

Application of cavity ring-down spectroscopy to the Boltzmann constant determination

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Abstract: The Boltzmann constant can be optically determined by measuring the Doppler width of an absorption line of molecules at gas phase. We propose to apply a near infrared cavity ring-down (CRD) spectrometer for this purpose. The superior sensitivity of CRD spectroscopy and the good performance of the near-ir lasers can provide ppm (part-per-million) accuracy which will be competitive to present most accurate result obtained from the speed of sound in argon measurement. The possible influence to the uncertainty of the determined Doppler width from different causes are investigated, which includes the signal-to-noise level, laser frequency stability, detecting nonlinearity, and pressure broadening effect. The analysis shows that the CRD spectroscopy has some remarkable advantages over the direct absorption method proposed before. The design of the experimental setup is presented and the measurement of C₂H₂ line near 0.8 μm at room temperature has been carried out as a test of the instrument.

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OCIS codes: (020.3690) Line shapes and shifts; (300.6360) Spectroscopy, laser; (120.3940) Metrology

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1. Introduction

The Boltzmann constant k_B is a fundamental constant that relates the thermodynamic temperature to thermal energy. The kelvin is currently defined such that the thermodynamic temperature of the triple point of water (TPW) is exactly 273.16 K. The international key comparisons have evidenced a significant inconsistency among different national primary TPW cells of participants. The thermometric community widely accepts that the isotopic abundances and the impurities in the water cells are the causes for that inconsistency. A proposal by Mills *et al.* [1] has been accepted by the International Committee for Weights and Measures (*Comité international des poids et mesures*, CIPM) to replace the present definition with a new one that redefines the kelvin unit on an exact value of k_B . Therefore, the new definition shall maintain the kelvin unit invariant. The specified value of k_B will be chosen to agree with the best measurements available. An optical method based on laser spectroscopy has received an increasing interest as an independent method in the activity of redetermination of the Boltzmann constant. The idea is to measure the Doppler width of an absorption line of atoms or molecules in a vapor cell in thermodynamic equilibrium [2]. At low pressure, the absorption line shape has a Gaussian profile with a Doppler width γ_D (Full Width at Half Maximum, FWHM), which is related to the equilibrium temperature T :

$$\frac{\gamma_D}{\nu_0} = \left(\frac{8k_B T \ln 2}{mc^2} \right)^{1/2} \quad (1)$$

where ν_0 is the central frequency of the line, m is the mass of the molecule, k_B and c are the Boltzmann constant and the speed of light, respectively. Since the speed of light is a fixed constant, the transition frequency ν_0 can be measured with an accuracy of 10^{-15} [3], and the atomic mass has been measured to the precision of $10^{-9} \sim 10^{-10}$ [4], accurate measurement of the sample temperature T and the Doppler width γ_D will result in a spectroscopic redetermination of the Boltzmann constant k_B . If the Boltzmann constant is fixed to an exact value, such Doppler width measurement based on laser spectroscopy can also serve as a universal gas thermometry [5].

The group in Université Paris 13 (France) has obtained k_B with uncertainty of 2×10^{-4} using a stabilized CO₂ laser to measure an absorption line of NH₃ at $\lambda \approx 10 \mu\text{m}$ [2]. They have improved the accuracy to 3.8×10^{-5} using a multi-pass cell to increase the signal-to-noise ratio (SNR) at lower sample gas pressure (below 1 Pa) [6] and approached to several ppm (part per million) level very recently [7]. The Italian group at Caserta applied a distributed feed back (DFB) diode laser to measure the absorption line of CO₂ at $2 \mu\text{m}$ and determined k_B with uncertainty of 1.6×10^{-4} [5]. They proposed to improve the accuracy by measuring the water absorption lines at the $1.4 \mu\text{m}$ region [8]. Yamada *et al.* proposed to measure a line of ¹³C₂H₂ in the near-ir region using a comb-stabilized diode laser [9, 10].

