

Measurements of pressure induced self-broadening and frequency shift coefficients of methane R9 manifold of $2\nu_3$ band

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An external-cavity diode laser (ECDL) has been used to investigate pressure-induced self-broadening as well as frequency shift of $2\nu_3$ band R9 manifold of methane. A phase sensitivity detection technology has been employed to determine the pressure induced frequency shift coefficient, however, which is obtained by line shape analyses of the recorded absorption spectrum. F1 and F2 unresolved double lines near 6105.626 cm^{-1} were measured as an object because they are often used to the high sensitivity detection of trace methane. The results show that the self-broadening and pressure induced frequency shift coefficients are 0.0232 ± 0.003 and 0.0055 ± 0.0007 MHz/Pa, respectively.

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Gas sensing based on diode laser spectroscopy is fast becoming the standard for real time noninvasive measurements of industrial gas emissions and the monitoring of gases used in manufacturing process. The monitor of methane (CH_4) concentration is essential to atmospheric chemistry, the safety of chemical facilities, gas plants, and mines because the accumulation of methane may cause the greenhouse effect. Besides methane is itself an inflammable, explosive gas^[1-4]. However there are large variations of operating conditions in different industrial processes. Therefore for the concentration measurement technique of the laser wavelength locking to absorption line center, the use of a reference cell may be impaired by a modification of spectral characteristics of the sample gas as a function of pressure. The investigation of pressure induced broadening and frequency shift coefficients of the target absorption lines will be necessary. Although the measurements on the effects of foreign gas-broadening are required in most conditions, it is also essential to know that self-broadening is important under the condition of high target gas concentration.

In this experiment we selected the methane vibrational overtone band $2\nu_3$ centered at $1.65\text{ }\mu\text{m}$, where ν_3 denoted the C-H stretching mode. Considering the theoretical research of molecular structure, the analysis of the variation of these two parameters due to pressure with the vibration and rotation quantum numbers is necessary. The experimental data of different vibration bands and rotation band have been researched, such as R3 manifold^[1] of $2\nu_3$ band and rotational lines of ν_3 ^[2], $3\nu_3$ ^[3], and ν_4 ^[4] bands. R9 manifold of $2\nu_3$ band has not been discussed by any researchers.

F1 and F2 lines of R9 manifold are an unresolved duplet with the frequency difference of 6 MHz (from HITRAN database^[5] and the results of Dong *et al.*^[6]). They are so closed that the profile can be treated as only a single line with strong line strength. So they can be used to the high sensitivity detection of trace methane.

For these applications, a good knowledge of pressure-induced self-broadening and frequency shift of the whole profile including F1 and F2 lines is required. The pressure induced broadening is obtained by measuring the direct absorption line width under various pressures. Generally phase sensitivity detection technology is mainly used to detect the trace gas because of its high sensitivity feature. Here we use the first harmonic ($1f$) signal to determine the pressure induced frequency shift of the absorbance, since the zero-crossing point is corresponding to the line center for arbitrary pressure.

The transmission of narrow line width radiation at frequency ν through a uniform medium is described by the Beer-Lambert Law

$$I = I_0 \exp[-\alpha(\nu)L], \quad (1)$$

where I and I_0 are the transmitted and incident light intensities, L is the absorption length of sample gas. The spectral absorption coefficient $\alpha(\nu)$ for pure gas can be expressed as

$$\alpha(\nu) = \sum_{i=0}^n S_i(T) \Phi_i(\nu - \nu_{0i}, a_i) P, \quad (2)$$

where P is the gas pressure; T is the temperature of the system; $S_i(T)$ is the line strength of transition i centered at ν_{0i} ; $\Phi_i(\nu - \nu_{0i}, a_i)$ is the line shape function normalized to $\int_V \Phi(\nu) d\nu = 1$. Φ depends on the temperature through Doppler broadening and depends on temperature, pressure, and perturbing species through collision broadening. Generally the line shape function for the transition i may be modeled as a Voigt profile characterized by a temperature and pressure dependent Voigt a parameter

$$a_i = \sqrt{\ln 2} \Delta\nu_{c,i} / \Delta\nu_{D,i}, \quad (3)$$

where $\Delta\nu_{c,i}$ and $\Delta\nu_{D,i}$ are the temperature, pressure dependent collision width and the temperature dependent

Doppler width.

The broadening and frequency shift of an absorption line as a function of pressure are originated from the variations of the relaxation time and energy of upper vibration state respectively because of the pressure collision. At a fixed temperature they could be described by^[7] $\Delta\nu_p = 2\gamma_{\text{self}}p$, and $\nu_p = \nu_R + \delta p$, where $\Delta\nu_p$ is the full width at half maximum (FWHM) of absorption line at the pressure p ; ν_p and ν_R are the frequency of the peak absorption profiles at pressure p and reference pressure R , respectively. $2\gamma_{\text{self}}$ and δ are the pressure induced self-broadening and frequency shift coefficients, respectively. When the process is analyzed by considering the interaction forces between molecules in the laser beam, the inelastic collisions mainly affect the broadening of line shapes; in contrast, the elastic collisions are responsible for the pressure induced frequency shift. In the low-pressure region, collisions may sometimes lead to a narrowing of the line width instead of a broadening (Dick narrowing^[8]). If the lifetime of the upper molecular level is long compared to the mean time between successive collisions, the velocity of the oscillator is often altered by elastic collisions and the mean velocity component is smaller than in the absence of such collisions, resulting in a smaller Doppler shift.

