, derived from

TABLE I Source of uncertainty in spectral line position.

Type	Source	Uncertainty/MHz
B	ULE drift	0.2
B	Radio frequency	< 0.01
B	Pressure shift	< 0.01
B	Power shift	< 0.01
B	PZT nonlinearity	0.2
B	interpolation	0.2–1.9
A	Baseline	< 0.01
A	Statistics	0.24
Total		0.3–2.0

multiple Fourier transform spectroscopy (FTS) studies [6]. These data were retrieved from Doppler-broadened spectra of methane with linewidths of several MHz. The HITRAN stated uncertainties of the line positions in this region are in the range of 0.001–0.01 cm^{-1} . Since the Doppler broadening is eliminated in saturated absorption spectroscopy, the accuracy of the line positions obtained in this work is better than 0.00001 cm^{-1} . By matching the Lamb dip positions and depths with the HITRAN Doppler-broadened line positions and intensities, we attributed the Lamb dips to the corresponding Doppler-broadened lines, which are detailed in Table II. Most of the differences between the line positions measured in this study and those listed in HITRAN are less than 0.005 cm^{-1} , reinforcing the correlations between the observed Lamb dips and the Doppler-broadened lines.

Meanwhile, energies, line positions, and intensities of methane can also be derived by *ab initio* potential energy surfaces (PES) and dipole moment surfaces (DMS). Although these computations have not attained the experimental accuracy of 10^{-3} cm^{-1} , they provide an extensive theoretical basis for comprehending ro-vibrational interactions across a wide spectral range, encompassing resonance coupling [13]. The Tomsk-Reims team [29] has recently offered highly precise PES and DMS, referred to as the NRT (Nikitin-Rey-Tyuterev) PES and DMS, with the objective of performing comprehensive first-principles calculations of absorption and emission lines for all methane isotopologues. In the $2\nu_3$ band around 6000 cm^{-1} , the Doppler-broadened absorption spectrum has multiple peaks, each consisting of several overlapped lines spreading in a range of approximately 0.1–0.2 cm^{-1} . Comparing theoretical calculations with observed data is crucial for validation, and experimental results have been incorporated directly in-

to these theoretical models. Accurate line positions are required to improve the calculations, particularly those “resonance-sensitive” transitions.

In Table II, we also list the line positions from the TheoReTS database [23]. By comparing HITRAN and TheoReTS, we observed that some transitions marked as a single line in HITRAN are divided into multiple lines in TheoReTS. For instance, the line with no rotational assignment (around 5997.19 cm^{-1}) consists of three lines in TheoReTS, with their lower state energies being 690.04940 cm^{-1} , 690.03974 cm^{-1} , and 689.87691 cm^{-1} , respectively. The combined intensity of the three TheoReTS lines ($2.788 \times 10^{-23} \text{ cm/molecule}$) closely matches the HITRAN value ($2.717 \times 10^{-23} \text{ cm/molecule}$). However, our Lamb-dip measurements found only one line within this range. Noting that the frequency intervals between the three TheoReTS transitions are much larger than our experimental resolution, we can confirm the presence of only one prominent line in this region. We adopted the same methodology to compare HITRAN and TheoReTS line-by-line. Similarly, the 10E 217<<10E 2 line at 5998.228010 cm^{-1} and 10F2326<<10F1 2 line at 5998.241620 cm^{-1} , which correspond to single lines in HITRAN but double lines in TheoReTS, are also confirmed to be single lines by the Lamb-dip measurements.

A completely different situation was found for the transition 10F131910<<F2 3 near 5998.21083 cm^{-1} , which corresponds to a single line in HITRAN but three lines in the TheoReTS database. In this frequency range, three Lamb dips were detected, as shown in FIG. 3(b). The intensities of the three lines are $4.755 \times 10^{-23} \text{ cm/molecule}$, $9.301 \times 10^{-23} \text{ cm/molecule}$, and $1.944 \times 10^{-24} \text{ cm/molecule}$ in TheoReTS, with partial percentages of 33.4%, 65.2%, and 1.4%. However, the results derived from the Lamb dip areas observed in this work are very different: they are 19.5%, 30.5%, and 50.0%.

FIG. 4 illustrates the comparison of our results with the HITRAN [26], WKLMC [21], and TheoReTS [23] databases. Within the spectral range, the HITRAN data were primarily based on FTIR measurements (GOSAT) [6, 30], while WKLMC was based on differential absorption spectroscopy (DAS) and high-sensitivity cavity ring-down spectroscopy (CRDS). These two databases are experimental lists, and comparing this work with them shows good consistency. The mean value of frequency differences is near zero and the largest

TABLE II Positions of the lines of $^{12}\text{CH}_4$.