The present Boltzmann constant value $k_B = 1.3806504(24) \text{ J K}^{-1}$, recommended by the Committee on Data for Science and Technology (CODATA) [4], has an uncertainty of 1.7 ppm. The value comes from the speed of sound in argon measurement which gives the molar gas constant R . The k_B value is derived with R/N_A where N_A is the Avogadro constant which has an uncertainty of 5×10^{-8} [4]. The uncertainty of the k_B value determined from Doppler width measurement is still one order of magnitude larger than the CODATA recommended value. The present uncertainty in the Doppler width measurement have varies of contributions. Cygan *et al.* discussed on the influence of the line-shape model applied in the spectral profile fitting [11]. It has been concluded from their simulation that using a mid-ir absorption line will result in a systematical error of several ppm. Instead of the conventional direct absorption measurement of a molecular line in the mid-ir region, we propose [12] to apply a near-ir continuous wave cavity ring down (cw-CRD) spectrometer, to take the advantage of the reduced relative deviation in γ_G/ν_0 . The excellent quality of the diode laser in the near-ir region also helps to obtain higher SNR in the measurements and are more competitive for portable applications. The enhanced sensitivity of cavity ring down spectroscopy (CRDS) will compensate the loss on the absorption line strength due to the shift from the mid-ir to near-ir.

CRDS has been introduced by O'Keefe and Deacon in 1988 [13] and a historic review of CRDS can be found in Ref. [14]. The main idea of CRDS is to measure the decay rate of the laser light inside a resonant cavity composed of two high-reflectivity mirrors. The absorption coefficient of the sample gas can be obtained by measuring the "ring-down time" of a single frequency laser pulse injected into the cavity. Using an optimized cw-CRDS setup [12], we has shown that the minimal detectable absorption coefficient α_{min} can be as low as $7 \times 10^{-11}/\text{cm}$. Consequently, for an absorption line with $\alpha \simeq 10^{-6}/\text{cm}$ (typical intensity of a strong molecular line in the near-ir), it is possible to determine the α value with uncertainty below 10^{-5} . Meanwhile, in order to determine the Doppler width of a molecular absorption line with ppm accuracy, it is also necessary to achieve sufficient frequency precision in the spectral scanning. This can be accomplished by using CRDS based on a frequency-locked laser. As will be shown in the Experimental Section, by locking the laser frequency to a thermo-stabilized etalon and using a scanning sideband as the light source of the CRDS, sub-kHz frequency accuracy can be achieved. A different approach of the frequency-stabilized CRDS has been established by Hodges *et al.* by locking the length of the ring-down cavity to a stabilized reference laser [15, 16]. The spectrometer has been applied for various quantitative measurements includ-

ing the sub-Doppler hyperfine structure measurements of O₂ molecule [17]. Very recently, they also locked the laser frequency to the stabilized ring-down cavity to increase the ring-down event acquisition rates and a minimal detectable absorption coefficient α_{min} of $2 \times 10^{-10}/\text{cm}$ has been achieved [18]. They also mentioned the possibility to apply the frequency-stabilized CRDS for the determination of the Boltzmann constant.

In the following sections, the error budget in determining the γ_D value in a CRDS measurement will be discussed and the experimental method toward ppm level accuracy k_B determination will be presented. Measurements of the C₂H₂ 788 nm line at room temperature will be given as a demonstration of the present CRD spectrometer.

2. CRDS measurement error analysis

In CRDS, the decay rate $1/\tau$ of the emitted light is proportional to the total optical losses inside the cavity, where τ is the “ring-down time” [19]:

$$\tau = \frac{L/c}{-\ln R + \alpha L} \quad (2)$$

L is the length of the cavity, c is the speed of light, R is the reflectivity of a cavity mirror, and α is the sample absorption coefficient. α can be determined using Eq. (2):

$$\alpha = \frac{1}{c\tau} + \frac{\ln R}{L} \quad (3)$$

Typically, using a pair of mirrors with reflectivity higher than 99.99% and a cavity of about 1 m long, the ring-down time τ will be of several tens micro-seconds. Since the $\frac{\ln R}{L}$ term can be treated in the baseline, the absorption line profile can be obtained by fitting the measured curve $\frac{1}{c\tau}$.