Figure 1 is a schematic diagram of the apparatus used for the measurement of frequency shift. Moreover the instruments in the broken line pane are applied to the measurement of self-broadening coefficient. A Littman-Metcalf external cavity diode laser (ECDL) system, including a laser head (Sacher TEC500) and a laser controller (LC) (Sacher MLD1000), is used for the spectroscopic investigation. Its output power is about 1.5 mW. The temperature of laser head is fixed at 20°C. The laser frequency is modulated at 5 kHz and ramped by a saw signal of 7 Hz, and the 1f signal is obtained by demodulating the modulated absorption signal via a lock in amplifier. The output from the laser is divided into three beams (power ratio 2:1:1) which propagate through the sample cell (SC) (4 cm of the length), reference cell (RC) (30 cm of the length) and Fabry-Perot cavity (FPC), then focus onto three InGaAs photoelectric detectors (PDs) (Hamamatsu G8605-23 NEP = 10⁻¹⁴ W/Hz^{1/2}),

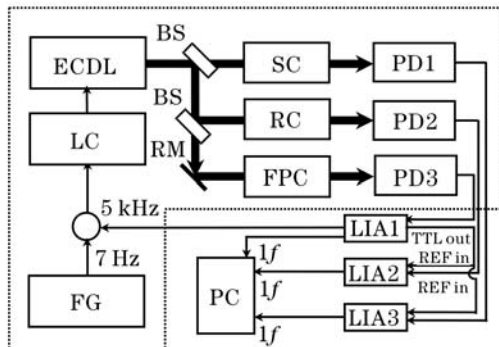


Fig. 1. Schematic diagram of the apparatus. The instruments in the broken line pane are applied to the measurement of self-broadening. FG: function generator, LIA: lock-in amplifier, BS: beam splitter, RM: reflection mirror, PC: personal computer, Ref In: reference input.

respectively. The pressure of sample cell is varied from 500 Pa to 80 kPa and that of the reference cell is fixed to 2 kPa. The high finesse confocal FP cavity is used to calibrate the frequency with the finesse and free spectral ranges (FSRs) of 130 and 735 MHz. The sample cell is evacuated to 10⁻⁴ Pa by molecular pump (Alcatel ATP 80/100) and then filled with pure methane. The pressure was measured by a pressure sensor (Motorola MPX100).

Two sets of experiments were performed to determine the pressure self-broadening and frequency shift coefficients. In order to extract the values of the pressure broadening from the direct absorption data, a Voigt profile is fit to the absorption spectrum. A line-shape-fitting Fortran program performs a general nonlinear least-squares fit of a Voigt profile. The free parameters consist of the frequency offset, the collision width, and absorption line strength. During the fitting process, the Doppler width was held as a fixed parameter and set to the calculated value for 296 K. This is appropriate since the temperature variation was less than ±0.5 K in the laboratory. The frequency axis was linearized using the marker fringes from the F-P etalon. The reduced methane line shape near 6105.626 cm⁻¹ was shown in the Fig. 2 on condition that $p = 1$ kPa, $l = 30$ cm, $\Delta\nu_D = 564$ MHz, $a = 0.035$, $T = 296$ K. In Fig. 2(b), the small circles represent the experimental direct absorption spectrum, and the theoretical fitting result is illuminated by the real line. The residual represents the normalized difference between the measured data and the theoretical profile, which is less than 5%. Figure 2(a) shows the cavity signal which was applied to convert the abscissa from the time domain to the frequency domain. Every interval is 735 MHz that is corresponding to a FSR. To obtain a precise frequency reference we fit the x -coordinate by considering the multiple FSR intervals with a 3rd order polynomial. Submitting the value of a into the Eq. (3), the pressure dependent collision width was 23.7 MHz at the pressure of 1 kPa.

The pressure induced broadening coefficient γ_{self} can be determined by the variations of collision width at different pressure. Figure 3 represents the measured collision width at various pressures, with the slope of 0.0232 MHz/Pa and the uncertainty of ±0.003 MHz/Pa. Compared with the theoretical self-broadening coefficients of

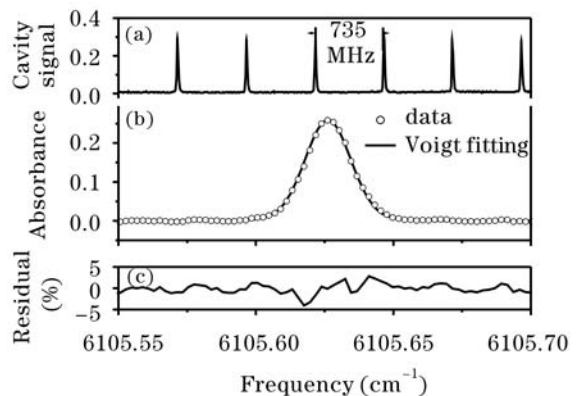


Fig. 2. The raw transmitted signals of the laser passing through the FP cavity (a), the sample cell with the pressure of 1 kPa (b), and the normalized difference between the measured data and the theoretical profile (c).