Rotation assignment	S_{HIT} ^a /(cm/molecule)	Position/cm ⁻¹		
		HITRAN	TheoReTS	CEAS (this work)
—	2.717×10 ⁻²³	5997.188090	5997.18375 5997.18404 5997.18889	5997.189720(11)
—<<11A2 1	3.960×10 ⁻²³	5997.276180	5997.27630	5997.275347(40)
—<<11A2 1	3.910×10 ⁻²³	5997.337000	5997.33749	5997.336688(18)
—<<11A2 1	3.915×10 ⁻²³	5997.359000	5997.35807	5997.358972(24)
—<<11A2 1	3.220×10 ⁻²³	5997.366000	5997.36811	5997.366566(11)
—<<11A2 1	2.800×10 ⁻²³	5997.423940	5997.42810	5997.424353(10)
—<<11A2 1	5.678×10 ⁻²³	5997.440010	5997.44385	5997.440732(12)
—<<11F2 2	4.608×10 ⁻²³	5997.491090	5997.49231	5997.490137(26)
—<<11A2 1	4.196×10 ⁻²³	5997.503830	5997.50751	5997.503450(27)
—<<11A2 1	2.005×10 ⁻²³	5997.526710	5997.52776	5997.526822(22)
11A1 <<11A2 1	9.666×10 ⁻²³	5997.552363	5997.55410	5997.552390(21)
—	3.218×10 ⁻²³	5997.618230	5997.61957	5997.617987(24)
—	1.357×10 ⁻²³	5997.659950	5997.66149	5997.659287(23)
10F1319<<10F2 3	1.414×10 ⁻²² ^b	5998.210830	5998.20772	5998.208551(10)
			5998.21125	5998.209796(10)
			5998.21857	5998.210980(10)
10E 217<<10E 2	9.440×10 ⁻²³	5998.228010	5998.22131	5998.227850(34)
			5998.22824	
10F2326<<10F1 2	1.354×10 ⁻²²	5998.241620	5998.24136	5998.240959(17)
			5998.24334	
10A2105<<10A1 1	2.216×10 ⁻²²	5998.280400	5998.28072	N.D ^c
10F2325<<10F1 1	1.323×10 ⁻²²	5998.319090	5998.31684	5998.318658(10)
			5998.31882	
10F1318<<10F2 2	1.247×10 ⁻²²	5998.334490	5998.33391	5998.333655(65)
10A1111<<10A2 1	1.904×10 ⁻²²	5998.439430	5998.43803	N.D ^c

^a The columns also display line intensities sourced from the HITRAN database [26] along with line positions from both HITRAN and TheoReTS [23].
^b According to this work, the intensity should be divided into three lines with percentages of 19.5%, 30.5%, and 50.0%.
^c Not detected due to low cavity transmittance and strong molecular absorption.

difference is within the database accuracy (0.001–0.01 cm⁻¹). In contrast, TheoReTS is from the variation calculation based on *ab initio* potential energy surfaces (PES) and dipole moment surfaces (DMS). The differences between this work and TheoReTS are reveal an overall offset of about 0.001 cm⁻¹. The results show that, while most experimental spectral data are limited by Doppler broadening, this work demonstrates that the error in the high-precision results is smaller than the nominal precision. Incorrect assignments in comparisons with TheoReTS have also been revealed.

The high density of methane lines within this region results in multiple lines overlapping within their Doppler width, complicating the acquisition of accurate results from Doppler-broadened spectra. Moreover, dense lines cause significant line-mixing effects, result-

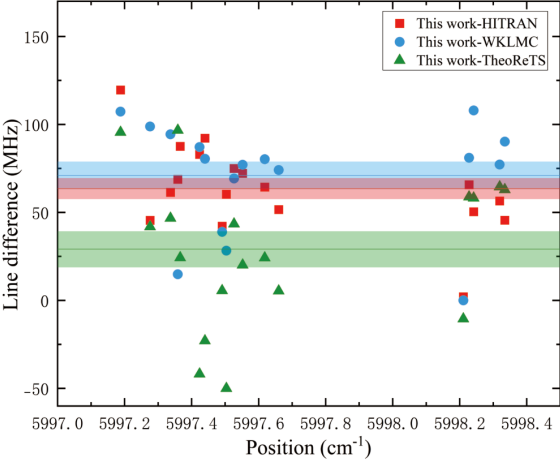


FIG. 4 Line positions compared with those given in the HITRAN database [26], WKLMC empirical line lists [21] and Theoretical Reims–Tomsk Spectral data (TheoReTS) [23].

