

Detection of Vibration–Rotational Band 5–0 of $^{12}\text{C}^{16}\text{O X } ^1\Sigma^+$ with Cavity Ringdown Absorption near $0.96 \mu\text{m}$

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We have recorded extremely weak absorption in the overtone band 5–0 of $^{12}\text{C}^{16}\text{O X } ^1\Sigma^+$ near $0.96 \mu\text{m}$ with cavity ringdown spectroscopy; the light source was a Raman-shifted dye laser pumped with a frequency-doubled Nd:YAG laser. This band shows lines in branch P to be much more intense than corresponding lines in branch R, in contrast to all lower overtone bands $\nu=0$ ($\nu = 1-4$). This reversal in relative intensity is explained quantitatively in terms of a radial function for the electric dipolar moment of CO. We have estimated absorption line strengths for P_3-P_{18} in band 5–0 of $^{12}\text{C}^{16}\text{O}$; these strengths are consistent with a pure vibrational matrix element $\langle 5|p(x)|0\rangle = (3.6 \pm 0.3) \times 10^{-36} \text{ C m}$ of the electric dipolar moment $p(x)$, a Herman–Wallis coefficient C_0^5 of about -0.1 , and a band strength of $(5.1 \pm 1.3) \times 10^{-29} \text{ m}$ at 293 K.

Introduction

Carbon monoxide CO plays an important role in the combustion of carbonaceous fuels and chemical and physical processes in the terrestrial atmosphere and has been detected through its spectral lines for pure rotational transitions in many extraterrestrial environments. The fundamental vibration–rotational band of CO in the mid-infrared region was the first spectral feature of a gaseous sample of a diatomic molecular substance to be measured in this region,¹ and subsequent measurements exploited a progressively increasing spectral resolution and accuracy. Overtone spectra of CO exhibit progressively decreasing strengths of bands. In our previous investigation,² we sought to observe also the fourth overtone band, $\nu = 5 - \nu = 0$ (designated 5–0) in terms of vibrational quantum number ν , but discerned no signal at predicted wavenumbers; an earlier search³ with product of length of absorbing path and pressure equal to 3000 mbar was equally unsuccessful. In the present work, we adapted a cavity ringdown spectral technique⁴ to the near-infrared region and have achieved detection and measurement of this band for the first time.

The radial function for the electric dipolar moment of CO in the electronic ground state has been investigated theoretically for many years.^{5–18} An initial discord about the absolute sign of the electric dipolar moment of CO between experimental results reported by Rosenblum et al.⁵ and calculations of molecular electronic structure was settled by Muentner.⁹ Chack-

erian¹⁰ predicted that, in the band 5–0 of CO, branch P is likely to be enhanced relative to branch R, whereas the opposite effect is observed in lower overtone bands. Chackerian and Tipping¹³ estimated Herman–Wallis coefficients¹⁴ of band 5–0 of CO that predicted the intensity of branch P of the fourth overtone to be more intense than that of branch R. Recently, Coxon and Hajigeorgiou¹⁸ reported an analysis of the frequency data of CO in its electronic ground state and indicated a preference for the dipolar moment function of CO by Kirschner et al.¹² over that given by Ogilvie et al.² A direct measurement of the absorption spectrum of CO in band 5–0 with cavity ringdown technique is thus useful both to verify predictions about the relative intensities of the P and R bands and to provide information that serves to extend the delineation of a function for the electric dipolar moment on an experimental basis.

Experiments

For spectra based on cavity ringdown absorption one relies on measurement of the decay of intensity of a light pulse trapped in an optical cavity formed between two highly reflective mirrors. The small proportion of light transmitted into the cavity through an entrance mirror is trapped during some temporal period as it is reflected back and forth; the intensity decays slowly because of finite losses of the cavity, due primarily to transmission of the mirrors. We monitor this process with a detector via a minute proportion of light transmitted through the exit mirror at each reflection. The envelope of decay is exponential because a constant fraction of intensity of a pulse is lost at each pass across the cavity. When the cavity contains

