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LETTER TO THE EDITOR

Pressure Self-shift of the $J = 1 \leftarrow 0$ Line of Carbon Monoxide

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The pressure self-shift parameter of the lowest rotational transition ($J = 1 \leftarrow 0$) of carbon monoxide in the ground vibrational state has been determined with an accuracy of about 2 kHz/Torr.

The study of the lineshape parameters of carbon monoxide is of particular interest with respect to its important role in planetary atmospheres (*1*, *2*). The knowledge of pressure-frequency shift parameter is also very important because the investigated line of $^{12}C^{16}O$ is useful as a secondary calibration standard in the 3-mm wavelength region (*3*).

The study was carried out using a RAD spectrometer (*4*) with a system of phase-lock-loop (PLL) stabilization described in (*5*). To avoid any instability, two different types of modulation techniques were used: either an amplitude modulation which employed a chopper wheel located between a PLL-stabilized BWO 78-118 GHz and a RAD cell or a frequency modulation which was achieved by a phase modulation of the PLL BWO reference synthesizer CH6-31.

Measurements using amplitude modulation were made according to the method described in (*5*, *6*). Briefly, the spectral line was digitally recorded with step-by-step frequency tuning of the radiation source. The data corresponding to the intensity of the spectral line were stored in a computer and were then fitted to the model of a Lorentzian lineshape which is valid for an optically thin sample

$$I(\nu_n) = A_0 \cdot (1 + k \cdot (\nu_n - \nu_0)) \cdot \frac{\Delta\nu}{(\nu_n - \nu_0)^2 + (\Delta\nu)^2} + b, \qquad [1]$$

where A_0 is an amplitude factor, $\Delta\nu$ the half-width at half-maximum (HWHM) of the Lorentzian lineshape, ν_n is the MW frequency, ν_0 is the line center frequency, k is the linear trend coefficient of the MW power, and b is a constant level of baseline. The results of the investigation using the amplitude-modulation technique are presented in Table 1 and Fig. 1. The data points for the three lowest pressures in Fig. 1 were obtained with a higher accuracy using a

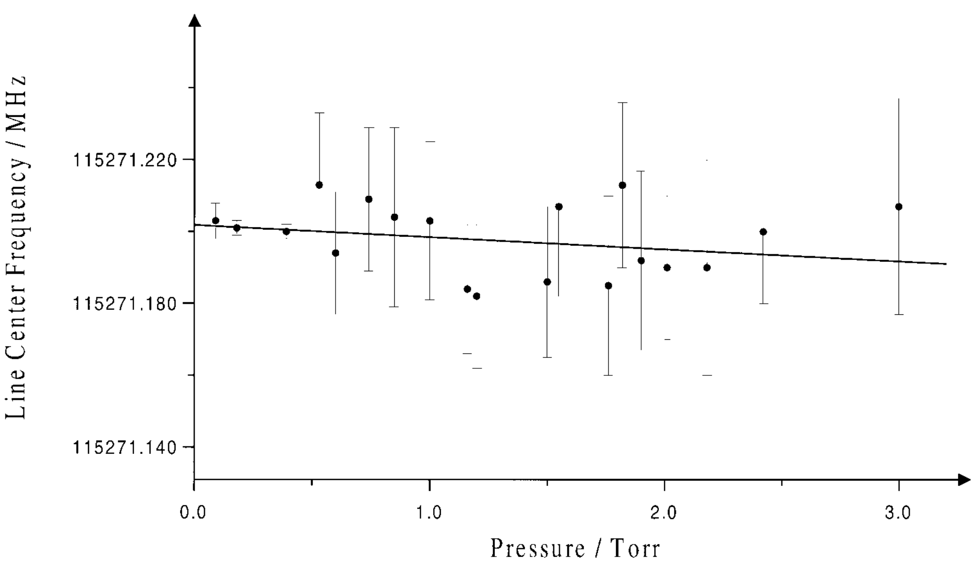

FIG. 1. Pressure dependence of the line center frequency of the $J = 1 \leftarrow 0$ transition of $^{12}C^{16}O$, using amplitude modulation of the mm radiation. The error bars indicate one standard deviation obtained from the least-squares fits of the line profiles.