The accuracy of the CRDS measurement is mainly limited by the noise level and frequency jitters during scanning. The causes contribute to the deviation in the Doppler line width are given below.

Frequency uncertainty: The line width derived from the fitting of experimental spectrum is perturbed by the experimental noise resulting from the measurements of the absorbance and frequency. The frequency measurement contributes directly an uncertainty to the determination of line width. A simulation of the uncertainty contribution by frequency measurement is illustrated in Fig. 1. The deviation in the line width is presented as the relative value: $\gamma_D/\gamma_D^0 - 1$, where γ_D is the Doppler width derived from the fitting of the simulation spectra, γ_D^0 is the physical true value of γ_D . Apparently, to achieve an accuracy of 10^{-6} level in the line width, comparative frequency accuracy is necessary. For an absorption line in the near infrared region, the Doppler width of a light molecule like C₂H₂ is about 1 GHz. In this case, it is necessary to apply a laser source with frequency stability better than 10 kHz, which is moderate for a frequency-stabilized diode laser.

Absorbance uncertainty, signal-to-noise ratio: For a direct absorption measurement, the vertical noise mainly results from the laser power instability, which is typically at a level of 0.01% - 0.1% [20, 21]. Such noise will directly contribute to an uncertainty to the determination of line width. To illustrate the influence by the experimental noise, we simulated a group of spectra with random noise at different SNR level, and the relative deviation in γ_D are presented in Fig. 1. As shown in the figure, only when SNR is better than 30,000, the γ_D accuracy can possibly reach the 1 ppm level, thus to determine the Boltzmann constant with a competitive accuracy by the optical Doppler width measurement. Since the cavity ring down spectroscopy is immune to the power fluctuation of the light source and has very large dynamic region, it is ideal for this application. In CRDS measurement, the SNR level is mainly governed by

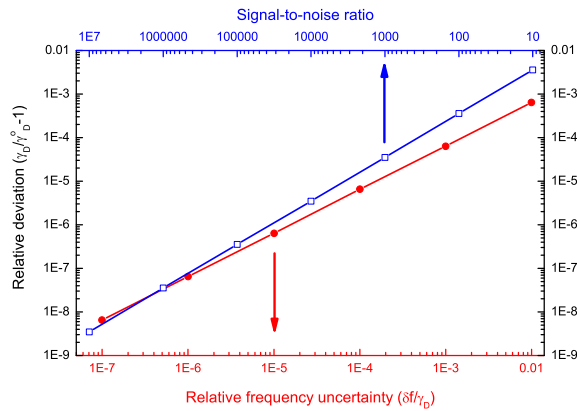


Fig. 1. Relative deviations in γ_D resulting from the noise level and frequency uncertainty.

the stability of the cavity loss. As shown in Eq. (2), it results from the fluctuations in the cavity length, the mirror reflectivity, and the speed of light (change of the refractive index). In a CRDS measurement with sample pressure below 10 Pa, drift of the refractive index can be well below 10^{-8} . We have achieved noise equivalent absorption coefficient of $7 \times 10^{-11}/\text{cm}$ using a ring-down cavity with temperature fluctuation about 1 K [12]. According to Eq. (2), the drift of the cavity length L due to temperature fluctuation will result in the drift of the measured decay time τ . In other word, it is possible to significantly improve the SNR if the whole ring-down cavity can be thermo-stabilized to 1 mK. In this case, a SNR at the 10^5 level will be achievable for an absorption line with strength over $1 \times 10^{-6}/\text{cm}$ which is moderate for a near-ir molecular line.

