PRECISE MILLIMETER-WAVE LABORATORY FREQUENCIES FOR CS AND C³⁴S

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ABSTRACT

Nine successive rotational lines in the ground vibrational state of CS and C³⁴S between 96 GHz ($J = 2-1$) and 500 GHz (10–9) were measured in the laboratory to an accuracy of a few kHz. When our measurements are combined with the submillimeter-wave measurements of Ahrens & Winnewisser, the entire rotational spectrum of both isotopic species is predicted to an accuracy of about 1 part in 10^8 up to 500 GHz and 5 parts in 10^8 near 1000 GHz. These frequencies should be useful for quantitative studies of cloud core collapse and star formation in the millimeter- and submillimeter-wave bands.

Subject headings: ISM: molecules — methods: laboratory — molecular data — molecular processes — radio lines: ISM — stars: formation

1. INTRODUCTION

Nearly 130 molecules have been detected in space by radio astronomers. The identifications are generally extremely secure because (1) nearly all are now based on laboratory frequencies, (2) several or many lines are typically assigned, and (3) the laboratory and astronomical frequencies typically agree to 1 km s^{−1} or better in equivalent radial velocity, i.e., 3 ppm. Most of these molecules were first detected at millimeter wavelengths either in the dense interstellar molecular clouds in Orion A and Sgr B2, or in the circumstellar envelope of the evolved carbon star IRC +10216. Of these three sources, the lines are narrowest in Orion, where the typical width (FWHM) is ~ 3 km s^{−1} (Ungerechts et al. 1997), and the corresponding Doppler width is about 1 MHz at a wavelength of 3 mm.³ In the millimeter-wave band the uncertainty in most laboratory frequency measurements is ~ 30 kHz. Precision such as this is quite adequate for the identification of new molecules, but it generally does not allow radial velocities to be measured accurately enough to study motions of star-forming molecular cloud cores.

With the development of low noise SIS receivers and digital correlators as standard equipment on millimeter-wave telescopes, it is now feasible to investigate the internal motions of low-mass star-forming cloud cores (Lee, Myers, & Tafalla 2001 and references therein). The technique used by radio astronomers is to measure lines of selected molecular species with a high signal-to-noise ratio and to quantitatively compare the profiles of optically thick and optically thin lines. Radiative transfer calculations indicate that a molecular line profile observed toward a uniformly contracting (infalling) core should have a symmetric

(Gaussian) shape centered on the systemic velocity if it is optically thin and an asymmetric shape skewed to the blue if the line is optically thick (Leung & Brown 1977 and references therein).

To identify inward motions in molecular cloud cores unambiguously, it is necessary to resolve the velocity shifts to a fairly small fraction of a line width. Because the line widths in optically thin tracers are only 0.2–0.3 km s^{−1} (Benson, Caselli, & Myers 1998), and the velocity shift between the peaks of the thick and thin lines is usually substantially less than a line width, the velocity shift must be determined to only about 0.05 km s^{−1}. For this application a frequency precision of 30 kHz is inadequate and can lead to ambiguity as to whether a particular velocity shift is due to inward motions or to uncertainties in the line frequencies (see Lee, Myers, & Tafalla 1999).

Determination of line frequencies in the laboratory to a few parts in 10^8 —equivalent to about 1% of the Doppler line width near 200 K—represents a challenge to the spectroscopist. In the past, few workers were able to report line frequencies to this accuracy, owing to difficulty in determining systematic uncertainties. Although the corresponding lines are 3–4 times wider in the laboratory than in narrow-line astronomical sources owing to some instrumental broadening in addition to the Doppler broadening, with gradual improvement in laboratory techniques it is now feasible to measure the frequencies of reasonably strong Doppler-broadened lines in the millimeter- and submillimeter-wave bands that are accurate to a few parts in 10^8 (Winnewisser et al. 1997 and references therein).

