The Astrophysical Journal Supplement Series, 165:432–437, 2006 July

ACCURATE LABORATORY WAVELENGTHS OF THE $A^1\Pi(v' = 0\text{–}5)\text{–}X^1\Sigma^+(v'' = 0)$ VIBRONIC BANDS OF $^{12}C^{17}O$ AND $^{12}C^{18}O$

Anton du Plessis,[1,2] Erich G. Rohwer,[1] and Christine M. Steenkamp[1]
Received 2005 December 2; accepted 2006 March 17

ABSTRACT

Twenty nine rovibronic lines of $^{12}C^{17}O$ for which laboratory wavelengths were previously unavailable were detected in laser-induced fluorescence excitation spectra of the six vibronic bands $A^1\Pi(v' = 0\text{–}5)\text{–}X^1\Sigma^+(v'' = 0)$. Rovibronic lines of $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{17}O$, and $^{12}C^{18}O$ were detected in each band, allowing accurate determination of the unknown wavelengths using neighboring $^{12}C^{16}O$ and $^{13}C^{16}O$ lines as reference. The new wavelength data yield consistent heliocentric velocity values when applied to vacuum ultraviolet observations of $^{12}C^{17}O$ and $^{12}C^{18}O$ in the interstellar medium.

Subject headings: ISM: molecules — methods: laboratory — molecular data — ultraviolet: general

1. INTRODUCTION

Carbon monoxide (CO) is the second most abundant molecule in interstellar gas clouds and is therefore of importance in astrophysics (Van Dishoeck & Black 1988). Spectral features of various isotopomers of CO in the vacuum ultraviolet (VUV) have been observed by satellite-based spectrographs. A comprehensive review of these observations is given by Morton & Noreau (1994). The fourth-positive system, $A^1\Pi(v')\text{–}X^1\Sigma^+(v'')$, dominates the spectrum of CO in the VUV. The VUV spectrum of CO isotopomers in the interstellar medium, which is observed in absorption, is restricted to transitions originating from the $v'' = 0$ vibrational level in the electronic ground state, as a result of the low temperature in the interstellar medium.

For the analysis and interpretation of astronomically observed spectra of CO in the interstellar medium, accurate laboratory measured wavelengths of the corresponding spectral lines of all isotopomers are required. Theoretical calculation of the wavelengths of less abundant isotopomers by appropriate isotopomeric corrections to the $^{12}C^{16}O$ wavelengths are not sufficiently accurate to produce consistent heliocentric velocity values, as pointed out in the analysis of the $A^1\Pi(v' = 2\text{–}5)\text{–}X^1\Sigma^+(v'' = 0)$ bands in the absorption spectra of $^{12}C^{17}O$ and $^{12}C^{18}O$ in the interstellar medium toward X Persei (Sheffer et al. 2002).

The relevant wavelength data for the more abundant isotopomers $^{12}C^{16}O$ and $^{13}C^{16}O$ are readily available, as compiled in the review paper of Morton & Noreau (1994). Term values for the $v' = 0\text{–}9$ vibronic bands of the $^{12}C^{18}O$ isotopomer have been published by Beaty et al. (1997). The only available laboratory wavelengths for the $^{12}C^{17}O$ isotopomer is of six lines in the $A^1\Pi(v' = 3)\text{–}X^1\Sigma^+(v'' = 0)$ band, which were recorded in our laboratory and published previously (Steinmann et al. 2003a, 2003b).

In the present study the determination of accurate laboratory wavelengths for $^{12}C^{17}O$ has been extended to the $v' = 0\text{–}5$ bands in the fourth-positive system, which are all of astrophysical interest. These spectroscopic results are presented here and applied to the recalculation of heliocentric velocity values associated with the observational data published by Sheffer et al. (2002). The wavelengths of the corresponding bands of $^{12}C^{18}O$ were remeasured in the present study, showing good agreement with the data published by Beaty et al. (1997).

