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# $N_2$ -shift coefficients in the $\nu_3$ band of $^{12}CH_4$ at room temperature.

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## ABSTRACT

Using a dual beam diode-laser spectrometer, we have studied with accuracy the N<sub>2</sub>-shift coefficients in the P-branch of the  $\nu_3$  band of methane. The experiments were performed at room temperature for 16 lines in the spectral range 2906-2948 cm<sup>-1</sup> with J values between 7 and 11. Each line was recorded at four different nitrogen pressures ranging from 17 to 302 mbar. The collisional shifts were obtained by fitting to the experimental lineshape a Rautian-Sobel'Man profile that takes into account the Dicke narrowing. The shift coefficients were determined using a procedure where a non perturbed line of pure CH<sub>4</sub> was simultaneously recorded with N<sub>2</sub>-shifted transitions. Finally, we give a comparison with previous published results.

## INTRODUCTION

Methane is an important trace gas in our atmosphere [1]. It is also a minor component in various planetary (or satellite) atmospheres like Jupiter [2], Mars [3] or Titan [4]. On earth, methane is the third greenhouse effect gas after water vapor and carbon dioxide [5, 6] and its global-warming potential is 21 times higher than those of CO<sub>2</sub> [7]. The quantity of methane in atmosphere are essentially dependant on industry activities, agriculture, temperature and humidity [7, 8].

The measurements of molecular parameters, like the shift coefficients, are useful for the understanding of the physical chemistry of our own atmosphere and the analyze of the infrared spectra of planetary atmospheres. These fields need very accurate measurements to improve their precision [9]. Thus we have studied with a great accuracy 16 individual N<sub>2</sub>-shift coefficients of CH<sub>4</sub> using a dual beam tunable diode-laser spectrometer with a high resolution ( $10^{-5}$  cm<sup>-1</sup>).

Some studies have already been devoted to the N<sub>2</sub>-shift coefficients in the  $\nu_3$  band of CH<sub>4</sub>. In 1993, Benner et al. [10] determined these coefficients using a Fourier transform spectrometer with a resolution of about 0.01 cm<sup>-1</sup> and by fitting a Voigt profile. In 1997, Pine [11] published new measurements realized by a tunable difference-frequency spectrometer using a Rautian-Sobel'Man profile and in 2000, Pine and Gabard [12] reinvestigated the results obtained by Pine by fitting more elaborated profiles taken into account the speed dependence and the line mixing effects.

## EXPERIMENTAL DETAILS

The spectra were recorded with an improved Aero Laser dual beam tunable diode-laser spectrometer (model L5004-IR) which will be described in details elsewhere [13]. Figure 1 gives an optical scheme of this apparatus; its resolution is about  $10^{-5}$  cm<sup>-1</sup> and its signal-to-noise ratio better than 2000. The signal provided by a diode-laser, cooled with liquid nitrogen, is divided into two components by a beam splitter 45/55. For this study, the first part of the laser beam is directed to a cell of 15 cm optical pathlength whereas the second part is passed through a 50 cm optical pathlength absorption cell.

The spectra from the two beams were recorded simultaneously and an homemade microprocessor signal averager was used for data acquisition. In order to increase the signal-to-noise ratio, each spectrum was averaged over 100 scans. For the relative calibration, a confocal étalon with a free spectral range of  $0.007958 \text{ cm}^{-1}$  was introduced in a laser beam.

Methane and nitrogen were supplied by Air Liquide Company with a stated purity of 99.95% and 99.999% respectively. The 50 cm cell contained the gas mixture with a small pressure of methane ( $\sim 0.7 \text{ mbar}$ ) diluted in the perturber gas (comprised between 170 and 300 mbar) whereas the 15 cm cell contained pure methane with a pressure between 0.2 and 1 mbar depending on the line under study. These two cells were placed in parallel in the two beams of the spectrometer. So, we recorded simultaneously two spectra: one with the unperturbed line, the other with the perturbed and shifted line. The fitting of experimental lineshapes can be done separately and the position of each line is known with a great accuracy. For each line, the measurements were realized at four perturber pressures. The pressures were measured by two MKS Baratron gauges with a full scale of 1.2 and 1200 mbar and all spectra were recorded at room temperature (297 K).