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an absorbing sample, which for these experiments is CO, the ringdown period is decreased at those wavenumbers at which absorption occurs; the effective length of the optical path is likewise decreased. The pertinent quantity is hence the absorption αl of a sample per pass through the cavity, in which $\alpha = \sigma N$ is the absorption coefficient and l is the length of the cell, σ is the cross section for absorption and N is the number density of absorbing molecules. In this equation

$$I = I_0 e^{-c(1-R+\alpha)l} \quad (1)$$

c is the velocity of light, t is time, R is the reflection coefficient of the mirror, and I_0 and I are the intensities of incident and transmitted light, respectively. The ringdown period τ is defined as the interval required for the intensity to decay to $1/e$ of its initial value. When there is no absorption, as in the absence of a sample so that $\alpha = 0$, the ringdown period of an empty cavity is

$$\tau = l/[c(1 - R)] \quad (2)$$

whereas in the presence of an absorbing species the ringdown period becomes

$$\tau' = l/[c(1 - R + \alpha)] \quad (3)$$

For mirrors with reflection coefficient $R \approx 0.9999$, the pulse undergoes about 5000 round trips before its intensity decays to $1/e$ of its initial value, resulting in a ringdown period about 30 μ s for a length of 0.90 m for our cavity. The total length of the optical path is thus about 9000 m at the ringdown period with no absorbing species in the cell. The absorption coefficient α is hence simply related to the cavity ringdown periods with

$$\alpha = \left(\frac{1}{\tau'} - \frac{1}{\tau}\right) \frac{1}{c} \quad (4)$$

Substituting τ' with $\tau - \Delta\tau$ and assuming $\Delta\tau$ is small, the minimum detectable value of α , α_{\min} , may be estimated as

$$\alpha_{\min} = \frac{\Delta\tau}{\tau^2} \frac{1}{c} \quad (5)$$

In our optical arrangement for cavity ringdown spectroscopy, we generated laser radiation in the near-infrared region, $\approx 0.96 \mu\text{m}$, with a single-pass Raman shifter employing gaseous H_2 at about 15 bar pumped with a dye laser (Spectra Physics, PDL-3, with Exciton dye LDS 698) and in turn pumped with a Nd:YAG laser (Spectra Physics, Lab 170, 30 Hz); output of this laser in the near-infrared region is about 1 mJ per pulse. The limiting spectral resolution of this laser system is about 0.1 cm^{-1} . Because the widths of lines of CO exceed 0.5 cm^{-1} due mostly to collisional broadening at the pressure required for this experiment, we scanned the wavenumber range in steps 0.01 nm (approximately 0.1 cm^{-1}), limiting the effective resolution accordingly. We calibrated the wavelength of the dye laser with a wavemeter (Burleigh, model 4500); lines of atmospheric water vapor absorption also served to calibrate the wavelength of radiation from the Raman shifter according to the HITRAN database.¹⁹ The accuracies of our measurements of wavelength are $\pm 0.012 \text{ nm}$.

The ringdown signal was recorded with a HgCdTe detector (Kolmar) cooled at 77 K. The signal was connected to a digital computer oscilloscope (14 bits, Gage Applied Technologies, Compuscope 14100) and then processed with a program for

data acquisition. Each data point at one wavelength is averaged typically over 120 laser pulses.

The path length between the mirrors (Los Gatos Research) is 0.90 m. The fractional loss R' (per pass)

$$R' = 1 - R + \alpha l = l/c\tau' \quad (6)$$

was determined from the ringdown time τ' . The fractional absorption (αl) of CO is thus the difference in fractional loss between a cavity filled with CO and an empty cavity. The fractional loss R' of an empty cavity ($\alpha = 0$) is shown in Figure 1A; the reflectivity of the mirrors was thus determined to be 0.999870–0.999857 in the spectral range of 10330–10500 cm^{-1} . On the basis of the reflectivity of the mirrors and the accuracy in ringdown time of 0.1–0.2 μ s, we estimate a minimal detectable absorption coefficient of our ringdown system to be $(0.6\text{--}1.5) \times 10^{-6} \text{ m}^{-1}$ according to eq 5.