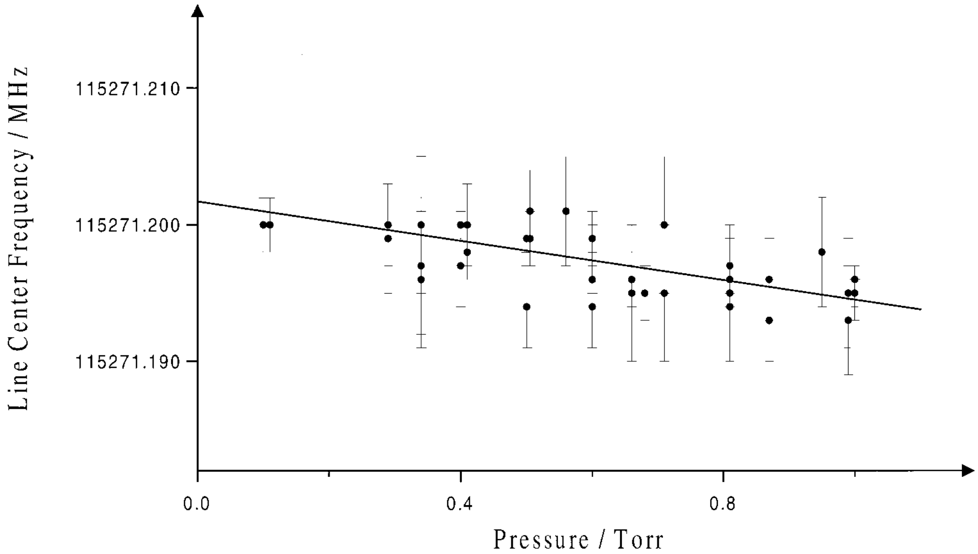

FIG. 2. Pressure dependence of the line center frequency $J = 1 \leftarrow 0$ transition of $^{12}C^{16}$, using frequency modulation of the mm radiation. The error bars indicate one standard deviation obtained from an ensemble averaging of frequency counter values.

modified ("quasi-resonant") RAD cell (*7*), which is only applicable for line-shape studies at low pressure.

The second method of pressure-frequency measurements using of a stabilization BWO PLL system is well known in the microwave spectroscopy (*8, 9*). In the case of using a square-wave frequency modulation, the frequency PLL reference synthesizer CH6-31 (30–50 MHz) was stabilized with respect to the derivative-shaped spectral line as was described in (*1*) together with a discussion of possible systematic errors in a RAD spectrometer. The main systematic error results from a frequency dependence of the MW power. Using the model of a Lorentzian lineshape with half-width $\Delta\nu$ and a square-wave frequency modulation with a deviation $\delta\nu$, the corresponding frequency shift ($\nu_0^{\text{obs}} - \nu_0$) can be shown to be given by

$$\nu_0^{\text{obs}} - \nu_0 \simeq \frac{P'_\nu}{2 \cdot P} \cdot ((\Delta\nu)^2 + (\delta\nu)^2), \qquad [2]$$

where P and P'_ν is the radiation power and the linear slope of the power, respectively. In order to estimate this shift of ν_0, we varied the gas pressure and the frequency deviation $\delta\nu$. As a result we found negligible systematic shift ($0 < \nu_0^{\text{obs}} - \nu_0 < 2$ kHz), when the gas pressure in the RAD cell was less than 1 Torr and $\delta\nu \leq 3$ MHz.

The signal-to-noise ration (S/N) was more than 10 000, which is about one order of magnitude better than the S/N ratio achieved with the amplitude modulation. The frequency of the reference synthesizer corresponding to the signal of the maximum absorption of the spectral line was measured with a frequency counter using a Rb-standard as reference. The value of the line center frequency was obtained by an average of 30 independent measurements of the line center frequency for each pressure. The measurements were performed at a period of a few weeks at room temperature (295 K) with an uncertainty of about 2 K. The results of the investigation of pressure-frequency self-shift with the frequency-modulation technique are presented in Table 1 and Fig. 2.

The value of the zero-pressure line center frequency determined in this work has a very good coincidence with the result from sub-Doppler measurements (*3*). The line has a slight negative frequency selfshift as in (*10*), but the accuracy of the pressure self-shift parameter is much higher in the present work.

TABLE 1
Line Center Frequency and Pressure Self-shift Parameter for the $J = 1 \leftarrow 0$ Transition of $^{12}C^{16}O$

Line Frequency MHz	Selfshift parameter kHz/Torr	Reference
115 271.2018(20)	-3.6(40)	this work [a]
115 271.2017(10)	-7.1(20)	this work [b]
115 271.2018(5)	-	(3)
115 271.199(7)	-27(24)	(10)

Note. One standard error in unit of the last digit quoted is given in parentheses.
[a] Measurements with amplitude modulation.
[b] Measurements with frequency modulation.

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