To support molecular studies of star formation, we have undertaken a program in laboratory spectroscopy to determine accurate line frequencies for the best tracers of small dynamical motions in narrow-line sources. Reported here are those for CS and C³⁴S in the millimeter-wave band. We began with CS for the following reasons: (1) its lines are typically strong so they provide an excellent means for assessing the accuracy in the measured line frequencies, (2) nine transitions of each isotopic species fall in the millimeter-wave band, (3) prior measurements for both isotopic species have large uncertainties, and (4) radio astronomers have shown that among neutral species, CS and C³⁴S are excellent tracers of depletion and infall motion in dense cores with no known associated stars (Lee et al. 1999).

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³ Approximately 15% of the known interstellar molecules were first detected at centimeter wavelengths in the narrow-line source TMC-1. The identifications of most of these were based on frequencies calculated from spectroscopic constants determined from millimeter-wave laboratory measurements. Because the line frequencies derived from the TMC-1 spectra are much more accurate, the astronomical lines were usually included in a reanalysis of the millimeter-wave laboratory spectra.

2. EXPERIMENT

Rotational line frequencies were measured with a free space millimeter-wave absorption spectrometer, which has been used to identify a number of reactive molecules of astrophysical interest in the laboratory. Millimeter-wave radiation in the range from 70 to 145 GHz is produced by solid state Gunn diode oscillators, efficient frequency multipliers then providing sufficient power to work at least as high as 500 GHz. The Gunn is phase-locked to a high harmonic of a frequency synthesizer in an arrangement described previously (see McCarthy et al. 1995). The spectral width of the phase-locked Gunn oscillator is less than 1 kHz. In the arrangement used here, the millimeter-wave radiation makes two passes through the 3 m long absorption cell and is then focused on a liquid-helium-cooled InSb hot-electron bolometer (Mollaaghababa et al. 1993). Frequency modulation of the Gunn and phase sensitive detection at the second harmonic of the modulation frequency significantly reduces $1/f$ noise and large amplitude standing waves between the radiation source and detector. The modulation source is a sine wave of high spectral purity (harmonic distortion < -60 dBc; Stanford Research Systems DS335). Owing to the fairly large bandwidth of the phase-lock loop (~ 5 MHz), the Gunn remains phase-locked when the modulation is applied to the 850 MHz reference oscillator. The modulation frequency (f) was 95 kHz, except for the (2–1) transition, which was observed with $f = 45$ kHz.

Carbon monosulfide (CS) was produced in a low-pressure DC discharge (20 mA) through a flowing mixture of CS₂ and Ar. The flow rate of Ar (at standard temperature and pressure) was ≤ 1 cm³ minute⁻¹, and the total pressure in the cell, measured near the pumping port with the discharge on, was ≤ 5 mtorr. The spacing between rotational levels is much less than kT , so to enhance the population of the lowest rotational levels the discharge was cooled to 220 K by flowing liquid nitrogen through a copper jacket on the outside of the cell. Cooling to a lower temperature was avoided to prevent the CS₂ from freezing out on the walls of the cell.

Because our goal was to determine line frequencies to an accuracy of a few kHz corresponding to roughly 1% of the FWHM, care was taken to minimize instrumental contributions either to line broadening or to distortion of the line profile. Specifically, the amplitude of the frequency modulation (Δf) was reduced from the level that gives the strongest peak line intensities, to a level that corresponds to about $\frac{1}{2}$ of the theoretical Doppler line width as determined from the relative amplitudes of the FM sidebands on the millimeter-wave carrier. The contribution to the line width from pressure broadening was minimized by operating at the lowest pressure that still gave fairly strong absorption lines. To minimize possible distortion of the line profile, the bandwidth of the preamplifier in the lock-in amplifier was set to maximum (i.e., flat response from 1 Hz to 210 kHz). To minimize possible offsets of the line center frequency, the spectra were recorded with a minimum lock-in amplifier time constant of less than 1 ms.

Spectra were obtained by stepping the frequency synthesizer, which is under computer control, and recording the output of the lock-in amplifier. The frequency was stepped very slowly (at a rate of 0.2 MHz s⁻¹), and the spectra were measured at 1024 points over a bandwidth (10 MHz) that was considerably greater than the width of the line profile.