2. EXPERIMENTAL METHOD

The experimental setup has been described in detail elsewhere (Steinmann et al. 2003a) and is only discussed briefly here. A wavelength-tunable pulsed laser source (pulse period ~25 ns) producing narrow-bandwidth ($\Delta\nu \sim 5$ GHz) VUV radiation is used to selectively excite the CO molecules. The undispersed fluorescence is recorded as function of excitation wavelength in the VUV. The CO gas sample, containing the CO isotopomers in natural abundance, is introduced by pulsed free supersonic expansion into vacuum.

In the VUV source, coherent VUV radiation is generated by sum frequency mixing of two visible laser beams produced by XeCl excimer pumped dye lasers in a magnesium vapor krypton gas medium (Yamanouchi & Tsuchiya 1995). Excitation of the $A^1\Pi(v' = 0\text{–}5)\text{–}X^1\Sigma^+(v'' = 0)$ bands, which lie in the range 1390–1550 Å, requires one of the dye lasers to be tuned over the range 3930–5450 Å, using a series of laser dyes: Coumarin 540A, Coumarin 480, Coumarin 440, Stilbene 3, and PBBO.

In the present work the experimental conditions were optimized for the detection of rare CO isotopomers, differing from the conditions used previously. A supersonic expansion consisting of pure CO gas expanding from a stagnation pressure of 4 bar into a vacuum of 5×10^{-6} mbar was typically used. The expansion was pulsed with a pulse duration of 0.3–0.8 ms and a repetition rate of 5 Hz. The estimated rotational temperature in the expansion was in the range 15–30 K. These experimental conditions constitute a compromise between efficient rotational cooling and sufficient sample density.

3. RESULTS AND DISCUSSION

The laser-induced fluorescence excitation spectra of the $A^1\Pi$ $(v' = 0\text{–}5)\text{–}X^1\Sigma^+(v'' = 0)$ bands of CO are shown in Figure 1. Each band spectrum contains lines of $^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, and $^{12}C^{17}O$. The positions of the band origins of the isotopomers are indicated by the labels A, B, C, and D, respectively.

A typical spectrum of the spectral region containing the $^{12}C^{17}O$ lines in the $A^1\Pi(v' = 2)\text{–}X^1\Sigma^+(v'' = 0)$ band is shown in Figure 2. From this spectrum, accurate wavelengths for the $R(0)$, $R(2)$, $R(3)$, $Q(1)$, $Q(3)$, and $P(2)$ lines of $^{12}C^{17}O$ were determined. For the $Q(1)$ and $P(2)$ lines of $^{12}C^{17}O$, the effect of

[1] Laser Research Institute, Physics Department, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa; egr@sun.ac.za, cmsteen@sun.ac.za.
[2] Current address: CSIR National Laser Centre, PO Box 395, Pretoria 0001, South Africa; adplessis2@csir.co.za.