Pressure dependence: A detailed theory of the absorption line shape of low-pressure gases has been presented recently by Bordé [22]. Cygan *et al.* pointed out that the collisional line width can introduce systematic error when pursuing Doppler limited line width even at very low pressure [11]. The measurement of NH_3 line at the $10.3 \mu\text{m}$ region carried out by Daussy *et al.* [2] with 1 - 10 Pa sample gas will include a systematic error of a few ppm. The use of a near-ir line can help to reduce this error, partly because the Doppler width increases linearly with the line frequency while the collisional line width does not. Regardless of the adopted model of the collisional line profile, linear extrapolation of the fitted Doppler width values to zero pressure can give good Doppler width value with accuracy better than 10^{-6} [11]. To investigate this effect in proposed CRDS measurements, spectra of C_2H_2 at 788 nm with sample pressure varying from 0.1 Pa to 60 Pa have been simulated with Voigt line profile. When fitting the spectra with pure Gaussian profile, the deviations of the retrieved line width γ_D to the true value γ_D^0 are plotted in Fig. 2. Note that the relative deviation is at the level of 10^{-4} at a sample pressure of 10 Pa. After extrapolation of the line width values to zero pressure, the relative deviation of the Doppler width at zero pressure is well below 2×10^{-7} .

Nonlinearity: Note that any nonlinearity in the detecting scheme will distort the experimental spectrum and bring direct influence on the accuracy of the retrieved linewidth. Moreover, such nonlinearity may introduce a systematic deviation which does not decrease after averaging. In this case, it is necessary to make sure that the instrumental nonlinearity is either negligible (for instance, below the noise level) or can be compensated. The cw-CRDS spectrometer also has the advantage of excellent linearity over a very large dynamic region of the absorption coefficient since the variation of the ring-down time instead of the absorption depth is measured in the CRDS experiment. Simulation of the CRDS result has been carried out assuming that the

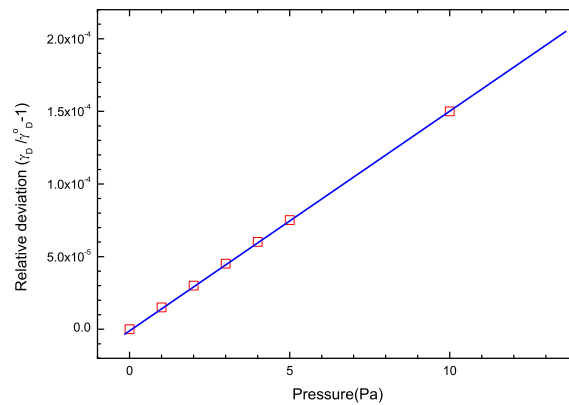


Fig. 2. Relative deviation on the Doppler line width from spectrum recorded with different sample pressure. The linear fit gives the extrapolation to the zero pressure limit.

detector (or the amplifier) has a fixed nonlinearity,

$$I' = I_0 + \delta I_0^2 \quad (4)$$

where I_0 is the true signal while I' is the detected (distorted) signal, δ is the nonlinearity coefficient. The ring-down signal was normalized to the one at the beginning of the ring-down ($t = 0$) for simplicity. The nonlinearity brings distortion on the measured ring-down curve. It imposes critical influence on the signal height. But the ring-down time τ' derived from the single-exponential fitting of the ring-down curve is still proportional to the true τ value with an almost fixed factor with a given nonlinear coefficient. In this case, the “measured” absorption line will have a line profile almost same as the true one, except that the line intensity is distorted. So the derived line width value is only perturbed with a much smaller amount. The relative deviation on the line width with a given nonlinear coefficient is plotted in Fig. 3. As a comparison, we also simulated direct absorption measurement with nonlinearity similar to the one given in Eq. (4). In the simulation, the transmission signal was normalized to the one without absorption and the absorbance at the line center was assumed to be 10%. In a direct absorption measurement, the nonlinearity in the detection brings direct influence to the line profile and the line width value derived from the fitting to the profile. For illustration, the relative deviation in the line width due to nonlinearity in direct absorption measurements is also plotted in Fig. 3. As shown in the figure, under the same nonlinearity in the detection, the influence to the CRDS measurement can be about two orders of magnitude smaller than the influence to a standard direct absorption measurement. However, because fast detection with bandwidth over several MHz is necessary in CRDS, which is usually much faster than that in the direct absorption measurement, the nonlinear effect is still need to be carefully investigated in quantitative CRDS measurement. Nevertheless, 1 ppm accuracy in line width determination is achievable when the nonlinearity is below 1% in CRDS.