FIG. 1.—Sample spectra of the (2–1) transition of CS and C³⁴S, each measured at 1024 points in a 10 MHz bandwidth for a total integration time of 5 minutes. The CS was produced in a DC discharge (20 mA) through a flowing mixture of CS₂ and Ar at a total pressure of less than 5 mtorr. A best-fit theoretical second derivative of a Voigt line profile with a small ($\leq 3\%$) contribution from the first derivative is superposed on the measured profile. The residual from the least-squares fit is plotted below the line profile.

As Figure 1 shows, the signal-to-noise ratio of the spectra for both isotopic species is greater than 100 at a typical integration time of about 5 minutes. Owing to the modulation and detection scheme employed, the instrumental line shape is approximately the second derivative of the underlying Voigt absorption profile.

Lines were generally observed near the Doppler limit with a negligible contribution from pressure broadening. A typical line width under these conditions was roughly 100 kHz (half-width at half-maximum) near 96 GHz. This is roughly 25 kHz larger than the theoretical Doppler line width for CS at 220 K (~ 75 kHz), owing to broadening of the line profiles by the modulation. The measured line width with $f = 45$ kHz and $\Delta f/f \sim 1$ is very close to that calculated for a

modulation-broadened Gaussian profile observed with second harmonic detection (Wilson 1963).

3. RESULTS

Carbon monosulfide (CS) in its $X^1\Sigma^+$ electronic ground state was one of the first reactive species to be observed by microwave spectroscopy (Mockler & Bird 1955). Lines of the normal (³²S) and the rare (³⁴S) sulfur isotopic species of CS are very strong in the laboratory, but in spite of that the uncertainties in most previously published millimeter-wave frequencies are fairly high (i.e., a few parts in 10⁷; Bogey, Demuyck, & Destombes 1982). In the submillimeter-wave band recent measurements in the range from 580 to 1100 GHz have been determined to much higher accuracy by Ahrens & Winnewisser (1999, hereafter AW99). Reported here are new line frequency measurements of CS and C³⁴S in the millimeter-wave band between 90 and 500 GHz. While this work was in progress, the fundamental (1–0) transition of CS and C³⁴S in the ground vibrational state near 48 GHz was measured very precisely by Fourier transform microwave (FTM) spectroscopy (E. Kim & S. Yamamoto 2001, private communication, hereafter KY01; owing to the lack of pulsed sources with adequate power in the millimeter-wave band, it is not yet feasible to observe higher transitions in CS by this high resolution technique).

3.1. CS and C³⁴S

The measured CS line frequencies (Table 1) were determined from a least-squares fit of a Voigt profile⁴ to the observed spectra. It was assumed in the fitting procedure that (1) the measured line profiles are symmetric about line center, and (2) the derived frequencies are unaffected when small residual baselines are removed by fitting a polynomial function to the observed spectra. The 1 σ uncertainties in the measured line frequencies determined in the least-squares fits were approximately equal to $\Delta\nu/(S/N)$, where $\Delta\nu$ is the FWHM and S/N is the signal-to-noise ratio. Although the lines at higher frequencies are wider, they are

also more intense, and therefore $\Delta\nu/(S/N)$ is fairly constant for the nine lines measured here. For each transition, the line frequency shown in Table 1 was obtained from the mean of 5–10 measurements. Each scan was given equal weight in determining the mean frequency, and the statistical uncertainties of each line frequency was taken as the 1 σ standard deviation of the mean. It is shown in the Appendix that systematic shifts in the line frequency due either to collisional effects or Doppler shifts from streaming motions of the gas through the discharge cell are at the level of $\leq 1 \times 10^{-8}$, and therefore negligible. Likewise, systematic effects that produce asymmetric line profiles, such as harmonic distortion of the frequency modulation, standing waves, or significant time constants in the detection system are at the level of $\leq 1 \times 10^{-8}$ and therefore negligible as well.

The millimeter-wave frequencies of CS and of C³⁴S are well described by the standard expression $\nu = 2B(J+1) - 4D(J+1)^3$, where J is the rotational angular momentum of the lower level of the transition, B is the rotational constant, and D is the centrifugal distortion constant. When this expression is least-squares fitted to the nine lines in Table 1, the reduced χ^2 of the fit (χ^2_ν) provides an independent estimate of the uncertainties in the measurements. For C³⁴S, the statistical uncertainties provide a good estimate of the measurement errors because $(\chi^2_\nu)^{1/2}$ is approximately unity (1.2). Using the same procedure for CS, we found that $(\chi^2_\nu)^{1/2} = 3.7$, indicating that the measurement errors for the CS lines are slightly larger than the statistical uncertainties.