ing in deviations from Lorentzian line shapes [31]. The dense and complex arrangement of most Q branch lines makes it difficult to accurately measure individual lines, particularly regarding line shape parameters such as pressure broadening and shift coefficients. Overlapping and mixing of adjacent lines in the Q branch make the analysis more complicated. Due to the congested nature of Q branches and the absence of suitable relaxation matrix models, it is generally more practical to study in the P and R branches of CH₄. However, information on the Q branches provides valuable cross-assessment of the P/R branches [32], encouraging a re-evaluation of the models. For atmospheric experiments (whether satellite-based or ground-based), it is crucial to have a set of consistent line parameters, considering both Q branch and P/R branch together to develop a correct model [33]. Studies on line-mixing effects in high-resolution spectroscopy often necessitate independent experiments or data to supply intensities and reference frequencies free of the pressure-induced shift [34]. Thus, high-precision line center measurements can greatly support this aspect of studies. In addition, efficient continuous coverage over specific spectral ranges can identify unobserved absorption lines to compare with databases and theoretical results, validating theoretical calculations and providing new experimental data to refine computational models.

IV. CONCLUSION

In this work, we used cavity-enhanced saturated absorption spectroscopy to determine the line positions of methane around the 1.66-micron atmospheric window. Doppler-broadened absorption features and saturated absorption Lamb dips were observed with sub-MHz precision through extensive spectral scans. Line positions in the Q branch of the $2\nu_3$ band near 5998 cm⁻¹ were determined with an accuracy better than 2 MHz. This work reveals the limitation of Doppler-broadened spectroscopy of highly congested spectra.

The experimental method applied in this work, cavity-enhanced absorption spectroscopy, can record both broad absorption features and narrow saturated lines simultaneously, offering considerable benefits in terms of easy operation, measurement speed, scanning range, and automation. The spectra obtained in this way can be directly compared with literature data obtained from Doppler-broadened spectroscopy measurements and

provide a crucial assessment of databases and theoretical models. This work fills in gaps in a region lacking high-precision spectral data and shows the potential to cover extensive spectral ranges. Accurate and reliable experimental methane line positions can not only refine the current spectral databases but also be used in the assessment of methane emissions.

V. ACKNOWLEDGEMENTS

This work was jointly supported by the Ministry of Science and Technology of China (No.2022YFF0606500) and the National Natural Science Foundation of China (No.22273096).

- [1] M. Etminan, G. Myhre, E. J. Highwood, and K. P. Shine, *Geophys. Res. Lett.* **43**, 12614 (2016).
- [2] IPCC, *Climate Change 2023: Synthesis Report. Contribution of Working Groups I, II and III to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*, H. Lee and J. Romero Eds., Geneva: IPCC, 35 (2023). DOI: [10.59327/IPCC/AR6-9789291691647](https://doi.org/10.59327/IPCC/AR6-9789291691647).
- [3] D. J. Jacob, A. J. Turner, J. D. Maasackers, J. X. Sheng, K. Sun, X. Liu, K. Chance, I. Aben, J. McKeever, and C. Frankenberg, *Atmos. Chem. Phys.* **16**, 14371 (2016).
- [4] P. Bergamaschi, C. Frankenberg, J. F. Meirink, M. Krol, M. G. Villani, S. Houweling, F. Dentener, E. J. Dlugokencky, J. B. Miller, L. V. Gatti, A. Engel, and I. Levin, *J. Geophys. Res.: Atmos.* **114**, D22301 (2009).
- [5] M. Buchwitz, R. de Beek, S. Noël, J. P. Burrows, H. Bovensmann, O. Schneising, I. Khlystova, M. Bruns, H. Bremer, P. Bergamaschi, S. Körner, and M. Heimann, *Atmos. Chem. Phys.* **6**, 2727 (2006).
- [6] A. V. Nikitin, O. M. Lyulin, S. N. Mikhailenko, V. I. Perevalov, N. N. Filippov, I. M. Grigoriev, I. Morino, Y. Yoshida, and T. Matsunaga, *J. Quant. Spectrosc. Radiat. Transfer* **154**, 63 (2015).
- [7] G. Ehret, P. Bousquet, C. Pierangelo, M. Alpers, B. Millet, J. B. Abshire, H. Bovensmann, J. P. Burrows, F. Chevallier, P. Ciais, C. Crevoisier, A. Fix, P. Flamant, C. Frankenberg, F. Gibert, B. Heim, M. Heimann, S. Houweling, H. W. Hubberten, P. Jöckel, K. Law, A. Löw, J. Marshall, A. Agusti-Panareda, S. Payan, C. Prigent, P. Rairoux, T. Sachs, M. Scholze, and M. Wirth, *Remote Sens.* **9**, 1052 (2017).
- [8] E. K. Conway, A. H. Souri, J. Benmergui, K. Sun, X. Liu, C. Staebell, C. Chan Miller, J. Franklin, J. Samra, J. Wilzewski, S. Roche, B. K. Luo, A. Chulakadabba, M. Sargent, J. Hohl, B. Daube, I. Gordon, K. Chance, and S. Wofsy, *Atmos. Meas. Tech.* **17**, 1347