3. Experimental

3.1. Optical layout

In order to perform precision CRDS measurement with sufficient frequency accuracy, the CRDS setup is built based on a frequency-locked laser. The schematics is shown in Fig. 4. A cw tunable laser (Coherent 899-21) is frequency locked on one longitude mode (ν_0) of

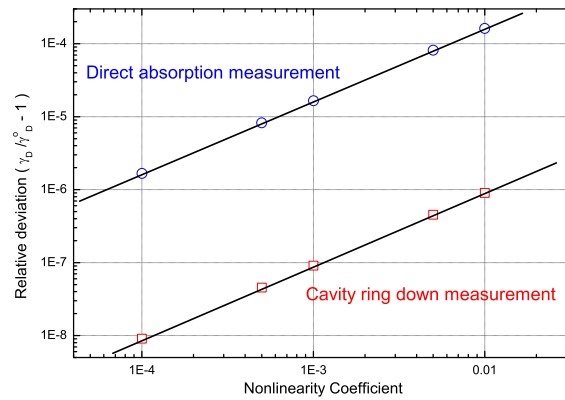


Fig. 3. Relative deviations in the determined line width with different nonlinearity coefficients in the detection, for direct absorption measurement (upper) and for cavity ring-down measurement (lower).

a temperature-stabilized Fabry-Perot interferometer (FPI). The FPI is made of ultra-low-expansion (ULE) glass and installed in a thermal-stabilized vacuum chamber. The free-spectral-range (FSR) of the ULE-FPI was determined to 1,497.029 MHz and the FSR drift is below 10 kHz for months. The laser beam passes a broadband fiber electro-optic modulator (EOM) driven by a digital radio-frequency (RF) source (Agilent 9320A) to produce tunable sidebands. One particular sideband $\nu_0 + \nu_m$ will be selected by passing the laser beam through another short FPI which is dynamically locked on resonance while the carrier and other sidebands will be blocked. The selected sideband is then coupled into the ring-down cavity. The cavity mirrors (Los Gatos Inc.) have a reflectivity of 99.995% and one of the two mirrors is mounted on a piezoelectric actuator. The piezoelectric actuator is driven with a triangle wave from a function generator. Once the cavity mode is resonated with the laser frequency, a trigger signal is produced to shut off the input laser beam through an acousto-optic modulator (AOM) and to start the measurement of the ring-down event. The ring-down signal is recorded with a fast digitizer (ADLINK PCI-9820) working at a sampling rate of 2 MS/s (Mega-samples per second) with 14-bit resolution. The detector, amplifier and digitizer are calibrated to ensure the overall non-linearity is below 0.1 %. A fitting program is applied to fit the exponentially decay curve and to give the ring-down time τ . With the carrier laser frequency ν_0 fixed and the RF frequency ν_m scanning, the laser sideband will scan over the resonance of the molecular absorption peak and the spectrum will be recorded. Since both the ν_0 and ν_m can be determined to kHz or below, sufficient frequency accuracy during the spectral scan can be readily obtained.

3.2. Ring-down cavity: temperature control

According to Eq. (1), the measurement for the temperature of gas sample in the cavity contributes an uncertainty to the redetermination of k_B . The ring-down cavity comprises a cylinder of stainless steel in a diameter of about 25 mm and a length 600 mm. The uncertainty by temperature measurement is produced by the following causes. The first is the fluctuation and the non-uniformity of the temperature on the cylinder during the period probing the Doppler width. This uncertainty contribution is governed by the thermal environment around the cylinder. The temperature non-uniformity appears a cause deserving a careful treatment. The cylindrical cavity has an optical path through both ends for the admitting laser beam. There are a gas fill duct