Because the CS and C³⁴S lines were measured under almost identical experimental conditions, the systematic errors should be nearly the same for both isotopic species. The only difference in the properties of the CS and C³⁴S lines that might affect these measurements is the optical depth, which is 23 times higher for CS than C³⁴S since C³⁴S was observed in natural abundance. The optical depth (τ) of the CS line is ~ 0.04 at 98 GHz, implying that τ approaches 1 in the higher frequency lines near 400 GHz. The slightly greater uncertainties in the CS frequencies are attributed to a small distortion (flattening) of the profile near line center, resulting in a slightly greater uncertainty in the least-squares fit of the theoretical line profile to the measured spectrum. The widths of the CS profiles near 400 GHz are roughly 15% wider than those of the corresponding transitions in C³⁴S, which is consistent with distortion of the CS profiles owing to the substantial optical depth in lines of the main isotopic species. To account for this source of systematic error, 1 kHz was added to the statistical uncertainties of each line with the result that $(\chi^2_\nu)^{1/2} = 1.2$ for CS.

Several independent tests indicate that the frequency measurements here are accurate to a few kHz. First, line frequencies determined from Doppler-limited profiles were compared with those determined in other laboratories from sub-Doppler profiles. Specifically, our measurements of the (1–0) line of C¹⁸O agreed to within ± 1 kHz with the sub-Doppler measurement of Klapper et al. (2001), with a claimed 1 σ uncertainty of 0.3 kHz. Second, the frequency of the fundamental (1–0) transition of CS and C³⁴S near 48 GHz, calculated with a B and D obtained from a fit to the nine millimeter-wave transitions (Table 2), agreed with those observed in a collision-free supersonic molecular beam by Fourier transform microwave spectroscopy to within the measurement uncertainties of ± 2 kHz (KY01). Third, blind predictions of two transitions that we subsequently measured (9–8

⁴ The Voigt profile is a convolution of a Gaussian (Doppler broadened) and a Lorentzian (pressure broadened) profile.

TABLE 1
MEASURED MILLIMETER-WAVE LINES OF CS AND C³⁴S

TRANSITION	CS		C ³⁴ S	
	Measured (MHz)	$O - C^a$ (kHz)	Measured (MHz)	$O - C^a$ (kHz)
2–1	97,980.9533 (23)	0.3	96,412.9495 (11)	–2.8
3–2	146,969.0287 (13)	3.0	144,617.1007 (14)	–0.4
4–3	195,954.2109 (16)	–2.9	192,818.4566 (12)	–0.4
5–4	244,935.5565 (28)	0.8	241,016.0892 (4)	–0.1
6–5	293,912.0865 (33)	–3.6	289,209.0684 (11)	1.5
7–6	342,882.8503 (50)	–4.9	337,396.4590 (6)	0.2
8–7	391,846.8898 (15)	0.1	385,577.3360 (34)	1.8
9–8	440,803.2320 (12)	0.1	433,750.7630 (12)	0.8
10–9	489,750.9210 (38)	0.7	481,915.8105 (12)	–1.2

NOTE—The 1 σ uncertainties (in parentheses) are in units of the last significant digits.

^a Calculated with the spectroscopic constants in Table 2 (this work).

TABLE 2
SPECTROSCOPIC CONSTANTS OF CS AND C³⁴S IN THE GROUND VIBRATIONAL STATE

CONSTANT	CS		C ³⁴ S	
	This Work ^a	Recommended ^b	This Work ^a	Recommended ^b
B	24,495.55876 (14)	24,495.55884 (15)	24,103.548377 (48)	24,103.548378 (53)
$D (\times 10^3)$	40.0637 (10)	40.0655 (15)	38.78896 (42)	38.78947 (60)
$H (\times 10^9)$		10.7 (5.5)		5.6 (1.6)

NOTE—Units are MHz. The 1σ uncertainties (in parentheses) are in units of the last significant digits.