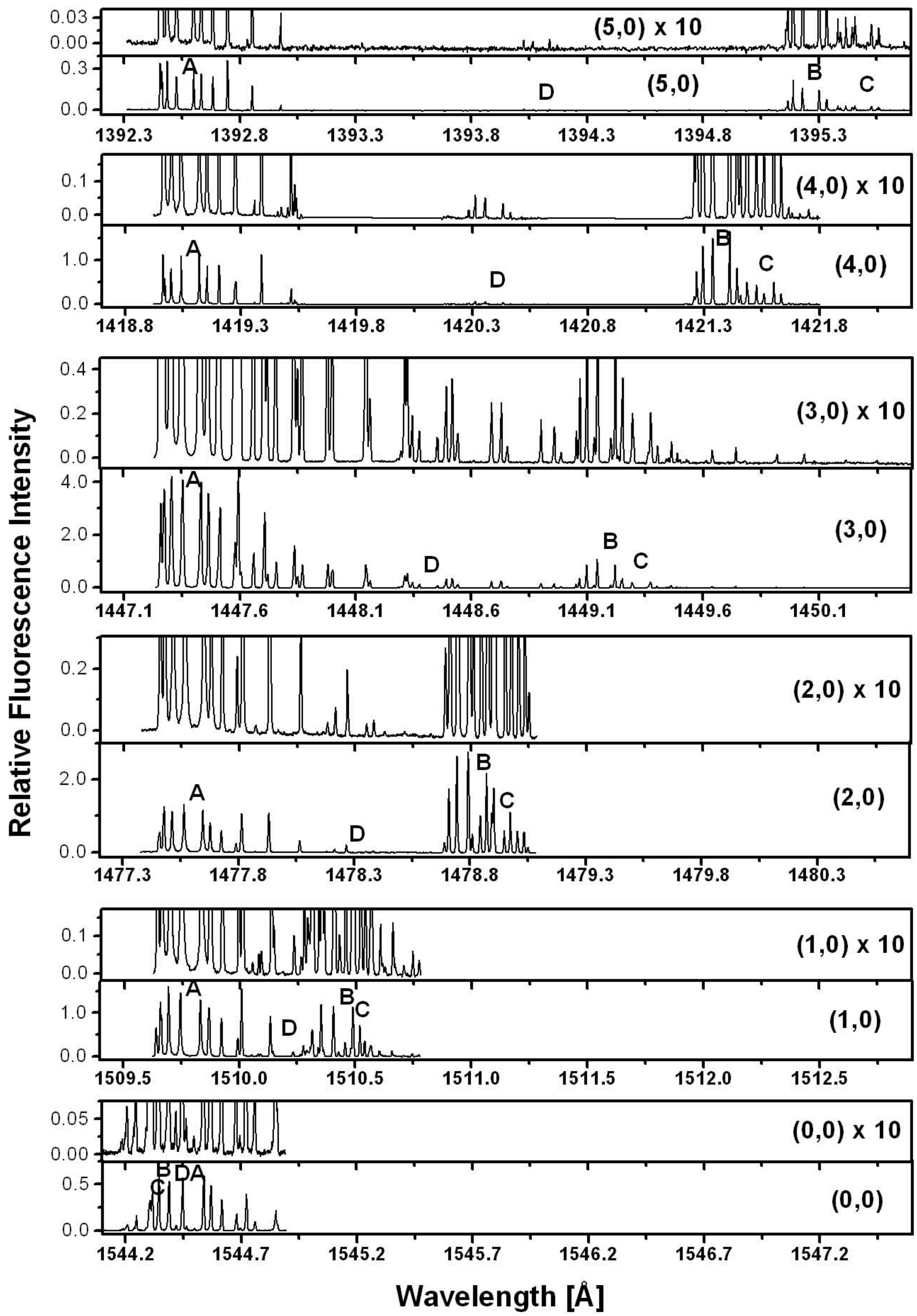

FIG. 1.— High-resolution laser-induced fluorescence excitation spectra of the $A^1\Pi(v' = 0\text{–}5)\text{–}X^1\Sigma^+(v'' = 0)$ bands of CO. The labels indicate the positions of the vibronic band origins of the following isotopomers: A for $^{12}C^{16}O$, B for $^{13}C^{16}O$, C for $^{12}C^{18}O$, and D for $^{12}C^{17}O$. The scale on the wavelength axes (Å per mm) are the same for all bands. The fluorescence intensities as indicated on the vertical scales approximately reflect the relative intensities of the bands. In the upper half of each window the spectrum is displayed at a tenfold magnification.