Before recording spectra, the purity of the mode was checked by the smoothness of the étalon fringe pattern, the laser emission regularity and the level of the saturated line. After being recorded the spectra were linearized, to correct the weak nonlinear tuning of the diode-laser, with a constant step of about  $1 \times 10^{-4} \text{ cm}^{-1}$ .

For each line under study, a set of 12 spectra was recorded: (1) diode-laser emission profile (100% transmission level); (2) low absorption line at low pressure of pure  $\text{CH}_4$  to avoid collisional effects (Doppler line) in view to determine the apparatus function; (3) confocal étalon fringes; (4) saturated line (0% transmission level); (5-8) the  $\text{N}_2$ -broadened lines at four different total pressures and (9-12) the unperturbed absorption line of pure methane. An example of the spectra obtained for the  $\text{N}_2$ -shift of the  $\text{P}(7)\text{F}_1$  line of the  $\nu_3$  band at  $2947.6679 \text{ cm}^{-1}$  is shown in figure 2. The assignments and wavenumbers of the measured lines of methane are taken from HITRAN [14]. The labelling of the transitions considered in our work is also explained in Ref. [14].

## DATA REDUCTION AND EXPERIMENTAL RESULTS

The measured absorbance  $\alpha(\nu)$  at wavenumber  $\nu$  ( $\text{cm}^{-1}$ ), for the light intensity transmitted through a gas column, is obtained through the Beer-Lambert law as

$$\alpha(\nu) = \ln I_0(\nu)/I_t(\nu) , \quad (1)$$

where  $I_0(\nu)$  and  $I_t(\nu)$  are transmitted intensities measured with the cell under vacuum and filled with the gas sample, respectively. The small instrumental distortion  $\gamma_{\text{app}}$  is taken into account as previously [15] through an effective Doppler width  $\gamma_{\text{D}}$  obtained from the pure  $\text{CH}_4$  lines at low pressure and systematically used in place of the true Doppler width  $\gamma_{\text{Dth}}$ . As the apparatus function can be assimilated to the Gaussian function [16] and theoretical Doppler, the apparatus half-width is given by:

$$\gamma_{\text{app}} = \sqrt{\gamma_{\text{D}}^2 - \gamma_{\text{Dth}}^2} \quad (2)$$

where

$$\gamma_{\text{Dth}} = 3.5812 \sqrt{\frac{T}{M}} \quad (3)$$

is the theoretical Doppler half-width with  $T$  (K) the temperature,  $M$  (a.m.u.) the molecular mass of  $\text{CH}_4$ , and  $\nu_0$  ( $\text{cm}^{-1}$ ) the line center wavenumber. The apparatus half-width  $\gamma_{\text{app}}$  deduced from Eq. (2) for recorded lines has a typical value of  $5 \times 10^{-4} \text{ cm}^{-1}$  in this work.

To determine the  $\text{N}_2$ -shift coefficient of a line, we assumed that the pressure broadened lines are symmetrical and they are considered sufficiently isolated to be individually fitted by a theoretical profile. We used the Rautian-Sobel'Man model [17] which incorporates the Dicke effect [18]. When the lines were not well isolated, like for P(7)E-1 and P(7)F<sub>2</sub>-2 lines, which are only separated of  $0.1 \text{ cm}^{-1}$ , a multiline fit method described in Ref. [19] was considered.

The collisional shift  $\delta_0$  (in  $\text{cm}^{-1} \text{ atm}^{-1}$ ), is determined for each line at each partial pressure of  $\text{N}_2$  and is the difference between the position of the unshifted line of pure methane and the  $\text{N}_2$ -shifted line of methane. The values of  $\delta_c$  (in  $\text{cm}^{-1}$ ) determined at the four different total pressures were plotted versus the pressure of the perturber ( $\text{N}_2$ ).