In the region of this band of CO, water vapor has significant absorption lines of $2\nu_1 + \nu_3$; we thus exercised particular care to minimize the presence of water vapor within the optical path. We transferred gaseous CO (Matheson, nominal purity 99.9%) to a steel cylinder of 1 L cooled with liquid N_2 ; retaining the cylinder at 180 K, we passed gaseous CO through a U-tube containing P_2O_5 into the optical cell. To attempt to eliminate water vapor, we baked the cell at 358 K under evacuation for 48 h before use. Using the line strengths of H_2O in the HITRAN database,¹⁹ 3.53 and $2.2 \times 10^{-24} \text{ m}$ for lines 10498.78 and 10475.00 cm^{-1} , respectively, we estimated that the concentration of H_2O in our sample of CO at 3.5 bar was at most 0.2 ppm ($1 \text{ ppm} = 10^{-6}$).

Theoretical Basis

For absorption by a diatomic molecular species in electronic state $X \ ^1\Sigma^+$ in a gaseous sample at temperature T , the strength S_1 of a line attributed to a spectral transition from a state $|0, J''\rangle$ to another state $|v', J'\rangle$ in a vibration–rotational spectrum is represented by²⁰

$$S_1 = \frac{8\pi^3}{3hc} \left[\frac{\exp\left(-\frac{hcE_{0,J''}}{k_B T}\right)}{4\pi\epsilon_0 Q} \right] \tilde{\nu}_0 \left[1 - \exp\left(-\frac{hc\tilde{\nu}_0}{k_B T}\right) \right] \times |\langle v', J' | p(x) | 0, J'' \rangle|^2 \quad (7)$$

with fundamental physical constants h , c , k_B , and ϵ_0 , total partition function Q , spectral term $E_{0,J''}$ of the initial state $|0, J''\rangle$ of a transition relative to $E_{0,0}$, and wavenumber $\tilde{\nu}_0$ of the transition; $\iota \equiv 1/2[J'(J'+1) - J''(J''+1)]$ is a running number of the value $J''+1$ for a line in branch R or $-J''$ for a line in branch P. In $|\langle v', J' | p(x) | 0, J'' \rangle|^2$, that is a square of an experimental matrix element for a transition between specified states, $p(x)$ is a radial function for the electric dipolar moment of an absorbing molecular species in terms of reduced displacement $x = (R - R_e)/R_e$ with internuclear distances instantaneous R and equilibrium R_e . The rotational dependence is factorable by²⁰

$$\langle v', J' | p(x) | 0, J'' \rangle^2 = \langle v' | p(x) | 0 \rangle^2 (1 + C_0 \iota + D_0 \iota^2) \quad (8)$$

in which $\langle v' | p(x) | 0 \rangle^2$ is the square of the pure vibrational matrix element of electric dipolar moment; the latter quantity is coefficient to a Herman–Wallis factor containing coefficients $C_0 \iota'$ and $D_0 \iota'^2$.^{14,20} The Herman–Wallis factor describes the influence of vibration–rotational interaction on line strengths within a vibration–rotational band.^{14,20} Even though the strengths of lines and bands are proportional to squares of matrix elements,