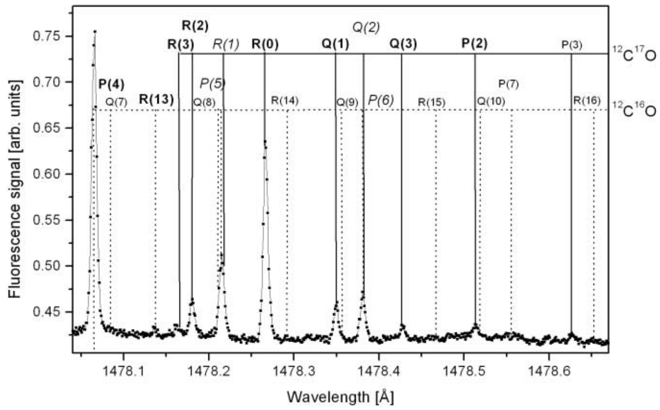

FIG. 2.—Spectrum showing the $^{12}C^{17}O$ and neighboring $^{12}C^{16}O$ lines in the $A^1\Pi(v'=2)$–$X^1\Sigma^+(v''=0)$ band. The observable lines are labeled in bold print, the unresolved overlapping lines are labeled in italics, and the positions of lines considered below the detection limit are labeled in small print.

overlap with the $Q(9)$ and $Q(10)$ lines of $^{12}C^{16}O$, respectively, were neglected, since the Q branch of $^{12}C^{16}O$ has relatively small signals in this region as seen from the signal of $Q(7)$. Wavelengths for the $R(1)$ and $Q(2)$ lines of $^{12}C^{17}O$ were not determined from this spectrum due to overlap with the $P(5)$ and $P(6)$ lines of $^{12}C^{16}O$, respectively. Since the $P(4)$ line of $^{12}C^{16}O$ produced a large signal, it must be assumed that the $P(5)$ and $P(6)$ lines also produced large signals.

The experimental wavelength data obtained for the $^{12}C^{17}O$ isotopomer are presented in Table 1. It includes laboratory wavelengths for 29 lines of $^{12}C^{17}O$ that have been determined for the first time. Data for the $A^1\Pi(v'=3)$–$X^1\Sigma^+(v''=0)$ band contain improved results obtained by recalibrating the spectra from the previous study (Steinmann et al. 2003a, 2003b), as well as new lines detected in recent experiments. Experimental wavelengths for 44 $^{12}C^{18}O$ lines have been determined for comparison with Beaty et al. (1997), as presented in Table 2. If a line has been detected in more than one experimental spectrum, the average wavelength is given in the relevant table. For a number of spectral lines experimental wavelengths have not been determined due to either the overlap of the line with another isotopomer line, or a signal below the noise limit. This is most pronounced in the congested $A^1\Pi(v'=0)$–$X^1\Sigma^+(v''=0)$ band, where only one line of $^{12}C^{17}O$ could be identified.

Flow cooling in the supersonic expansion facilitated the detection of the astrophysically relevant lines of the rare isotopomers. The low rotational temperatures reached in the expansion approaches the temperature of the interstellar medium. The resulting rotational population distribution enhances the signals of the lines of interest. In some cases lines were resolved by changing the effective rotational temperature in the supersonic expansion, which changes the relative rotational line intensity. For example, the spectrum of the $A^1\Pi(v'=3)$–$X^1\Sigma^+(v''=0)$ band in Figure 1 was measured at an exceptionally high temperature. The lower temperature of the other spectra in Figure 1 is more typical for our experiment.

In the previous study (Steinmann et al. 2003a), wavelength calibration of the experimental spectra was done using a linear fit on the $^{12}C^{16}O$ and $^{13}C^{16}O$ lines as wavelength references, with reference data taken from Morton & Noreau (1994) for lines with $J' \leq 6$, and from Tilford & Simmons (1972) for lines with $J' > 6$. In the previous study, the data from Tilford & Simmons (1972) were adjusted to correct for a systematic shift observed between the two data sets. In the present study, calibration was done using only the data of Morton & Noreau (1994). This decision was based on the wide acceptance of the data compiled by Morton & Noreau (1994) and evidence that the data from Tilford & Simmons (1972) deviate from those of Morton & Noreau