The  $\delta_0$  collisional shift coefficient is determined by the following relation :

$$\delta_0 = \delta_c^{N_2} P_{N_2} \quad (4)$$

where  $\delta_c^{N_2}$  represents the  $N_2$ -shift of  $CH_4$ ,  $P_{N_2}$  is the partial pressure of  $N_2$ . The slope of the best fit line passing through the experimental points gives the  $N_2$ -shift coefficient. Figure 3 shows an example of these fits for the P(11) $A_2$ -1 line. The small contribution of self-shift was neglected because of its weak value due to the low pressure of active gas. However, the difference of pressure in the two absorption cells (factor 2.5) can explain why the best fit line does not pass by the origin. These  $N_2$ -shift coefficients  $\delta_0$  and their experimental errors are listed in Table 1, while Figure 4 presents, for A, E and F-species, these coefficients versus the wavenumbers. The absolute errors are estimated to be twice the standard deviation given by the linear least-squares procedure plus 2% of  $\gamma_0$  representing experimental error. This experimental error comes mainly from the baseline location, the perturbations due to neighboring lines, the slight nonlinear tuning of the laser and the lineshape model used.

As may be seen on Figure 4, it is not possible to highlight a general behaviour for both symmetries of methane lines. But, we can observe a possible scattering of the values of the shift coefficients with the increasing value of the wavenumbers. That has been also observed in the work of Antony et al. [20].

Figure 5 compares our results obtained for six P(10) symmetries of the  $\nu_3$  vibrational band with earlier published determinations from Pine [11], Benner et al. [10] and, Pine and Gabard [12] for the A-, E- and F-species. Generally, our values are in good agreement with these previous data.

### Conclusions

Using a tunable dual beam diode laser spectrometer, the  $N_2$ -shift coefficients for 17 lines belong to the P-branch of the  $\nu_3$  vibrational band of  $CH_4$  were measured at room temperature. The trend of our results for the  $\nu_3$  band with rotational state is essentially the same than for those observed by Antony et al. [18]. The comparison with earlier published data [10-12] is in good agreement.

