THE ASTROPHYSICAL JOURNAL, 393:848–851, 1992 July 10

IMPROVED LABORATORY REST FREQUENCY MEASUREMENTS AND PRESSURE SHIFT AND BROADENING PARAMETERS FOR THE $J = 2 \leftarrow 1$ AND $J = 3 \leftarrow 2$ ROTATIONAL TRANSITIONS OF CO

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Received 1991 October 7; accepted 1992 January 16

ABSTRACT

The $J = 2 \leftarrow 1$, $3 \leftarrow 2$, and the $4 \leftarrow 3$ rotational transitions of CO have been measured using the RAD-2 microwave spectrometer at the Applied Physics Institute in Nizhny Novgorod. Pressure shift and broadening parameters were measured for the $J = 2 \leftarrow 1$ and $J = 3 \leftarrow 2$ transitions. This was done with CO (self-broadening) and CO_2 (foreign gas-broadening). The new laboratory rest frequency measurements are accurate to ± 2 kHz (2 σ uncertainty). These improved frequency measurements should be useful in planetary atmosphere research to determine more accurate wind velocities in the Venusian atmosphere.
Subject headings: line: identification — molecular data

1. INTRODUCTION

In a recent paper, Buhl, Chin, & Goldstein (1991) have observed that the millimeter line of the $J = 2 \leftarrow 1$ rotational transition of CO in the atmosphere of Venus exhibits a complex profile consisting of a broad pedestal base with a narrow Doppler profile on top of the broad pedestal. The broad profile is attributed to pressure-broadened CO absorption below about 100 km. The narrow feature is attributed to CO above 100 km. The narrow feature is approximately 600 kHz FWHM. From a statistical average of seven groups of three measurements, they derived an uncertainty of 7.3 m s^{-1} in the average wind velocity above 100 km.

Unfortunately there are a number of uncertainties that affect the accuracy of these measurements that completely overshadow the precision of 7.3 m s^{-1}. These uncertainties arise from two separate artifacts. One is the uncertainty associated with the rest frequency which for the $J = 2 \leftarrow 1$ is 230,537.990 MHz with 2 σ error bar of 17 kHz (22 m s^{-1} at 230 GHz) (Lovas 1985). Winnewisser, Winnewisser, & Winnewisser (1984) have recently made improved measurements on the frequencies of a number of low-J transitions of CO. For the $J = 2 \leftarrow 1$ transition they arrive at 230,538.0016 (50) MHz, which is much more precise than the earlier number, but it still carries at 5 kHz uncertainty. There is also a current lack of knowledge of the pressure shift in line frequency associated with both the laboratory measured rest frequency and with the spectra observed in the Venusian atmosphere. Ab initio calculations indicate pressure shifts could be as large as 0.75 kHz Pa^{-1} (100 kHz $torr^{-1}$) (Hillman 1990). This would correspond to about a 2 kHz (3 m s^{-1}) shift at 230 GHz at the line core pressures and temperatures (Buhl et al. 1991). In addition, superposition of the Doppler core onto the pressure-shifted broader pedestal could induce a core shift of 3 kHz (4 m s^{-1}) if the broad feature has significant contributions down to 85 km (Buhl et al. 1991).

There are also additional uncertainties associated with the radiotelescope that need to be considered. A slope in the baseline of the broad pedestal results from the slow source/sky switching rates. This uncertainty could be as much as 6 kHz (8 m s^{-1}). Pointing errors could also introduce systematic offsets which could result in shifts of up to 15 m s^{-1} (Buhl et al. 1991).

While there is nothing that can be done in the laboratory to improve the second category of uncertainties associated with the radiotelescope itself, clearly, improved laboratory measurement of the rest frequency and associated pressure shifts from self-broadening and foreign gas (CO_2)–broadening at a number of different temperatures would greatly lower the overall uncertainty associated with the measurement of the Venus wind velocities using this technique.

2. EXPERIMENTAL

Spectrometer description.—All of the new frequency measurements were done using a submillimeter spectrometer with acoustic detection. The spectrometer is a variant of the RAD-2 design which has been previously described by Krupnov (Krupnov 1979). The spectrometer consists of a chain of phase-locked backward-wave oscillators (BWOs) which are referenced to a rubidium standard. For the measurements reported here, the frequency measurements were double-checked against two independent rubidium frequency standards. The instrument employs 180 Hz frequency modulation of the source with frequency deviations up to several megahertz. The spectral lines are detected by lock-in amplification of the signals, providing a first derivative line shape of the rotational transitions. This method is very useful for frequency measurements since it allows automatic frequency tuning of the spectrometer to the zero crossing (line center) of the rotational transitions. The zero-pressure (rest frequencies) are obtained by least-squares fitting of the individual frequency measure-

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ments made at the various pressures shown in the self-broadening plots of Figure 1. The rest frequencies are determined by extrapolating the plots to zero pressure.