TABLE 1
SUMMARY OF EXPERIMENTAL WAVELENGTH DATA FOR THE $A^1\Pi(v'=0$–$5)$–$X^1\Sigma^+(v''=0)$ BANDS OF $^{12}C^{17}O$

Line	Wavelength (Å)	Line	Wavelength (Å)	Line	Wavelength (Å)
$A^1\Pi$–$X^1\Sigma^+(5,0)$		$A^1\Pi$–$X^1\Sigma^+(4,0)$		$A^1\Pi$–$X^1\Sigma^+(3,0)$	
$R(1)$	1394.027	$R(3)$	1420.274	$R(3)$	1448.282*
$R(0)$	1394.066	$R(2)$	1420.285	$R(2)$	1448.298*
$Q(1)$	1394.138	$R(1)$	1420.312	$R(1)$	1448.328
$Q(2)$	1394.171	$R(0)$	1420.356	$R(0)$	1448.376*
		$Q(1)$	1420.433	$Q(1)$	1448.454*
		$Q(2)$	1420.465	$Q(2)$	1448.486*
		$Q(3)$	1420.514	$Q(3)$	1448.532*
				$Q(4)$	1448.597
				$P(2)$	1448.610
$A^1\Pi$–$X^1\Sigma^+(2,0)$		$A^1\Pi$–$X^1\Sigma^+(1,0)$		$A^1\Pi$–$X^1\Sigma^+(0,0)$	
$R(3)$	1478.162	$R(3)$	1510.030	$R(0)$	1544.363
$R(2)$	1478.181	$R(2)$	1510.052		
$R(0)$	1478.268	$R(1)$	1510.092		
$Q(1)$	1478.350	$R(0)$	1510.146		
$Q(3)$	1478.429	$Q(1)$	1510.232		
$Q(4)$	1478.490	$Q(2)$	1510.263		
$P(2)$	1478.514				
$P(3)$	1478.628				

NOTE.—All $^{12}C^{17}O$ wavelengths, except those marked with asterisks, are new spectral data. The asterisks indicate wavelengths that were obtained by recalibrating spectra of Steinmann et al. (2003a, 2003b).

TABLE 2

COMPARISON OF EXPERIMENTAL WAVELENGTH DATA FOR THE $A^1\Pi(v'=0\text{–}5)\text{–}X^1\Sigma^+(v''=0)$ BANDS OF $^{12}C^{18}O$ (Å) FROM THIS WORK AND BEATY ET AL. (1997)

Line	This Work	Beaty	Line	This Work	Beaty	Line	This Work	Beaty
	$A^1\Pi\text{–}X^1\Sigma^+(5,0)$			$A^1\Pi\text{–}X^1\Sigma^+(4,0)$			$A^1\Pi\text{–}X^1\Sigma^+(3,0)$	
$R(2)$	1395.395	1395.392	$R(2)$	1421.460	1421.461	$R(3)$	1449.204	1449.203
$R(1)$	1395.418	1395.416	$R(1)$	1421.486	1421.487	$R(1)$	1449.250*	1449.248
$R(0)$	1395.457	1395.455	$R(0)$	1421.529	1421.530	$R(0)$	1449.296*	1449.294
$Q(1)$	1395.528	1395.526	$Q(1)$	1421.603	1421.604	$Q(1)$	1449.375*	1449.371
$Q(2)$	1395.560	1395.558	$Q(2)$	1421.635	1421.635	$Q(2)$	1449.405*	1449.402
$Q(3)$	1395.608	1395.606	$Q(3)$	1421.683	1421.683	$Q(3)$	1449.450	1449.448
$P(2)$	1395.670	1395.669	$P(2)$	1421.753	1421.752	$Q(4)$	1449.514	1449.510
$P(3)$	1395.770	1395.772				$P(2)$	1449.527	1449.525
	$A^1\Pi\text{–}X^1\Sigma^+(2,0)$			$A^1\Pi\text{–}X^1\Sigma^+(1,0)$			$A^1\Pi\text{–}X^1\Sigma^+(0,0)$	
$R(2)$	1478.811	1478.811	$R(3)$	1510.341	1510.341	$R(2)$	1544.200	1544.196
$R(1)$	1478.845	1478.845	$R(2)$	1510.365	1510.364	$R(1)$	1544.237	1544.235
$R(0)$	1478.895	1478.895	$R(0)$	1510.457	1510.457	$R(0)$	1544.292	1544.290
$Q(1)$	1478.975	1478.975	$Q(1)$	1510.540	1510.540	$Q(2)$	1544.407	1544.408
$Q(2)$	1479.005	1479.006	$Q(2)$	1510.570	1510.570	$Q(4)$	1544.517	1544.517
$Q(3)$	1479.051	1479.051	$Q(3)$	1510.616	1510.615			
$Q(4)$	1479.111	1479.112	$Q(4)$	1510.670	1510.675			
$P(2)$	1479.136	1479.136	$Q(5)$	1510.745	1510.750			
$P(3)$	1479.248	1479.246	$P(2)$	1510.708	1510.707			
$P(4)$	1479.375	1479.372						
$P(5)$	1479.515	1479.512						