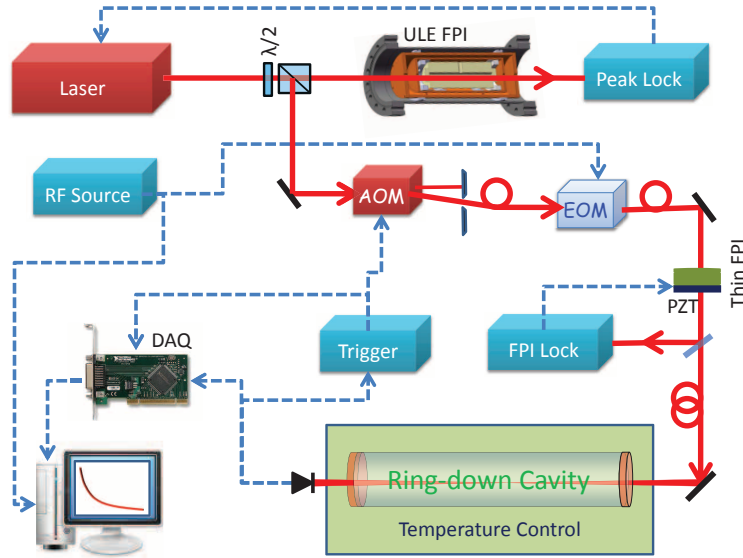


Fig. 4. Schematics of a frequency-stabilized CRDS setup. AOM: acousto-optic modulator; EOM: electro-optic modulator. DAQ: Data acquisition card.

on the cavity, and three thermometry wells in the cavity to house the capsule standard platinum thermometers (CSPRTs). These components comprise the paths of heat leak and yield disturbances to the temperature uniformity.

One of the authors has practical experience of using high stable thermostat of a stability of 0.05 mK per 24 hours [23]. Based on the experience, we have designed a thermostat consisting of a vacuum jacket for the cavity. The outer cylindrical container is cooled by the methanol to hold the temperature 2.5 °C below the objective triple point of water for the ring-down cavity. The inner wall of the container is gold plated to diminish thermal radiation. An active radiation shield is set between the cavity and the outer container. Both sides of the shield are gold plated to increase their reflection to thermal radiations from both the cavity and the inner wall of the container. A line heater is installed on the outside of the shield. The shield is heated to track the temperature of the cavity. The wire of the heater shall have an optimal distribution based on a heat transfer simulation to achieve satisfied temperature uniformity. The temperature difference between the shield and the cavity is controlled within 1 mK. The leads of thermometers and the gas duct for the cavity are thermally anchored on the shield to diminish heat leak from those paths. The outside wall of the cavity is also gold plated to reduce the thermal radiation. The space housing the cavity and the shield is filled with pure argon at beginning to let the cavity and the shield quickly approximate the objective temperature. Once the triple point of water is approximated, the space is evacuated. Therefore, the left paths for heat leaks are thermal radiation and conduction. Both paths are controlled to their minimum by tracking the temperature of the shield to that of the cavity.

The objective temperature of the cavity is the triple point of water. Three thermometry wells are set at the middle and both ends of the cavity. The temperature gradient along the cavity is then read by three CSPRTs. The temperature of gas sample is measured by the average value of three CSPRTs when thermal equilibrium is approached. A temperature gradient below 1 mK

is expected. The temperature fluctuation shall be within 0.1 mK according to our previous practical experience. We have good practice to use the CSPRTs made by the HartScientific of Fluke. The temperature reproducibility (or short term stability) during repeated calibrations is better than 0.05 mK by the application of a special designed copper jacket to house thermometer. Accordingly, a relative uncertainty of better than 3.7 parts per million is expected for the thermometry.

3.3. $^{12}\text{C}_2\text{H}_2$ 788 nm line measured at room temperature

To demonstrate the viability of CRDS for precise Doppler width measurement, we performed CRDS measurement of an absorption line of acetylene near 788 nm at room temperature. The line at 12696.4 cm^{-1} is the R(9) line of the $\nu_1 + 3\nu_3$ band of $^{12}\text{C}_2\text{H}_2$. This band has been reported by Zhan and Halenon using photoacoustic spectroscopy [24]. The C_2H_2 line near 788 nm is over 10 times stronger than the O_2 line near 687 nm proposed by Cygan *et al.* [11]. In this case, measurement with lower sample pressure is possible. In addition, because the atmospheric absorption is negligible in this spectral region, it avoids any possible interference from air in the open optical path or trace water vapor in the ring-down cavity. Our simulation shows that SNR of about 10^5 is achievable with C_2H_2 sample gas pressure of 0.1 - 10 Pa.