Linewidths are measured by using a variable low-frequency synthesizer centered near 30 MHz to step across the transition. Using this technique, F_{min} and F_{max} can be recorded for the derivative shaped line yielding a $\Delta F = F_{min} - F_{max}$. The values of $\Delta\nu$ recorded in this paper were obtained from ΔF by equation (1):

$$\Delta\nu = \Delta F \frac{\sqrt{3}}{2}, \quad (1)$$

where $\Delta\nu$ represents the half-width at half-height (HWHM) for a Lorentzian line shape.

The sample mixture used for the $J = 2 \leftarrow 1$ CO_2 shift and broadening measurements consisted of 10% CO in CO_2. The mixture used for the $J = 3 \leftarrow 2$ measurements was 20% CO in CO_2. The pressure measurements were made using a capacitance manometer type pressure gauge and should be accurate to better than 1.0%.

Error analysis.—The uncertainties associated with the line frequency measurements were considered in some detail since the accuracy of the frequency measurements is extremely important for the wind velocity measurements. The uncertainties are of two types; the first are those associated with statistics. In principal the uncertainty in the frequency measurement arising from the line width, $\delta\nu_{lw}$, is given by equation (2):

$$\delta\nu_{lw} = \frac{2\Delta\nu}{S/N}, \quad (2)$$

where $\Delta\nu$ is given by equation (1) and S/N is the signal-to-noise ratio associated with the measurement. For the measurements at low pressures, $\Delta\nu \sim 1$ MHz and S/N $\sim 10^4$ so $\delta\nu_{lw} \sim 200$ Hz, which is quite small compared to other uncertainties. The uncertainty of the frequency counter reading, $\delta\nu_c$ is on the order of 1×10^{-10} which at 200–500 GHz corresponds to uncertainties of 20–50 Hz.

More significant are the uncertainties due to systematic errors. The nature of the spectrometer requires that a frequency modulation be applied to the BWO in order for the acoustic detection system to work. In these experiments a square wave (on-off) modulation frequency of 180 Hz was used. The uncertainty, $\delta\nu_{mod}$, is given by equation (3):

$$\delta\nu_{mod} = \delta \frac{T_1 - T_2}{T_1 + T_2}, \quad (3)$$

where T_1 and T_2 are the times of the first and second half-periods of the frequency modulation, δ is the difference in the frequency of the BWO radiation, $F_1 - F_2$, when the modulation is on and off, respectively. Generally $\delta = F_1 - F_2 \leq 1$ MHz and $(T_1 - T_2)/(T_1 + T_2)$ is less than 1×10^{-3}, so $\delta\nu_{mod} \leq 1$ kHz.

The largest uncertainty, $\delta\nu_{VSWR}$, in the frequency measurements is due to an influence of the absorption cell on the BWO radiation frequency. In terms of standard radio theory this term could be referred to as an effect caused by the variable standing wave ratio (VSWR). At pressures ≤ 133.3 Pa (≤ 1 torr) the influence is linear and minimal (1–2 kHz), where this represents the total variation in amplitude of the effect. Furthermore, since the effect is approximately sinusoidal in nature, the rms value ($\sim 0.7 \times$ peak-to-peak) is a more reasonable number to use. At pressures greater than 133.3 Pa (1 torr), the influence is more pronounced and deviation from linearity begins to show up. The uncertainty can be still be estimated by recording a number of measurements at each pressure where the relative position of the BWO with respect to the absorption cell is changed slightly. Typically, the total movement necessary is only $\lambda/2$ where λ is the wavelength of the radiation of the BWO. In the 200–500 GHz frequency region $\lambda/2 = 0.75$–0.3 mm. From this one can determine the total peak-to-peak variation in amplitude of the effect. The best value for the frequency determination is then chosen to be the center of this range of values.