NOTE.—Asterisks indicate wavelengths that were obtained by recalibrating spectra of Steinmann et al. (2003a, 2003b).

(1994) in a more complex manner than originally believed. Since the majority of our experimental spectra were recorded at temperatures at which lines with $J' > 6$ were generally below the detection limit, the calibrations were done using the $^{12}C^{16}O$ and $^{13}C^{16}O$ lines with $0 \le J' \le 6$. Previously recorded spectra were recalibrated, and the improved results are included in Tables 1 and 2. The accuracy of the calibration was estimated from the difference between the literature wavelengths of the reference lines and their wavelengths as given by the calibration function. In Figure 3 this difference is plotted versus the literature wavelength of the line for every $^{12}C^{16}O$ and $^{13}C^{16}O$ reference line in the six observed bands. The standard deviations of the data in the respective bands are between 1.1×10^{-3} and 2.1×10^{-3} Å. These standard deviations are smaller than the measured linewidths (full width at half-maximum) of the spectral lines, which are typically $4-8 \times 10^{-3}$ Å. The standard deviation over all bands, 1.7×10^{-3} Å, is considered the uncertainty in the wavelength values.

As an additional test of the accuracy of the experimental wavelengths, the differences between the calibrated wavelengths of the $^{12}C^{18}O$ lines and the wavelengths obtained from the term values of Beaty et al. (1997) were calculated. The results are plotted in Figure 4. The standard deviation averaged over all bands, 1.9×10^{-3} Å, corresponds well to the uncertainty of the calibration. Although there is no significant offset from zero when averaging over all bands, individual bands in Figure 4 show small offsets in

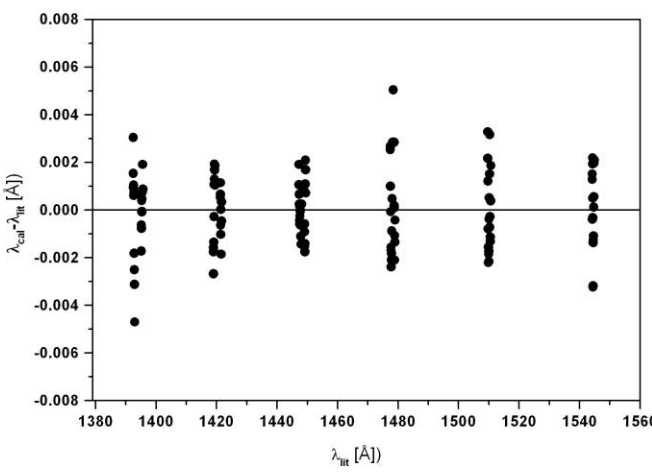

FIG. 3.—Differences between the literature wavelengths ($\lambda_{\rm lit}$) of the $^{12}C^{16}O$ and $^{13}C^{16}O$ reference lines and the wavelengths given by the calibration function ($\lambda_{\rm cal}$), showing the calibration accuracy for all six vibronic bands $A^1\Pi(v'=0\text{–}5)\text{–}X^1\Sigma^+(v''=0)$