^a From a least-squares fit to the millimeter-wave lines in Table 1.

^b From a least-squares fit to the millimeter-wave lines (this work); the 1–0 line measured by KY01; and the submillimeter-wave lines in AW99.

and 10–9), were accurate to within 3 kHz or better (i.e., to about 1 part in 10^8). Fourth, the frequency of the (2–1) line of C³⁴S inferred from astronomical measurements in L1512—the same quiescent low-mass cloud core in Taurus in which the hyperfine structure of N₂H⁺ was determined to very high precision (~ 1 kHz) by Caselli, Myers, & Thaddeus (1995)—is in excellent agreement with the frequency in Table 1 on the assumption that the radial velocity is the same as that of the (1–0) line of C¹⁸O (Lee et al. 2001).

To facilitate future astronomical observations between 500 and 1000 GHz, the millimeter-wave lines in Table 1 were analyzed simultaneously with the submillimeter-wave measurements of AW99. In the fit to the combined measurements, it was necessary to include the next term H in the centrifugal expansion in order to accurately

reproduce the submillimeter-wave frequencies. As shown in Tables 3 and 4, the submillimeter-wave lines of both isotopic species are predicted to a fraction of the quoted measurement uncertainties and the calculated frequencies are in excellent agreement with the much more accurate millimeter-wave lines. The three spectroscopic constants determined from the combined analysis (Table 1, recommended constants) allow us to predict the rotational spectra of CS (Table 3) and C³⁴S (Table 4) to an accuracy of 1 part in 10^8 below 500 GHz and to 5 parts in 10^8 near 1000 GHz.

4. DISCUSSION

The present measurement of the CS (2–1) line frequency has already been of value for the interpretation of kinematic

TABLE 3
CS LINE FREQUENCIES

TRANSITION	CALCULATED ^a (RECOMMENDED) (MHz)	MEASURED		
		Frequency (MHz)	$O - C^a$ (kHz)	References
1–0	48,990.957 (1)	48,990.9549 (24)	–2.5	1
2–1	97,980.953 (1)	97,980.9533 (23)	–0.3	2
3–2	146,969.026 (1)	146,969.0287 (13)	3.0	2
4–3	195,954.214 (1)	195,954.2109 (16)	–3.0	2
5–4	244,935.556 (1)	244,935.5565 (28)	1.2	2
6–5	293,912.090 (1)	293,912.0865 (33)	–4.0	2
7–6	342,882.855 (1)	342,882.8503 (50)	–5.0	2
8–7	391,846.889 (1)	391,846.8898 (15)	0.6	2
9–8	440,803.232 (1)	440,803.2320 (12)	0.1	2
10–9	489,750.921 (2)	489,750.9210 (38)	–0.1	2
11–10	538,688.996 (2)	...	...	
12–11	587,616.495 (4)	587,616.485 (20)	–10.2	3
13–12	636,532.458 (6)	636,532.460 (30)	2.2	3
14–13	685,435.923 (10)	...	...	
15–14	734,325.929 (14)	...	...	
16–15	783,201.516 (21)	...	...	
17–16	832,061.724 (30)	...	...	
18–17	880,905.591 (41)	...	...	
19–18	929,732.157 (56)	929,732.125 (80)	–31.7	3
20–19	978,540.462 (76)	...	...	
21–20	1,027,329.545 (99)	...	...	
22–21	1,076,098.448 (129)	1,076,098.525 (200)	77.0	3

^a Calculated frequencies are derived from the recommended spectroscopic constants (Table 2) determined in a least-squares fit to the measured lines shown here. The 1σ uncertainties (in parentheses) are in the units of the last significant digits.

REFERENCES.—(1) E. Kim & S. Yamamoto 2001, private communication; (2) this work, Table 1; (3) AW99.