The signal, S, from a spectral line in the RAD spectrometer is given by equation (4):

$$S = \kappa \cdot P \cdot \gamma \cdot l, \quad (4)$$

where κ is a constant, P is the power of the BWO radiation, γ is the Lorentzian profile of the spectral line given by equation (5):

$$\gamma = \frac{\gamma_0(\Delta\nu)^2}{(\nu - \nu_0)^2 + \Delta\nu^2}, \quad (5)$$

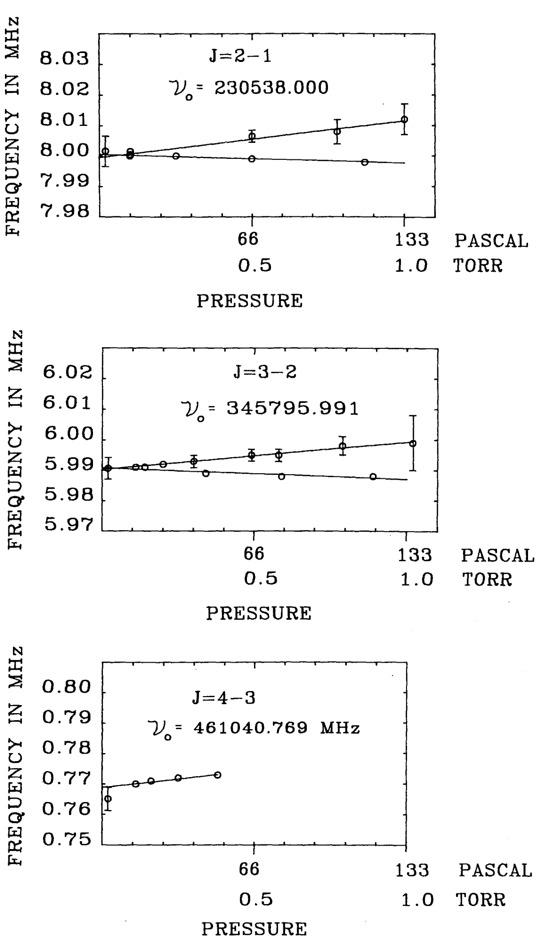

FIG. 1.—Plots of the pressure shift of CO rotational transitions. The upper plots (positive slope) for the $J = 2 \leftarrow 1$ and $J = 3 \leftarrow 2$ transitions are the shift function when CO_2 is added, while the lower line (negative slope) is obtained for the pure CO sample. The points with the large error bars near zero pressure are the data from Winnewisser et al. (1984). See text for discussion and Table 1 for the derived values.

and l is the length of the radiation path through the absorption cell. In order to estimate the uncertainty in S we must take the first derivative with respect to the two variables, γ and P. By substituting the expression for γ into equation (4) and letting $x = (\nu - \nu_0)/\Delta\nu$ and taking the derivative with respect to x we obtain

$$S' = \kappa\gamma_0 l \frac{1}{1+x^2}\left(P'_x - \frac{2x}{1+x^2}\right). \tag{6}$$

At the maximum and minimum values of the expression, $S' = 0$, so

$$P'_x - P\frac{2x}{1+x^2} = 0 ,$$

from which we can obtain the final expression for $\delta_{\rm VSWR}$

$$\delta_{\rm VSWR} \to \nu - \nu_0 = \frac{(\Delta\nu)^2}{2}\frac{P'_\nu}{P} .$$

Experimentally we find that P'_ν/P is different for each BWO and it changes slightly during the course of the scan, however, in the worst case it is $\leq 10^{-3}$ MHz^{-1}. This leads to values of $\delta_{\rm VSWR}$ which are ~ 500 Hz at 26.7 Pa (0.2 torr) to values of $\simeq 8$–12 kHz in the pressure region of 133.3 Pa (1 torr). As previously mentioned, because of the sinusoidal nature of this effect, one can usually extrapolate to a value in the middle of the range of variation, which in actuality leads to a much smaller uncertainty. The total estimated uncertainty in the measurements is reduced further by making the measurements at a number of different pressures below 133.3 Pa (1 torr) and extrapolating to zero pressure using a linear least-squares fit of the data.

Summarizing the results and adding up all the uncertainties described above we obtain

$$\delta\nu_{\rm tot} = \delta\nu_{\rm lw} + \delta\nu_c + \delta\nu_{\rm mod} + \delta\nu_{\rm VSWR} \tag{9}$$

and by substitution of the values obtained as described above one arrives at $\delta\nu_{\rm tot} \leq \sim 2$ kHz for pressures in the range of 13.3–40 Pa (0.1–0.3 torr) for the frequency measurements presented here.