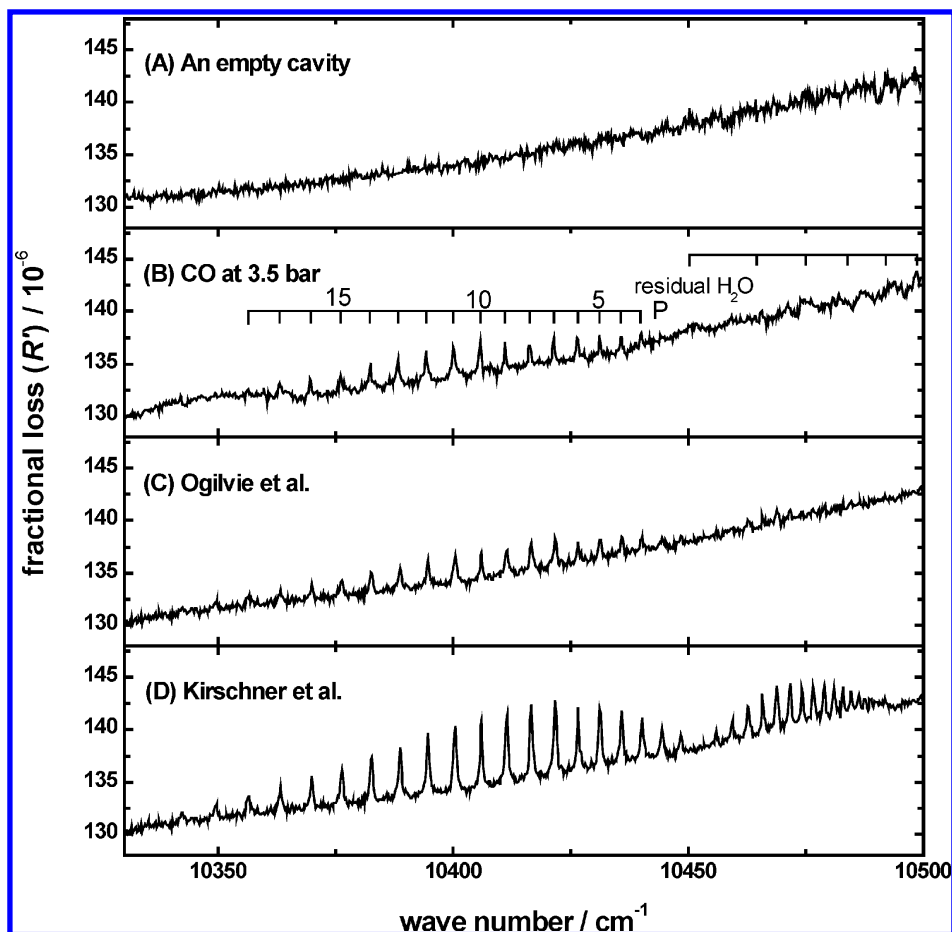


Figure 1. Fractional loss R' of an empty cavity (A) and of CO at 3.5 bar (B) in the spectral region 10330–10500 cm^{-1} observed in a cavity ringdown experiment. Spectra simulated with functions for electric dipolar moment by Ogilvie et al. (C) and Kirschner et al. (D) are compared; the mirror reflectivity and a random noise of 0.2×10^{-6} are incorporated in the simulation.

because coefficients $C_0^{v'}$ and $D_0^{v'}$ are linearly proportional to coefficients p_j in an expansion of $p(x)$, one might apply this information to deduce the sign of $\langle v'|p(x)|0\rangle$ with the present experiment $v' = 5$.

An experimental measure of a band strength S_b is a sum of measured strengths S_1 of all lines in that band

$$S_b = \sum S_1 \quad (9)$$

whereas a theoretical measure is proportional to the pure vibrational matrix element of electric dipolar moment

$$S_b = \frac{8\pi^3 \tilde{\nu}_c |\langle v'|p(x)|0\rangle|^2}{3hc4\pi\epsilon_0} \quad (10)$$

in which $\tilde{\nu}_c$ is the wavenumber characterizing the origin of the band. A line strength is derived from the integrated absorbance of a particular spectral line, a known number density N of molecules per unit volume in a gaseous sample at temperature T , and the effective length l of an optical path,

$$S_1 = \frac{1}{Nl} \int \ln \left(\frac{I_0(\tilde{\nu})}{I(\tilde{\nu})} \right) d\tilde{\nu} = \int \sigma d\tilde{\nu} \quad (11)$$

Of two forms to represent the dependence of electric dipolar moment $p(x)$ as a function of the reduced displacement variable x , one is a simple polynomial of an order sufficient for a particular purpose²⁰

$$p(x) = \sum_{j=0} p_j x^j \quad (12)$$

Another form is a Pade function^{13,20} that is a ratio of polynomials such that successive derivatives with respect to x , apart from factorial factors, agree exactly with as many coefficients p_j in eq 12 as can be evaluated from available data,

$$p(x) = \frac{q_0(1 + q_1x + q_2x^2)}{1 + q_3x + q_4x^2 + q_5x^3 + C_\infty x^6} \quad (13)$$

in which $q_0 = p_0$ and other q_j values are accordingly fitted from various p_j values. A rational function thus constructed has a qualitatively appropriate form throughout a large range of molecular existence; although it appears well behaved beyond the range of internuclear distance to which experimental data pertain, unlike a mere polynomial form, it is quantitatively unreliable beyond that defined range, like any other formula that might be employed for the purpose of extrapolation. Nevertheless, because such a rational formula has a realistic form, it might serve as a tentative basis for modest extrapolation, unlike a polynomial form that might diverge rapidly outside a region for which its parameters reflect experimental data.