- (2024).
- [9] C. Chan Miller, S. Roche, J. S. Wilzewski, X. Liu, K. Chance, A. H. Souri, E. Conway, B. K. Luo, J. Samra, J. Hawthorne, K. Sun, C. Staebell, A. Chulakadabba, M. Sargent, J. S. Benmergui, J. E. Franklin, B. C. Daube, Y. Li, J. L. Laughner, B. C. Baier, R. Gautam, M. Omara, and S. C. Wofsy, *Atmos. Meas. Tech.* **17**, 5429 (2024).
 - [10] K. Kefala, V. Boudon, S. N. Yurchenko, and J. Tennyson, *J. Quant. Spectrosc. Radiat. Transfer* **316**, 108897 (2024).
 - [11] C. Frankenberg, J. F. Meirink, M. van Weele, U. Platt, and T. Wagner, *Science* **308**, 1010 (2005).
 - [12] S. Kassi, T. Stoltmann, M. Casado, M. Daëron, and A. Campargue, *J. Chem. Phys.* **148**, 054201 (2018).
 - [13] M. Rey, A. V. Nikitin, B. Bézard, P. Rannou, A. Coustenis, and V. G. Tyuterev, *Icarus* **303**, 114 (2018).
 - [14] A. M. Zolot, F. R. Giorgetta, E. Baumann, W. C. Swann, I. Coddington, and N. R. Newbury, *J. Quant. Spectrosc. Radiat. Transfer* **118**, 26 (2013).
 - [15] A. A. Madej, A. J. Alcock, A. Czajkowski, J. E. Bernard, and S. Chepurov, *J. Opt. Soc. Am. B* **23**, 2200 (2006).
 - [16] A. V. Nikitin, O. M. Lyulin, S. N. Mikhailenko, V. I. Perevalov, N. N. Filippov, I. M. Grigoriev, I. Morino, T. Yokota, R. Kumazawa, and T. Watanabe, *J. Quant. Spectrosc. Radiat. Transfer* **111**, 2211 (2010).
 - [17] S. Kassi, B. Gao, D. Romanini, and A. Campargue, *Phys. Chem. Chem. Phys.* **10**, 4410 (2008).
 - [18] A. Campargue, L. Wang, A. W. Liu, S. M. Hu, and S. Kassi, *Chem. Phys.* **373**, 203 (2010).
 - [19] A. Campargue, O. Leshchishina, L. Wang, D. Mondelain, S. Kassi, and A. V. Nikitin, *J. Quant. Spectrosc. Radiat. Transfer* **113**, 1855 (2012).
 - [20] L. S. Rothman, I. E. Gordon, Y. Babikov, A. Barbe, D. Chris Benner, P. F. Bernath, M. Birk, L. Bizzocchi, V. Boudon, L. R. Brown, A. Campargue, K. Chance, E. A. Cohen, L. H. Coudert, V. M. Devi, B. J. Drouin, A. Fayt, J. M. Flaud, R. R. Gamache, J. J. Harrison, J. M. Hartmann, C. Hill, J. T. Hodges, D. Jacquemart, A. Jolly, J. Lamouroux, R. J. Le Roy, G. Li, D. A. Long, O. M. Lyulin, C. J. Mackie, S. T. Massie, S. Mikhailenko, H. S. P. Müller, O. V. Naumenko, A. V. Nikitin, J. Orphal, V. Perevalov, A. Perrin, E. R. Polovtseva, C. Richard, M. A. H. Smith, E. Starikova, K. Sung, S. Tashkun, J. Tennyson, G. C. Toon, V. G. Tyuterev, and G. Wagner, *J. Quant. Spectrosc. Radiat. Transfer* **130**, 4 (2013).
 - [21] A. Campargue, O. Leshchishina, L. Wang, D. Mondelain, and S. Kassi, *J. Mol. Spectrosc.* **291**, 16 (2013).
 - [22] A. V. Nikitin, I. S. Chizhmakova, M. Rey, S. A. Tashkun, S. Kassi, D. Mondelain, A. Campargue, and V. G. Tyuterev, *J. Quant. Spectrosc. Radiat. Transfer* **203**, 341 (2017).
 - [23] M. Rey, A. V. Nikitin, Y. L. Babikov, and V. G. Tyuterev, *J. Mol. Spectrosc.* **327**, 138 (2016).