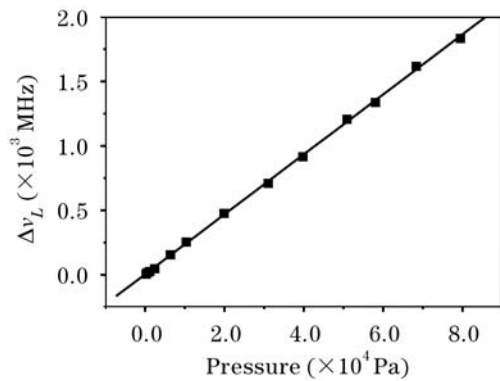


Fig. 3. Pressure induced broadening line width as the function of pressure at 296 K.

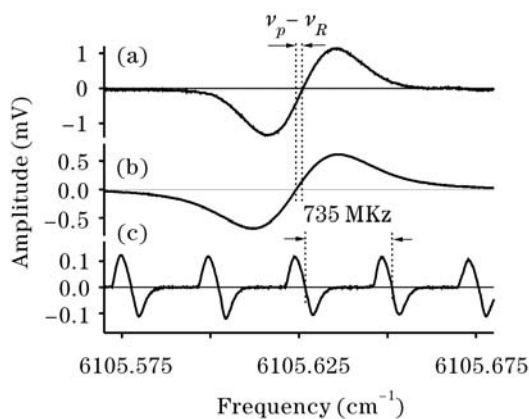


Fig. 4. The typical $1f$ component of the transmitted signals of the reference cell (a), sample cell with the pressure of 10 kPa (b), and FP cavity (c).

0.0234 MHz/Pa of F1 and F2 single line, there is a bit difference between them. The detected lowest pressure is 200 Pa in this experiment. The pressure broadening induced by the collision articles is weaker, the observable pressure of Dicke narrowing effect is higher. From the results of measurement, the Dicke narrowing phenomena will be relatively weak. Therefore the effect was not observed near the pressure of 200 Pa.

Figure 4 represents the $1f$ components of the three transmitted signals of PD1, PD2 and PD3 with the pressure of 10 kPa in the sample cell. Figure 4(a) is corresponding to the absorption of reference cell with the pressure of 2 kPa. It was used as a spectral marker against which the $1f$ signal in the sample cell (shown in Fig. 2(b)) was compared. By varying the pressure of sample cell we can determine the relation of the frequency shift versus pressure easily. The $1f$ signal of cavity transmission (shown in Fig. 2(c)) was used as a frequency reference. The calibration method of the frequency is the same with the measurement of the pressure broadening. Here the frequency shift $\nu_p - \nu_R$ is 54 MHz. The dots in Fig. 3 represent the frequency shifts at different pressures from 200 Pa to 80 kPa relative to the reference pressure of 2 kPa. When the pressure increases, the red shift will occur at the absorption line center. The frequency shift coefficient δ was determined from the slope of the linear fit to these measured shifts. The solid line is the linear fit result with the slope of 0.0055 MHz/Pa and the uncertainty was ± 0.0007 MHz/Pa. Here the frequency

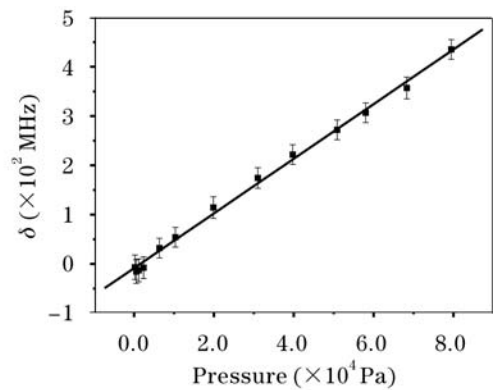


Fig. 5. Measured spectral line shift versus pressure at 296 K.

shift was yielded because the different line broadening and different frequency shift of the two lines included in the profile.

In conclusion the pressure induced broadening coefficient was measured by detecting direct absorption spectra. However $1f$ signal of the absorption line was applied to determine the absorption peak frequency shift coefficient since the zero-crossing point of $1f$ is corresponding to the line center. For the wide absorption line such a method can obtain a better precision than previously detection technology by the use of direct absorption. The two parameters of absorption profiles are important in the spectral sensing system employing a line-locking technique and absorption analysis in a non-standard pressure environment, and they also would be useful in testing the model of intermolecular potentials.

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