Results

In Figure 1, trace B presents a spectrum measured between 10330 and 10500 cm^{-1} (952–968 nm) for a sample of CO at 3.5 bar and 293 K; this spectrum shows also a few weak lines due to residual water vapor within the optical path. We detected

TABLE 1: Wavenumbers Predicted and Measured, Height, Width, and Strengths of Lines Measured and Calculated in Branch P of Band 5–0 of CO at 293 K

J''	$\tilde{\nu}/\text{cm}^{-1}$		height/ 10^{-6}	$S_l/10^{-30}$ m		
	predicted	measured		width/ cm^{-1}	observed	calculated
1	10448.378					0.39
2	10444.358					0.87
3	10440.163	10439.90	1.31	0.56	1.43	1.41
4	10435.794	10435.60	1.57	0.47	1.44	1.96
5	10431.251	10431.15	2.07	0.49	1.99	2.47
6	10426.533	10426.44	2.05	0.86	3.25	2.91
7	10421.641	10421.41	2.30	0.57	2.43	3.25
8	10416.575	10416.28	2.10	0.67	2.74	3.46
9	10411.335	10411.01	2.69	0.46	2.44	3.53
10	10405.922	10405.60	2.76	0.65	3.37	3.48
11	10400.335	10399.98	2.79	0.81	4.27	3.32
12	10394.574	10394.19	2.67	0.72	3.76	3.06
13	10388.641	10388.20	2.12	0.82	3.38	2.75
14	10382.534	10382.28	2.28	0.86	3.68	2.4
15	10376.254	10375.99	1.34	0.70	1.75	2.04
16	10369.802	10369.57	1.75	0.52	1.78	1.69
17	10363.177	10362.95	1.34	0.65	1.66	1.36
18	10356.379	10356.32	0.64	0.64	0.78	1.07

and estimated strengths of lines P_3 – P_{18} in branch P of band 5–0 of $^{12}\text{C}^{16}\text{O}$; because of decreased reflectivity of mirrors, and consequently decreased ratio of signal-to-noise, signals at expected wavenumbers of the lines of CO in the region of branch R are doubtful. Fits of wavenumber, height (the net maximum absorbance relative to an interpolated baseline), width, and area of individual lines in the spectrum in trace B of Figure 1 yielded the results presented in Table 1. No signal was clearly discernible for the first two lines P_1 and P_2 in branch P. Although the spectrum might appear to indicate an envelope for branch R, no feature is distinct with a satisfactory ratio of signal-to-noise; some features identifiable in the same region are due to residual water vapor. Although lines of water vapor occur also in the region of branch P, their intensities under our conditions of measurement were much smaller than those due to CO at the positions of the latter lines. The area, equal to the integral in eq 11, of each line from a fit according to a Lorentzian profile was converted to a line strength, listed as S_l observed in Table 1.

The almost exact agreement between the wavenumber of every observed line in an evident series and a corresponding calculated wavenumber for $^{12}\text{C}^{16}\text{O}$ for a particular band proves unambiguously the carrier of this spectrum. A few lines measured at wavenumbers greater than 10450 cm^{-1} correlate exactly with known features of water vapor;¹⁹ other weak features in the same region might correlate with the lines of CO expected in branch R, but, as these measurements are unreliable, we omit them from further consideration. The mean uncertainty of the fitted measurement of a wavenumber of each line of CO is $(1.11 \pm 0.33) \times 10^{-2}\text{ cm}^{-1}$, but because the precision of calibration is $\approx 0.12\text{ cm}^{-1}$, we specify a wavenumber of $\pm 0.12\text{ cm}^{-1}$. The height of each line has a mean uncertainty of 0.03×10^{-6} . The apparent mean uncertainty of most measurements of width is $(3.8 \pm 1.1) \times 10^{-2}\text{ cm}^{-1}$ apart from the weakest lines that are severely distorted by noise. The software used to fit these lines provides no uncertainty associated with an integrated area under a particular spectral line, but the minimum uncertainty of a line strength is likely 15% of a listed value or 0.4×10^{-30} m, whichever is greater. We converted each strength S_l of a vibration–rotational line in branch P to a square of a vibration–rotational matrix element of electric dipolar moment according to eq 7. Mostly because of the lack of observed values of strengths for lines in branch R but also