Figure 1 shows the results of the line frequency measurements of CO, recorded as a function of pressure for the $J = 2 \leftarrow 1$, $J = 3 \leftarrow 2$, and $J = 4 \leftarrow 3$ transitions. The data were least-squares fitted to determine the intercept (zero-pressure line frequency). The points near zero pressure with larger error bars (~ 3–5 kHz) are from the data of Winnewisser et al. (1984). These points were not included in the least-squares analysis but are shown to indicate that at least for the $J = 2 \leftarrow 1$ and $J = 3 \leftarrow 2$ transitions, the measurements are in close agreement with the measurements recorded here. The slope of the line determines the pressure shift. The data for self-shift (CO–CO) are straightforward. The shift with added CO_2 is more complex and must be corrected for the concentration factor. In addition, the adjustment for the CO–CO shift must be subtracted in order to obtain the shift for adding CO_2. The pressure shift for added CO_2 was not determined for the $J = 4 \leftarrow 3$ transition. From the least-squares fits one can obtain a more precise value of the frequency than previously existed. The results of these fits are given in Table 1. The correction for the CO–CO frequency shift is quite small in all cases, causing a variation of ~ 7.5 kHz mPa^{-1} (~ 1 kHz torr^{-1}) in the measurements. The slight negative slopes for the $J = 2 \leftarrow 1$ and $J = 3 \leftarrow 2$ transitions may be due in part (or entirely) to the effect described by $\delta\nu_{\rm VSWR}$. At present there is no way to deconvolve this effect from the true self-shift. In any case, the important point is that the numbers are quite small, being ≤ -15 kHz mPa^{-1} (≤ -2 kHz torr^{-1}) for the $J = 2 \leftarrow 1$ transition and ≤ -28 kHz mPa^{-1} (≤ -3.8 kHz torr^{-1}) for the $J = 3 \leftarrow 2$ transition). In Table 1, values for the CO_2 shifts are shown for both cases, i.e., shifts of 0 and -15 kHz mPa^{-1} (0 and -2 kHz torr^{-1}) and 0 and -28 kHz mPa^{-1} (0 and -3.8 kHz torr^{-1}) for the $J = 2 \leftarrow 1$ and $J = 3 \leftarrow 2$ transitions, respectively. The variation in the CO_2 pressure shift values, regardless of the CO self-shift values chosen, is quite small ranging from 82 to 97 kHz mPa^{-1} (11–13 kHz torr^{-1}). The absolute values are also smaller than the

TABLE 1

PRESSURE SHIFT AND LINE-BROADENING PARAMETERS FOR CO

$J' \leftarrow J''$	ν_0 (MHz)	CO Shift[a] (kHz mPa^{-1}) [kHz torr^{-1}]	CO_2 Shift[a] (kHz mPa^{-1}) [kHz torr^{-1}]	CO-Broadening[a] (MHz mPa^{-1}) [MHz torr^{-1}]	CO_2-Broadening[a] (MHz mPa^{-1}) [MHz torr^{-1}]
$2 \leftarrow 1$..............	230538.000 (1)[b]	0 to 5	+90 (15)[c]	30.0 (15)	33.7 (15)
		[0 to 2]	[+12 (2)]	[4.0 (2)]	[4.5 (2)]
		0[d]	+98 (15)		
		[0]	[+13 (2)]		
		−15[e]	+98 (15)		
		[−2]	[+13 (2)]		
$3 \leftarrow 2$..............	345795.991 (1)	0 to −28.5	+68 (15)[f]	30.0 (15)	34.5 (15)
		[0 to −3.8]	[+9 (2)]	[4.0 (2)]	[4.6 (2)]
		0[d]	+82.5 (75)		
		[0]	[+11 (1)]		
		−28.5[e]	97.5 (75)		
		[−3.8]	[+13 (1)]		
$4 \leftarrow 3$..............	461040.769 (2)				

[a] Shift and broadening parameters are given in both kHz mPa^{-1} and [kHz torr^{-1}] and MHz Pa^{-1} and [MHz torr^{-1}] units, respectively.

[b] The numbers in parentheses are the uncertainties associated with each measurement.

[c] Raw data from the graph in Fig. 1, using a mixture of 10% CO in CO_2.

[d] If the self-shift is assumed to be zero, then the CO_2 shift is calculated after correcting for the concentration effect.

[e] If the self-shift is assumed to be this value, then the CO_2 shift is calculated after correcting for the concentration effect.

[f] Raw data from the graph in Fig. 1, using a mixture of 20% CO in CO_2.