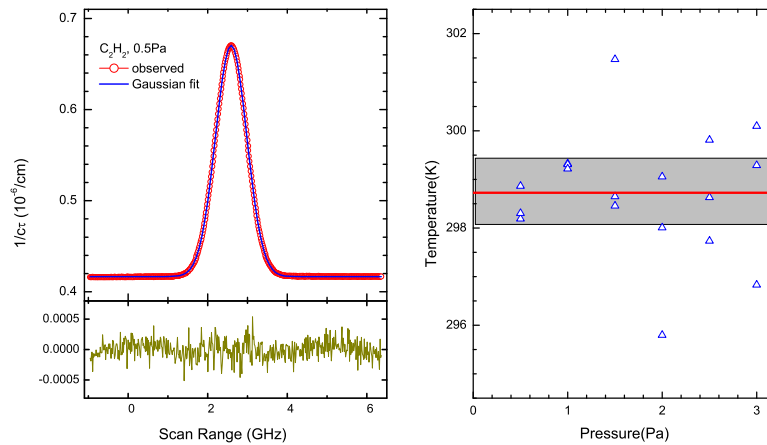


Fig. 5. Spectrum of a $^{12}\text{C}_2\text{H}_2$ line near 788 nm at the room temperature. Left panel: observed and simulated spectrum (upper) and the fitting residual (lower). Right panel: temperature values derived from the Gaussian widths of a series of spectrum obtained with different sample gas pressure.

The ring-down cavity was directly placed on an optical table and the spectra with acetylene sample gas pressure ranging from 0.5 Pa to 3 Pa were recorded. The spectrum with 0.5 Pa sample is presented in Fig. 5 (left panel). The spectrum can be well fitted by a Gaussian profile and the fitting residual is also shown in Fig. 5. The line width (FWHM) γ_D obtained from the fitting was used to retrieve the sample gas temperature following Eq. (1). The temperature values obtained from each recorded spectrum are also shown in Fig. 5 (right panel). The determined sample temperature is 298.7 ± 0.6 K which agrees with the readout from a thermometer used to monitor the room temperature. The present accuracy 2×10^{-3} is limited by the temperature fluctuation of the sample cell during the measurement since no temperature-stabilizing has been applied in present experiment. That is why the present accuracy is lower than those reported in Refs. [2, 5, 6, 8] where temperature stabilized sample cells were used. A chamber

with temperature stabilized within 1 mK at the triple point of water is under construction and a dramatic improvement of the accuracy is expected when the ring-down cell is installed in the temperature-stabilized chamber. The residual shown in Fig. 5 also implies the Gaussian profile adopted in the fitting may be oversimplified. As discussed in Refs. [22, 11], more proper treating of the line profile can further improve the accuracy for spectrum with higher SNR.

4. Summary

We have explored the possibility to apply a near infrared cavity ring-down spectrometer to the determination of the Boltzmann constant by measuring the Doppler width of a molecular absorption line. Compared with the direct absorption measurement in the mid-infrared region, the signal-to-noise level can be raised to the 10^{-5} level, the influence from detecting nonlinearity will be negligible, and the enhanced sensitivity will compensate the loss in the molecular absorption strength due to switching from the mid-infrared to the near infrared. Using a diode laser with frequency stabilized to sub-10 kHz level and a ring-down cavity with temperature stabilized to 1 mK, measuring the Doppler width of the absorption line of C_2H_2 near 0.8 μm , we expect an optical determination of the Boltzmann constant to the ppm accuracy. Since compact near infrared diode laser can be applied, the instrument can be developed as a portable universal gas thermometry if the Boltzmann constant is fixed.

Acknowledgments

This work is jointly supported by NSFC (90921006, 20903085 & 20873132), by NKBRSF (2007CB815203) and by the Fundamental Research Funds for the Central Universities.