 - [24] L. Yang, H. Lin, M. D. Plimmer, X. J. Feng, Y. J. Ma, J. T. Luo, J. F. Luo, and J. T. Zhang, *J. Quant. Spectrosc. Radiat. Transfer* **245**, 106888 (2020).
 - [25] C. Ishibashi, M. Kourogi, K. Imai, B. Widiyatmoko, A. Onae, and H. Sasada, *Opt. Commun.* **161**, 223 (1999).
 - [26] I. E. Gordon, L. S. Rothman, R. J. Hargreaves, R. Hashemi, E. V. Karlovets, F. M. Skinner, E. K. Conway, C. Hill, R. V. Kochanov, Y. Tan, P. Wcisło, A. A. Finenko, K. Nelson, P. F. Bernath, M. Birk, V. Boudon, A. Campargue, K. V. Chance, A. Coustenis, B. J. Drouin, J. M. Flaud, R. R. Gamache, J. T. Hodges, D. Jacquemart, E. J. Mlawer, A. V. Nikitin, V. I. Perevalov, M. Rotger, J. Tennyson, G. C. Toon, H. Tran, V. G. Tyuterev, E. M. Adkins, A. Baker, A. Barbe, E. Canè, A. G. Császár, A. Dudaryonok, O. Egorov, A. J. Fleisher, H. Fleurbaey, A. Foltynowicz, T. Furtenbacher, J. J. Harrison, J. M. Hartmann, V. M. Horneman, X. Huang, T. Karman, J. Karns, S. Kassi, I. Kleiner, V. Kofman, F. Kwabia-Tchana, N. N. Lavrentieva, T. J. Lee, D. A. Long, A. A. Lukashetskaya, O. M. Lyulin, V. Y. Makhnev, W. Matt, S. T. Massie, M. Melosso, S. N. Mikhailenko, D. Mondelain, H. S. P. Müller, O. V. Naumenko, A. Perrin, O. L. Polyansky, E. Raddaoui, P. L. Raston, Z. D. Reed, M. Rey, C. Richard, R. Tóbiás, I. Sadiek, D. W. Schwenke, E. Starikova, K. Sung, F. Tamassia, S. A. Tashkun, J. Vander Auwera, I. A. Vasilenko, A. A. Vigasin, G. L. Villanueva, B. Vispoel, G. Wagner, A. Yachmenev, and S. N. Yurchenko, *J. Quant. Spectrosc. Radiat. Transfer* **277**, 107949 (2022).
 - [27] Y. R. Xu, A. W. Liu, Y. Tan, C. L. Hu, and S. M. Hu, *Phys. Rev. A* **109**, 042809 (2024).
 - [28] Y. Tan, Y. R. Xu, T. P. Hua, A. W. Liu, J. Wang, Y. R. Sun, and S. M. Hu, *J. Chem. Phys.* **156**, 044201 (2022).
 - [29] A. V. Nikitin, M. Rey, and V. G. Tyuterev, *J. Quant. Spectrosc. Radiat. Transfer* **200**, 90 (2017).
 - [30] L. R. Brown, K. Sung, D. C. Benner, V. M. Devi, V. Boudon, T. Gabard, C. Wenger, A. Campargue, O. Leshchishina, S. Kassi, D. Mondelain, L. Wang, L. Daumont, L. Régalia, M. Rey, X. Thomas, V. G. Tyuterev, O. M. Lyulin, A. V. Nikitin, H. M. Niederer, S. Albert, S. Bauerecker, M. Quack, J. J. O'Brien, I. E. Gordon, L. S. Rothman, H. Sasada, A. Coustenis, M. A. H. Smith, T. Carrington, X. G. Wang, A. W. Mantz, and P. T. Spickler, *J. Quant. Spectrosc. Radiat. Transfer* **130**, 201 (2013).
 - [31] S. Nordebo, *J. Quant. Spectrosc. Radiat. Transfer* **310**, 108731 (2023).
 - [32] A. S. Pine and T. Gabard, *J. Mol. Spectrosc.* **217**, 105 (2003).
 - [33] V. M. Devi, D. C. Benner, R. R. Gamache, H. Tran, M. A. H. Smith, and R. L. Sams, *J. Quant. Spectrosc. Radiat. Transfer* **206**, 409 (2018).
 - [34] A. S. Pine, *J. Quant. Spectrosc. Radiat. Transfer* **224**, 62 (2019).