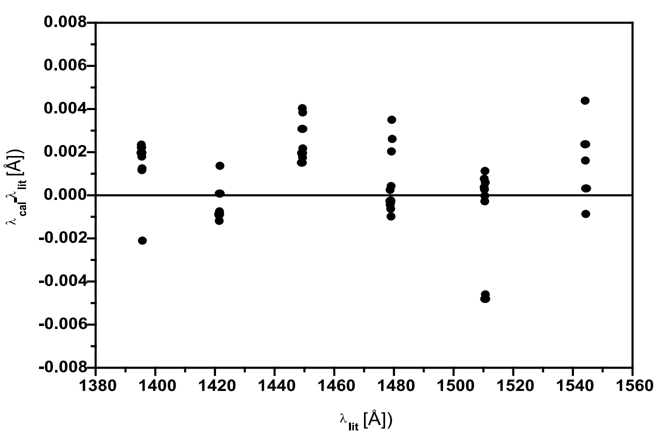

FIG. 4.—Differences between the observed $^{12}C^{18}O$ lines identified in calibrated spectra ($\lambda_{\rm cal}$) and the corresponding literature wavelengths ($\lambda_{\rm lit}$) taken from Beaty et al. (1997).

TABLE 3
COMPARISON OF HELIOCENTRIC VELOCITIES (km s^{-1}) FOR ^{12}C^{17}O AND ^{12}C^{18}O CALCULATED BY SHEFFER ET AL. AND FROM THE SPECTRAL DATA OBTAINED IN THE PRESENT STUDY

	Sheffer et al. (2002)			This Work		
Band	^{12}C^{18}O	^{12}C^{17}O	Difference	^{12}C ^{18}O	^{12}C ^{17}O	Difference
$A^1\Pi$–$X^1\Sigma^+(2, 0)$	14.8	13.8	1.0	14.8	14.3	0.5
$A^1\Pi$–$X^1\Sigma^+(3, 0)$	15.0	13.5	1.5	14.5	14.3	0.2
$A^1\Pi$–$X^1\Sigma^+(4, 0)$	14.4	13.4	1.0	14.6	14.9	−0.3
$A^1\Pi$–$X^1\Sigma^+(5, 0)$	15.9	13.5	2.4	14.4	14.2	0.2
Average	15.03	13.55	1.48	14.58	14.43	0.15

the range of -8×10^{-4} to 2.5×10^{-3} Å, in contrast to Figure 3, where all offsets are negligible. This indicates that there are systematic differences, the magnitude of which varies from band to band, between the wavelengths assigned to the ^{13}C^{16}O and ^{12}C^{18}O lines by Morton & Noreau (1994) and Beaty et al. (1997), respectively. Additional measurements with an independent wavelength calibration would be needed to resolve these differences.

The new spectral data were used as rest wavelengths in the calculation of heliocentric velocities from the spectra of ^{12}C^{17}O and ^{12}C^{18}O observed in the same interstellar region (Sheffer et al. 2002). In Table 3 the heliocentric velocities obtained from the new spectral data are compared to those calculated from the rest wavelengths that were available to Sheffer et al. The difference between the average heliocentric velocities calculated from the ^{12}C ^{17}O and ^{12}C^{18}O data has been reduced by a factor 10 by the use of the new spectral data, to a value within the experimental uncertainty of 0.4 km s^{-1}. The improvement was mostly due to the correction of a systematic error in the ^{12}C^{17}O rest wavelength values. The heliocentric velocity of the diffuse gas cloud toward X Persei can be concluded to be 14.5 ± 0.4 km s^{-1}, based on both the ^{12}C^{17}O and ^{12} C^{18}O data.