because of rough values for branch P reflecting a small ratio of signal-to-noise, an attempt to plot these squared matrix elements versus ι according to eq 8 yielded insignificant values of all parameters. We therefore calculated a spectrum according to eqs 7 and 8, with $\langle 5|p(x)|0\rangle = 3.6 \times 10^{-36}\text{ C m}$ and $C_0^5 = -0.1$ that produces a sum-of-line strengths the same as measured; the corresponding values appear in Table 1 as S_l calculated. Comparison between observed and calculated values of line strengths indicates a relative precision of about 25% for the pure vibrational matrix element and thereby a band strength of $(5.1 \pm 1.3) \times 10^{-29}$ m at 293 K according to eq 10. Under our conditions of measurement of this spectrum, with its modest ratio of signal-to-noise, we are unable to derive more precise values of either line strengths or Herman–Wallis coefficients C_0^5 and D_0^5 .

Discussion

According to Table 1, measured line positions of transitions in branch P of band 5–0 of $^{12}\text{C}^{16}\text{O}$ are systematically smaller by $(0.25 \pm 0.10)\text{ cm}^{-1}$ than predicted values, which are known accurately to about $5 \times 10^{-3}\text{ cm}^{-1}$.² Collisional effects in the gaseous sample at a pressure of 3.5 bar partly contribute to this difference. The mean pressure shift of $(0.0065 \pm 0.0007)\text{ cm}^{-1}\text{ bar}^{-1}$ for lines in band 4–0 is small,² but a larger shift for band 5–0 is possible. The mean width of lines in the present branch P is $(0.65 \pm 0.13)\text{ cm}^{-1}$, with no evident trend of narrowing with increasing value of J'' ; this value partly reflects the limited spectral resolution of the experiment but is mainly influenced by collisional broadening. The extent of such broadening of lines in band 4–0 of $^{12}\text{C}^{16}\text{O}$ is about $0.15\text{ cm}^{-1}\text{ bar}^{-1}$,² which would correspond analogously to widths of about 0.52 cm^{-1} for the 5–0 transition.

As an indication of an expected strength of this band 5–0 of $^{12}\text{C}^{16}\text{O}$, one can predict the value of the pure vibrational matrix element of electric dipolar moment through use of a rational function,²⁰ as in eq 13, based on data of measured transitions or calculations of molecular electronic structure. Chackerian and Tipping¹³ integrated numerically their rational function and fitted calculated line strengths to yield values $\langle 5|p(x)|0\rangle = 6.588 \times 10^{-36}\text{ C m}$, $C_0^5 = -0.0529$, and $D_0^5 = 0.00040$; the former value implies a band strength $S_b = 1.70 \times 10^{-28}$ m that might rationalize the failure of Herzberg and Rao to detect this band in their experiments.³ The intensity of a line in branch P of band 5–0 is hence predicted to be enhanced with respect to a corresponding line for a transition in branch R originating in the same vibration–rotational state $|0, J''\rangle$, as we observe, in contrast to other measured vibration–rotational bands originating in $\nu = 0$.²

As an independent test of two functions for electric dipolar moment, one from Kirschner et al.¹² and another from Ogilvie et al.,² we employed program RKR1 2.0 (ref 21) to construct a potential curve of CO and program LEVEL 7.5 (ref 22) to obtain the vibration–rotational matrix elements for band 5–0 of CO by extrapolation. The fractional loss R' predicted with these two functions are presented as traces C (Ogilvie et al.) and D (Kirschner et al.) of Figure 1; the mirror reflectivity and a random noise of 0.2×10^{-6} are also included in the simulation. The simulated spectrum with the function for dipolar moment from Ogilvie et al.² evidently conforms closely to our direct experimental measurements because its maximum fractional absorption of CO is about 2.8×10^{-6} in branch P, rather than 7×10^{-6} corresponding to the function of Kirschner et al.¹² As the predicted maximum fractional absorption of CO is less than

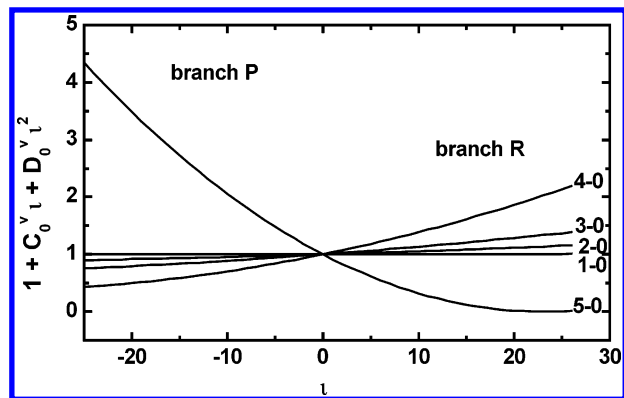


Figure 2. Calculated Herman–Wallis factors for bands $v'' = 0$, $v = 1-5$.