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## FIGURE CAPTIONS

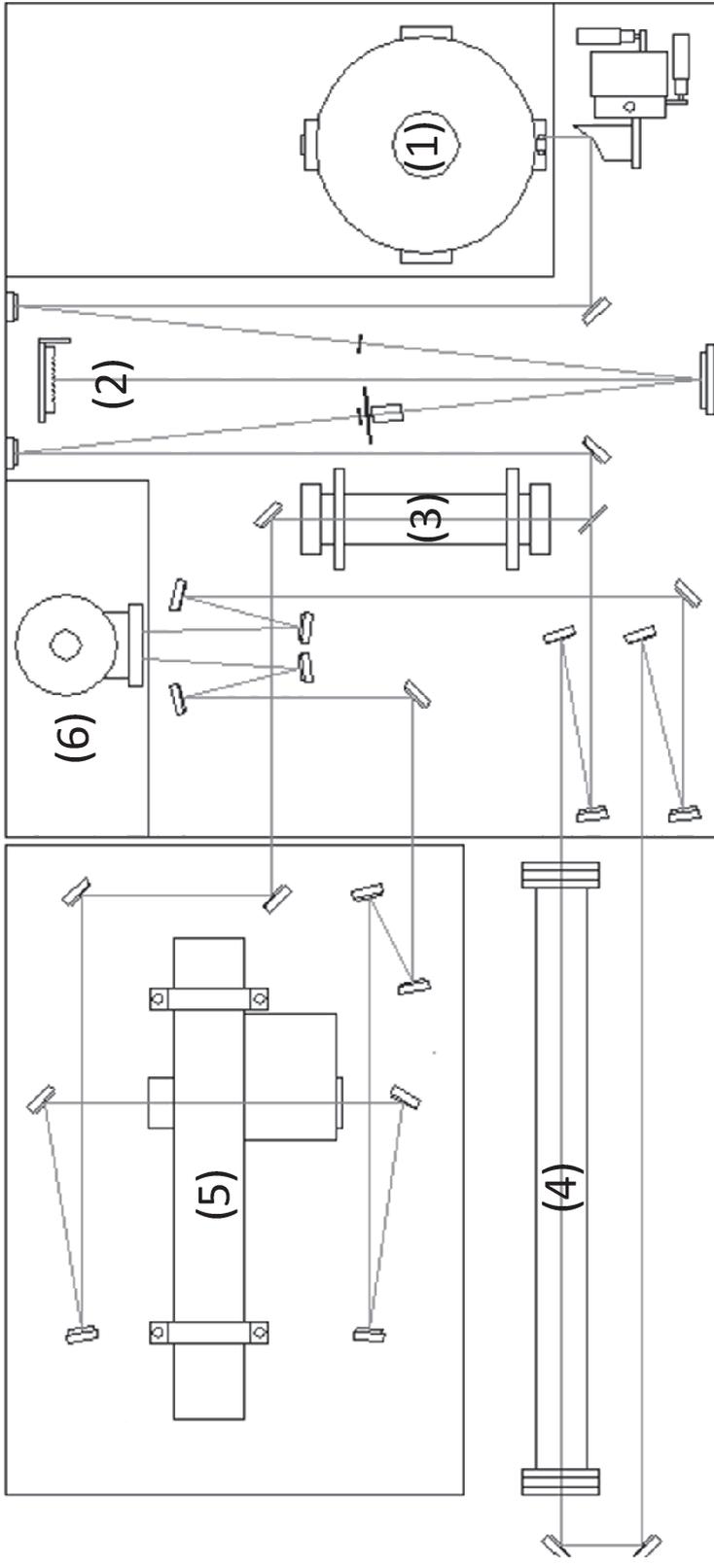
- Fig. 1. Aero Laser dual beam tunable diode-laser spectrometer : (1) diode-laser Dewar, (2) monochromator, (3) and (4) absorption cells, (5) confocal étalon and (6) double detector.
- Fig. 2. Example of the spectra recorded for shift determination at 296 K for the P(7)F<sub>1</sub> line in the  $\nu_3$  band of CH<sub>4</sub> perturbed by N<sub>2</sub>. (1) diode-laser emission profile (100% transmission level); (2) low absorption line at low pressure of pure CH<sub>4</sub> (Doppler line), (3) confocal étalon fringes, (4) saturated line (0% transmission level), (5-8) perturbed line at different pressures of N<sub>2</sub> (154.3, 202.2, 252.1 and 302.0 mbar respectively) and (9-12) unshifted line of CH<sub>4</sub>.
- Fig. 3. Pressure dependence of the N<sub>2</sub>-shift coefficient  $\delta_c$  of P(11)A<sub>2</sub> absorption line belong to the  $\nu_3$  vibrational band of CH<sub>4</sub> at 2906.7348 cm<sup>-1</sup>. The collisional shift coefficient is the slope of the best fit line.
- Fig. 4. N<sub>2</sub>-shift coefficients of P(7), P(10) and P(11) absorption lines belong to the  $\nu_3$  vibrational band of CH<sub>4</sub>. They are represented in function of their symmetries and their wavenumbers.
- Fig. 5. Comparison of the N<sub>2</sub>-shift coefficients of the P(10) absorption lines belong to the  $\nu_3$  vibrational band of CH<sub>4</sub> obtained with the Rautian-Sobel'Man profile with those earlier published by Pine [11] ( $\square$ ), Benner et al. [10] ( $\Delta$ ), Pine and Gabard [12] ( $\circ$ ).

Table 1  
 $N_2$ -shift coefficients  $\delta_0$  in the  $\nu_3$  band of  $^{12}CH_4$  at room temperature.