TABLE 4
C³⁴S LINE FREQUENCIES

TRANSITION	CALCULATED ^a (RECOMMENDED) (MHz)	MEASURED		
		Frequency (MHz)	$O - C^a$ (kHz)	References
1-0	48,206.942 (1)	48,206.9411 (24)	-0.5	1
2-1	96,412.952 (1)	96,412.9495 (11)	-2.3	2
3-2	144,617.101 (1)	144,617.1007 (14)	0.0	2
4-3	192,818.457 (1)	192,818.4566 (12)	0.0	2
5-4	241,016.089 (1)	241,016.0892 (4)	-0.2	2
6-5	289,209.067 (1)	289,209.0684 (11)	1.3	2
7-6	337,396.459 (1)	337,396.4590 (6)	0.3	2
8-7	385,577.334 (1)	385,577.3360 (34)	1.7	2
9-8	433,750.763 (1)	433,750.7630 (12)	0.3	2
10-9	481,915.813 (1)	481,915.8105 (12)	-1.0	2
11-10	530,071.555 (1)	...	...	
12-11	578,217.057 (2)	578,217.069 (20)	12.4	3
13-12	626,351.388 (2)	626,351.384 (20)	-4.4	3
14-13	674,473.619 (3)	...	...	
15-14	722,582.819 (4)	...	...	
16-15	770,678.056 (6)	...	...	
17-16	818,758.402 (8)	...	...	
18-17	866,822.924 (11)	...	...	
19-18	914,870.693 (15)	914,870.705 (50)	11.8	3
20-19	962,900.779 (20)	962,900.785 (50)	6.0	3
21-20	1,010,912.251 (26)	1,010,912.265 (50)	13.8	3
22-21	1,058,904.180 (34)	1,058,904.175 (50)	-4.7	3

^a Calculated frequencies are derived from the recommended spectroscopic constants (Table 2) determined in a least-squares fit to the measured lines shown here. The 1σ uncertainties (in parentheses) are in the units of the last significant digits.

REFERENCES.—(1) E. Kim & S. Yamamoto 2001, private communication; (2) this work, Table 1; (3) AW99.

motions and abundances in low-mass dense cores. From previous laboratory measurements, for example, it could not be determined whether double-peaked profiles in the optically thick CS (2–1) line toward low-mass starless cores with no embedded *IRAS* source or associated T Tauri star are produced by two independent velocity components or by a collapsing gas cloud with depletion and self-absorption (Lee et al. 1999). On the basis of our line frequency, Lee et al. (2001) showed that the latter interpretation is correct—i.e., inward motions are a significant feature in a number of starless cores believed to be in a very early stage of star formation.

As new, high-resolution radio interferometers, such as the Submillimeter Array (SMA) and the Atacama Large Millimeter Array (ALMA) come into operation, the need for more accurate line frequencies in the millimeter- and submillimeter-wave bands will increase. The work of Lee et al. (1999, 2001) has shown that without improvements in rest frequencies, it will not be possible to unambiguously compare and analyze the narrow-line profiles characteristic of low-mass star- and planet-forming regions. We have demonstrated here that it is possible in the laboratory to determine line frequencies from Doppler-limited profiles in the millimeter-wave band to the required accuracy of a few parts in 10^8 .

A critical review of the spectroscopic literature reveals that many of the published laboratory measurements in the millimeter-wave band are inadequate because (1) they are very old, or (2) they are preliminary measurements

whose purpose was to confirm the astronomical identifications and guide searches for additional transitions, rather than to provide very precise line frequencies for detailed kinematic investigations. At least 10 molecules were identified as needing improvement in their line frequencies according to the following criteria: (1) relevance of the lines for studies of star and planet formation, (2) detectability of the species according to past observations, and (3) velocity precision significantly worse than 0.02 km s^{-1} . These include neutral tracers of depletion and infall (*c*-C₃H₂, H₂CS, and SO), shock chemistry (SiO), and disk surface chemistry (CN and CCH); and ionic tracers of ion budget and infall (HCO⁺, N₂H⁺, and HCS⁺). For most of these molecules the uncertainties in the line frequencies in the millimeter-wave band are roughly 10 times too large (i.e., typically 2–6 parts in 10^7).