TABLE 2: Band Origin, Pure Vibrational Matrix Element, and Strength of Vibration–Rotational Bands of $^{12}\text{C}^{16}\text{O}$

band	origin/cm $^{-1}$	$\langle v' p(x) 0\rangle/\text{C m}$	S_b/m
0–0	0	3.6632×10^{-31} ^a	
1–0	2143.2711	-3.53×10^{-31} ^b	1.00×10^{-19}
2–0	4260.0622	2.22×10^{-32} ^b	7.83×10^{-22}
3–0	6350.4391	-1.36×10^{-33} ^b	4.42×10^{-24}
4–0	8414.4693	6.95×10^{-35} ^b	1.53×10^{-26}
5–0	10452.2222	3.6×10^{-36} ^c	5.1×10^{-29}

^a Reference 9. ^b Reference 2. ^c Present work.

1×10^{-6} for lines in branch R of band 5–0 (trace C of Figure 1), this is just less than our detectability of 1.4×10^{-6} in this region.

For calculations of Herman–Wallis factors of CO in various vibration–rotational transitions, we employed program LEVEL 7.5 (ref 22) with the function for the dipolar moment from Ogilvie et al.,² the results appear in Figure 2. In contrast to lower overtones, the Herman–Wallis factor of band 5–0 of CO clearly indicates, through a negative value of C_0^5 , the intensity of lines in branch P to be greater than that of the corresponding lines of branch R. Several factors are responsible for such a condition, including the mutual interactions between higher-order terms of mechanical and electrical anharmonicities. In general, according to ref 20, once the sign of $C_0^{v'}$ becomes negative, the intensity of branch P becomes more intense than that of branch R, after taking into account frequency factors. Such an intensity alteration of branches P and R occurs also for other molecules, such as HCl and HBr.²³

Table 2 presents a summary of reported data² pertaining to intensities of vibration–rotational transitions of $^{12}\text{C}^{16}\text{O}$ from its vibrational ground state, for comparison with an expectation value $\langle 0|p(x)|0\rangle$ for the vibrational ground state⁹ and the present result for band 5–0. The ratios of band strengths between successive overtones are thus 128, 177, 289, and 301, in contrast with the corresponding ratios for NO,²⁴ which are 65.2, 48.1, 22.1, 13.4, and 8.6. Despite this contrast, functions for the electric dipolar moment of CO and NO share a common form incorporating two significant extrema and only small values of their permanent dipolar moments, represented by p_0 . Moreover, the sign of p_0 , corresponding to $^-\text{CO}^+$ or $^-\text{NO}^+$ contradicts in each case an expectation according to conventional atomic electronegativities.

On the basis of these pure vibrational matrix elements, we deduce a radial function^{2,20} for electric dipolar moment in this polynomial form according to eq 12 as follows,

$$p(x)/10^{-30} \text{ C m} = 0.407871 - 11.8633x + 1.3064x^2 + 13.369x^3 - 2.826x^4 + 0.17x^5 \quad (14)$$

for which the uncertainty of p_5 (0.17) propagated from the value of $\langle 5|p(x)|0\rangle$ is 1.2; this function has a range $R/10^{-10}$ m of validity [0.99, 1.33]. Apart from an additional term resulting from a further vibrational matrix element, this function differs only slightly from that in our preceding report.² The small magnitude of the coefficient of x^5 reflects the small magnitude of $\langle 5|p(x)|0\rangle$; as this coefficient is zero within experimental error, our new data for line strengths fail to provide a significant extension of $p(x)$ from previous work.²

Conclusion

Detecting the vibration–rotational band 5–0 of $^{12}\text{C}^{16}\text{O}$ with cavity ringdown spectroscopy for the first time, we obtained estimates of the band strength, $(5.1 \pm 1.3) \times 10^{-29}$ m at 293 K, and the pure vibrational matrix element of electric dipolar moment, $\langle 5|p(x)|0\rangle = (3.6 \pm 0.3) \times 10^{-36}$ C m. Branch P is observed to be enhanced over branch R as previously predicted.