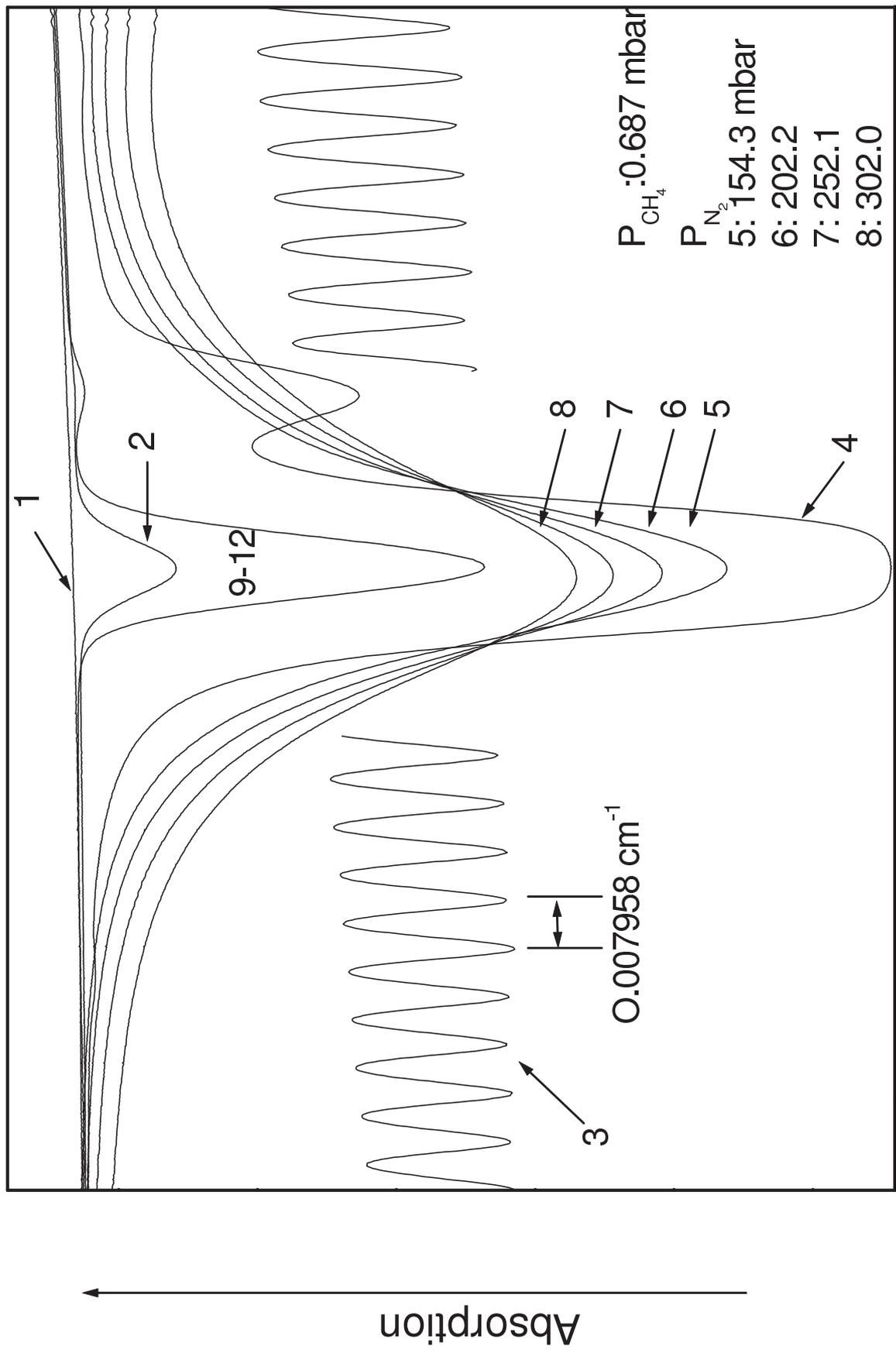
Lines	$\nu_0$ ( $cm^{-1}$ )	$\delta_0$ ( $10^{-3} cm^{-1} atm^{-1}$ )
P(11) $F_2(42) \leftarrow F_1(2)$	2906.2824	$5.84 \pm 0.27^*$
P(11) $E(28) \leftarrow E(1)$	2906.5886	$6.11 \pm 0.35$
P(11) $F_1(40) \leftarrow F_2(2)$	2906.6477	$6.43 \pm 0.67$
P(11) $A_1(15) \leftarrow A_2(1)$	2906.7348	$6.79 \pm 0.20$
P(10) $F_1(37) \leftarrow F_2(3)$	2916.2014	$3.98 \pm 0.41$
P(10) $E(24) \leftarrow E(2)$	2916.3017	$6.04 \pm 0.28$
P(10) $F_2(36) \leftarrow F_1(2)$	2916.3961	$7.61 \pm 0.38$
P(10) $A_2(14) \leftarrow A_1(1)$	2916.7538	$5.85 \pm 0.31$
P(10) $F_2(37) \leftarrow F_1(1)$	2916.9661	$5.11 \pm 0.45$
P(10) $F_1(38) \leftarrow F_2(2)$	2917.0662	$7.78 \pm 0.48$
P(7) $F_2(26) \leftarrow F_1(2)$	2947.6680	$2.81 \pm 0.73$
P(7) $E(17) \leftarrow E(1)$	2947.8109	$7.76 \pm 0.33$
P(7) $F_1(24) \leftarrow F_2(2)$	2947.9121	$8.60 \pm 0.27$
P(7) $A_1(10) \leftarrow A_2(1)$	2947.1079	$6.35 \pm 0.81$
P(7) $F_1(25) \leftarrow F_2(1)$	2947.4214	$4.75 \pm 0.49$
P(7) $F_2(27) \leftarrow F_1(1)$	2947.4741	$8.43 \pm 0.36$