From the ^{12}C^{17}O spectral data, term values were calculated for the lowest rotational states of the $A^1\Pi(v' = 0–5)$ bands of the isotopomer, as presented in Table 4. The wavenumber values given in Table 4 are subject to experimental errors of ± 0.79 cm^{-1}, and the energy splitting between levels of *e* and *f* parity is therefore not resolved. The number of term values available was not considered sufficient for a deperturbation analysis, which would have made the smoothing of the experimental errors possible.

TABLE 4
SUMMARY OF EXPERIMENTAL TERM VALUES (cm^{-1}) FOR THE $A^1\Pi(v' = 0–5)$ LEVELS OF ^{12}C^{17}O

v'	J'	T_e	T_f
0	1	64751.62	...
1	1	66218.76	66218.74
	2	66224.88	66224.88
	3	66234.13	...
	4	66246.34	...
2	1	67646.73	67646.73
	2	67652.75	...
	3	67661.96	67661.85
	4	67674.07	67674.05
3	1	69042.89	69042.88
	2	69048.88	69048.85
	3	69057.81	69057.90
	4	69069.81	69069.79
4	1	70404.88	70404.82
	2	70410.81	70410.73
	3	70419.65	70419.54
	4	70431.44	...
5	1	71732.62	71732.66
	2	71738.37	71738.46

4. CONCLUDING REMARKS

The combination of a tunable, narrow-bandwidth VUV source and a supersonic expansion of CO has allowed us to resolve rovibronic lines in the $A^1\Pi(v' = 0-5)$–$X^1\Sigma^+(v'' = 0)$ bands for the CO isotopomers ^{12}C^{16}O, ^{13}C^{16}O, ^{12}C^{17}O, and ^{12}C^{18}O and to determine accurate laboratory measured wavelengths for ^{12}C^{17}O and ^{12}C^{18}O. The spectral results presented on 29 of the ^{12}C^{17}O lines have never been measured experimentally before. The new spectral data were used to resolve a discrepancy in the calculation of heliocentric velocities from ^{12}C^{17}O and ^{12}C^{18}O spectra measured in the interstellar medium. Experimental term values for the $J' \leq 4$ rotational states of the $A^1\Pi(v' = 0–5)$ bands of ^{12}C^{17}O were calculated, but more data on higher rotational states are needed for a deperturbation analysis. The vibronic bands that have been characterized spectroscopically in this study constitute the most relevant rovibronic CO bands in astronomical observations. Extension of this investigation to the $A^1\Pi(v' \geq 6)$–$X^1\Sigma^+(v'' = 0)$ and $A^1\Pi(v' \geq 0)$–$X^1\Sigma^+(v'' = 1)$ bands could be useful in future (Morton & Noreau 1994), although these bands have not been detected in astronomical observations yet. In addition, there is a need for laboratory measurements of a number of triplet bands of ^{12}C^{16}O, which are lacking in the literature (Eidelsberg & Rostas 2003). Some of these triplet bands have been detected in our laboratory, and a more comprehensive study is envisaged.

A. du Plessis acknowledges the South African Department of Labour for his Ph.D. bursary. The project was supported by the CSIR National Laser Centre of South Africa.

REFERENCES

Beaty, L. M., Braun, V. D., & Huber, K. P., & Le Floch, A. C. 1997, ApJS, 109, 269
Eidelsberg, M., & Rostas, F. 2003, ApJS, 145, 89
Morton, D. C., & Noreau, L. 1994, ApJS, 95, 301
Sheffer, Y., Lambert, D. L., & Federman, S. R. 2002, ApJ, 574, L171
Steinmann, C. M., Rohwer, E. G., & Stafast, H. 2003a, ApJ, 590, L123
———. 2003b, ApJ, 591, L167
Tilford, S. G., & Simmons, J. D. 1972, J. Phys. Chem. Ref. Data, 1, 147
Van Dishoeck, E. F., & Black, J. H. 1988, ApJ, 334, 771
Yamanouchi, K., & Tsuchiya, S. 1995, J. Phys. B, 28, 133