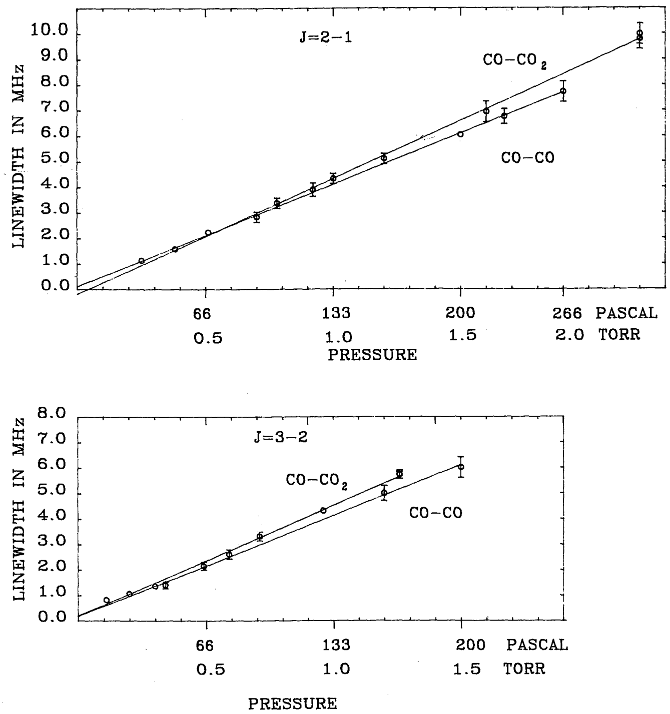

FIG. 2.—Plots of the line width vs. pressure for the $J = 2 \leftarrow 1$ and $J = 3 \leftarrow 2$ transitions of CO. Note both slopes are similar with the CO_2 plots showing slightly larger slopes.

predicted value of $\sim$0.75 kHz Pa^{-1} ($\sim$100 kHz $torr^{-1}$) as predicted by theory (Hillman 1990).

The pressure-broadening behavior for the $J = 2 \leftarrow 1$ and $J = 3 \leftarrow 2$ transitions of CO is shown in Figure 2, where the line width, $\Delta\nu$, is plotted as a function of pressure for both pure CO and for the CO–CO_2 mixtures. The results of least-squares fitting of these data are also given in Table 1. The pressure broadening for pure CO is slightly smaller than 30 MHz mPa^{-1} (4.0 MHz $torr^{-1}$) compared with the experiments when CO_2 is added where the value is 34.5–35.25 MHz mPa^{-1} (4.6–4.7 MHz $torr^{-1}$). For the plot of the $J = 2 \leftarrow 1$ data, the two slopes do not extrapolate to the same zero pressure value. This is most likely due to small differences in the pressure measurements of the two samples when they were prepared. In any respect, the effect is minimal and does not affect the results.

3. SUMMARY

Frequency measurements, pressure shift, and pressure-broadening measurements have been made for the $J = 2 \leftarrow 1$ and the $J = 3 \leftarrow 2$ rotational transitions of CO. These results have lowered the rest frequency uncertainties of these transitions by at least a factor of 3 over the previous literature values of Winnewisser et al. (1984). Since only three transitions have been measured in this work, no new rotational analysis was attempted; however, Varberg & Evenson (1991) have recently carried out precise frequency measurements of CO transitions with J'' ranging from 5 to 37 using a tunable far-infrared spectrometer. They have incorporated the measurements reported in this paper into their least-squares fit of rotational transitions. The observed – calculated values for the three transitions measured here are $\sim$1 kHz which is the same as the estimated uncertainties in our measurements. These improved frequency measurements along with the careful pressure shift and preassure-broadening measurements decrease the overall uncertainty associated with the Venusian wind velocity measurements by at least one order of magnitude. The measurements reported here for the $J = 4 \leftarrow 3$ rotational transition of CO should be regarded as preliminary especially since the agreement with the previous measurement of Winnewisser et al. (1984) is not as good as for the $J = 3 \leftarrow 2$ and $J = 2 \leftarrow 1$ transitions. This as well as other frequency measurements for rotational transitions higher up the energy ladder will be reported in a later paper.

The authors are deeply indebted to A. F. Krupnov for many stimulating conversations during the course of this work. One of us, R. D. S., thanks A. F. Krupnov and the members of his research group at the Applied Physics Institute for their generous hospitality extended to me during my stay in Nizhny Novgorod. In particular I wish to thank Eugene Karyakin for assisting me with travel while in Russia and Oleg Polyansky for acting as interpreter on many occasions.

We also thank Tom Varberg of NIST in Boulder, CO, for reading the manuscript prior to publication and offering a number of useful suggestions.

REFERENCES

Buhl, D., Chin, G., & Goldstein, J. J. 1991, ApJ, 369, L17
Hillman, J. J. 1990, private communication
Krupnov, A. F. 1979, in Modern Aspects of Microwave Spectroscopy, ed. G. W. Chantry (London: Academic), 217
Lovas, F. J. 1985, J. Phys. Chem. Ref. Data, 15, 251
Varberg, T. D., & Evenson, K. M. 1992, ApJ, 385, 763
Winnewisser, M., Winnewisser, B. P., & Winnewisser, G. 1984, in Molecular Astrophysics; State of the Art and Future Directions, 375