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References and Notes

- Angstrom, K. *Ofvers. Kongl. Vet. Akad. Forh. Stockholm* **1889**, *46*, 203.
- Ogilvie, J. F.; Cheah, S.-L.; Lee, Y.-P.; Sauer, S. P. A. *Theor. Chem. Acc.* **2002**, *108*, 85.
- Herzberg, G.; Rao, K. N. *J. Chem. Phys.* **1949**, *17*, 1099.
- Busch, K. W.; Busch, M. A. *Cavity-Ringdown Spectroscopy – An UltraTrace-Absorption Measurement Technique*; American Chemical Society: Washington, DC, 1999.
- Rosenblum, B.; Nethercot, A. H., Jr.; Townes, C. H. *Phys. Rev.* **1958**, *109*, 400.
- Toth, R. A.; Hunt, R. H.; Plyler, E. K. *J. Mol. Spectrosc.* **1969**, *23*, 74.
- Toth, R. A.; Hunt, R. H.; Plyler, E. K. *J. Mol. Spectrosc.* **1969**, *32*, 85.
- Billingsley, F. P.; Krauss, M. *J. Chem. Phys.* **1974**, *60*, 4130.
- Muenter, J. S. *J. Mol. Spectrosc.* **1975**, *55*, 490.
- Chackerian, C., Jr. *J. Chem. Phys.* **1976**, *65*, 4228.
- Kirby-Docken, K.; Liu, B. *J. Chem. Phys.* **1977**, *66*, 4309.
- Kirschner, S. M.; Le Roy, R. J.; Ogilvie, J. F.; Tipping, R. H. *J. Mol. Spectrosc.* **1977**, *65*, 306.
- Chackerian, C. Jr.; Tipping, R. H. *J. Mol. Spectrosc.* **1983**, *99*, 431.
- Herman, R.; Wallis, R. F. *J. Chem. Phys.* **1955**, *23*, 637.
- Chackerian, C., Jr.; Farrenq, R.; Guelachvili, G.; Rossetti, C.; Urban, W. *Can. J. Phys.* **1984**, *62*, 1579.
- Langhoff, S. R.; Bauschlicher, C. W., Jr. *J. Chem. Phys.* **1995**, *102*, 5220.
- Bouanich, J.-P. *J. Quant. Spectrosc. Radiat. Transfer* **2001**, *69*, 1.
- Coxon, J. A.; Hajigeorgiou, P. G. *J. Chem. Phys.* **2004**, *121*, 2992.
- Rothman, L. S.; Rinsland, C. P.; Goldman, A.; Massie, S. T.; Edwards, D. P.; Flaud, J.-M.; Perrin, A.; Camy-Peyret, C.; Dana, V.; Mandin, J.-Y.; Schroeder, J.; McCann, A.; Gamache, R. R.; Wattson, R. B.; Yoshino, K.; Chance, K. V.; Jucks, K. W.; Brown, L. R.; Nemtchinov, V.; Varanasi, P. J. *Quant. Spectrosc. Radiat. Transfer* **1998**, *60*, 665.
- Ogilvie, J. F. *The Vibrational and Rotational Spectrometry of Diatomic Molecules*; Academic Press: London, 1998 and references therein.
- Le Roy, R. J. *RKRI 2.0: A Computer Program Implementing the First-Order RKR Method for Determining Diatomic Molecule Potential Energy Functions*; University of Waterloo Chemical Physics Research Report CP-657R, 2004.
- Le Roy, R. J. *LEVEL 7.5: A Computer Program for Solving the Radial Schrodinger Equation for Bound and Quasibound Levels*; University of Waterloo Chemical Physics Research Report CP-655, 2002.
- Ogilvie, J. F.; Rodwell, W. R.; Tipping, R. H. *J. Chem. Phys.* **1980**, *73*, 5221.
- Lee, Y.-P.; Cheah, S.-L.; Ogilvie, J. F. *Infrared Phys. Technol.* **2005**, in press.