For a few species (e.g., CN, CCH, N₂H⁺, and N₂D⁺) hyperfine structure (hfs) will not be resolved in the Doppler-limited spectra of the higher rotational transitions. What can be done in those cases is to calculate the hfs with the spectroscopic constants determined from high-quality spectra observed in a narrow-line astronomical source (see Caselli et al. 1995). The line frequencies of the individual hyperfine components can then be determined by fitting the theoretical blended line shape to the observed Doppler-limited laboratory profiles. A similar procedure was used successfully in a comprehensive analysis of the Doppler-limited spectrum of NO

(Varberg, Stroh, & Evenson 1999). It remains for spectroscopists to provide accurate frequencies for those neutral and ionic species that radio astronomers will use to probe motions and chemical processes in star-forming dense cores and planet-forming circumstellar disks.

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APPENDIX

SOURCES OF SYSTEMATIC ERROR

A careful consideration of both statistical and systematic errors is required to yield realistic uncertainties for the measurements here. Statistical uncertainties associated with the determination of the line centers from least-squares fits of a theoretical profile to the measured spectra are discussed in § 3.1. Here we consider systematic errors caused by instrumental effects that can produce either shifts of the line centroid or small asymmetries in the line profile.

A1. FREQUENCY SHIFTS

Systematic errors in the line frequencies may result from collision- (pressure-) induced shifts or Doppler shifts from streaming motions of the gas as it is slowly pumped through the absorption cell.

A1.1. *Pressure-Induced Shifts*

Collision-induced shifts of the line frequency arise in weak binary collisions (i.e., at large values of the impact parameter b) as a molecule is perturbed by a second in a close encounter. Such shifts are usually largest in the lowest rotational transitions of molecules with large dipole moments, those with degenerate or nearly degenerate levels such as symmetric tops, and those molecules which have closely spaced inversion doublets such as NH_3 . In the few molecules for which line shifts have been measured in the microwave region, the self-shifts are typically only a few percent of the pressure-broadened line width, except in NH_3 , for which the shifts are much larger (Belov et al. 1982). On the other hand, in diatomic and linear molecules only upper limits for the pressure-induced shifts have been determined. For example, in CO the self-shift is $\leq 2 \text{ kHz torr}^{-1}$ (Belov, Tretyakov, & Suenram 1992). Similarly, several investigators have attempted to measure the shift parameter for OCS, but only an upper limit of less than $0.02 \text{ MHz torr}^{-1}$ could be established (Cazzoli & Dore 1990).

On the basis of the exceedingly small shift parameters for CO and OCS, it might appear that collision-induced line shifts are negligible for CS at the very low pressures in the measurements reported here (pressure $\leq 5 \text{ mtorr}$). Nevertheless, owing to the large dipole moment of CS (1.958 D) relative to CO (0.112 D) or OCS (0.715 D), it is important to establish that the collision-induced shifts are indeed negligible for CS. We therefore examined the (2–1) line of C^{34}S at 96 GHz, because it has the smallest Doppler width of the lines measured here and the optical depth is $\ll 1$. Starting at the Doppler limit the pressure in the cell was increased incrementally from about 1 to 7 mtorr, such that the pressure-broadened width was 2 times the Doppler width. Under these conditions there was no evidence of a pressure-induced line shift of the (2–1) line of C^{34}S to within the measurement precision of $\pm 1 \text{ kHz}$.

A1.2. *Gas Streaming*

The velocity of the gas flowing through the present absorption cell is very small ($\sim 30 \text{ cm s}^{-1}$) because of the modest pumping speed ($\sim 6 \text{ liter s}^{-1}$). The Doppler shift caused by the streaming gas is largely cancelled because the millimeter-wave beam makes two passes through the cell; the cancellation, however, is not complete because the powers in the forward and reflected beams are not identical. Nevertheless, the Doppler shift produced by the streaming velocity of the gas is extremely small, and the shift in the measured line frequencies of $\leq 1 \text{ part in } 10^9$ is negligible.

A2. MILLIMETER-WAVE SOURCE

Determination of absolute line frequencies requires precise measurement and control of the millimeter-wave carrier. In the present spectrometer, the reference to the microwave frequency counter and the 850 MHz reference to the Gunn oscillator phase-lock loop are derived from the same local frequency standard: a 10 MHz quartz oscillator. Frequent comparisons with the time signal broadcast by WWVB, which is accurate to better than 1 part in 10^{12} , confirmed that our quartz frequency standard was accurate to 1 part in 10^9 or better during the course of the measurements here.