\* The errors quoted are twice the standard deviation plus 2% of  $\delta_0$

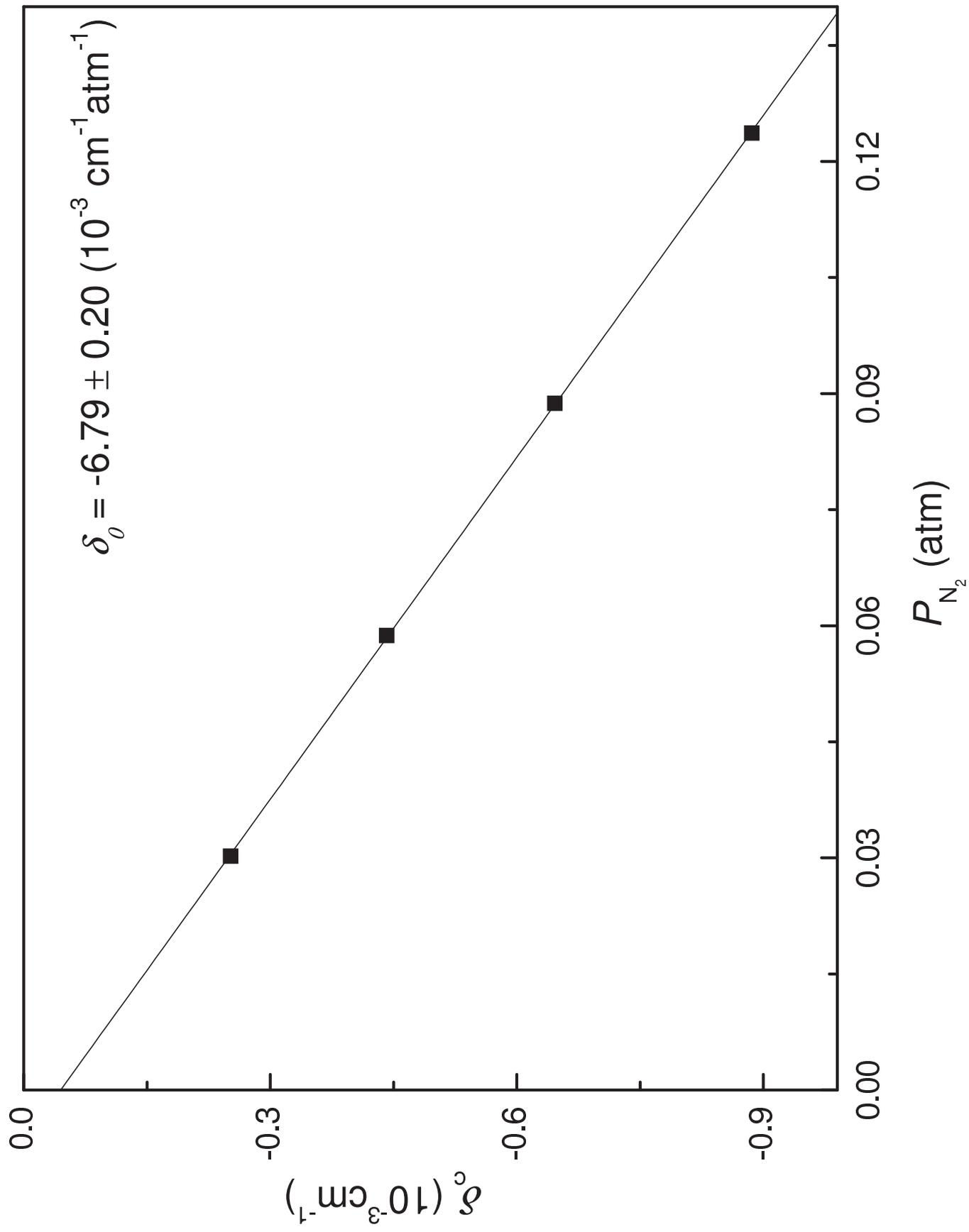
Figure



Figure



Figure





Figure