A3. ASYMMETRIC LINE PROFILES

Line asymmetry can arise from harmonic distortion, standing waves, or time constants in the detection system. The degree of asymmetry in the actual profiles is very small; typically the fractional difference in the peak-to-peak amplitudes of the two halves of a line profile is ≤ 0.03 (see Fig. 1). Possible causes of the asymmetry are (1) harmonic distortion in the frequency modulation of the millimeter-wave source, (2) standing waves between the source and detector, and (3) time constants in the detection circuit. Because the line profiles are generally fitted with a function that is symmetric about the line center,

asymmetries in the line profiles could produce apparent shifts of the line center frequency when theoretical symmetric profiles are fitted to the measured spectra.

A3.1. *Distortion of the Frequency Modulation*

Asymmetries in the line profiles that we observe are not caused by harmonic distortion of the frequency modulation. De Vreede, Gillis, & Dijkerman (1988) showed analytically that the effect of distortion of the frequency modulation on the line profile decreases with increasing modulation amplitude. We found that the degree of asymmetry was independent of the modulation amplitude.

A3.2. *Standing Waves*

The standing wave pattern in our spectrometer is due to reflections from several objects in the millimeter-wave beam. The voltage standing wave ratio (VSWR) measured at a single point in the propagation path with our InSb detector is about 1.04. It is difficult to identify the principal sources of the millimeter-wave reflections from a single point measurement of the VSWR, because the voltages of the reflected waves add and the amplitude and phase of each component cannot be determined separately (Montgomery, Dicke, & Purcell 1948). On the basis of test measurements made some time ago, we established that the main sources of standing waves are (1) reflection between the horn that launches the radiation from the source and the detector and its associated quasi-optical components, and (2) internal reflections in the discharge cell. In these tests the VSWR was reduced from 1.04 to about 1.02 (i.e., the reflected power measured outside the cell was reduced by a factor of 3–4) by introducing baffles consisting of standard absorbing material in a cell that was not evacuated. In practise, we have been unable to much reduce reflections in the discharge cell because common absorbing materials (e.g., carbon-impregnated foam) cannot be used in vacuum, the discharge causes erosion of the few absorbing materials that can be used (e.g., neoprene), and the baffles interfere with the discharge.

Although we were not able to eliminate the standing wave entirely, the phase can be shifted by translating the position of the polarizing grid by a fraction of a wavelength. This allowed us to find a point on the standing wave pattern at which the amplitude was fairly constant at the line frequency. Nevertheless, the power typically varied by a few percent over the 10 MHz frequency range of the measurements, which may account for the residual asymmetry in the line profiles.

Two steps were taken to ensure that derived frequencies are not affected by the instrumental standing wave. First, each line was measured at several different points (phases) on the standing wave. When the polarizing grid was adjusted between successive scans, there was no evidence of a shift in the derived line frequency to within the (1 σ) measurement uncertainty for an individual scan of ~ 1.5 kHz. As a further check, a distortion term was included in the theoretical expression for the line profile (de Vreede et al. 1988). Comparison of derived line frequencies with and without the distortion term confirmed that small asymmetries in the profiles from standing waves are not a significant source of uncertainty in the frequencies determined here—i.e., the effect of standing waves on the derived line frequencies are less than the stated uncertainties.

A3.3. *Time Constants*

Time constants in the detection system, which includes the InSb detector, the detector preamplifier, and the lock-in amplifier, is another instrumental source that can give rise to asymmetric line profiles. The response times of the detector and the preamplifier are too short (≤ 1 μ s) to affect the line profile. In our spectrometer, the recorded spectrum is the sum of successive pairs of up and down sweeps in frequency. From sample measurements of the (1–0) line of C¹⁸O with lock-in amplifier time constants ranging from less than 1 to 10 ms, we showed that the very small minimum time constant of the lock-in amplifier of less than 1 ms combined with the very slow sweep rate of 0.2 MHz s^{−1} does not affect the line frequency measurements.

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