The Astrophysical Journal Letters, 714:L268–L270, 2010 May 10 doi:10.1088/2041-8205/714/2/L268

ACCURATE LABORATORY WAVELENGTHS OF THE $e^3\Sigma^-(\nu' = 5) - X^1\Sigma^+(\nu'' = 0)$ BAND OF $^{12}C^{16}O$

G. D. Dickenson[1,3], A. C. Nortje[1], C. M. Steenkamp[1], E. G. Rohwer[1], and A. Du Plessis[2]
[1] Laser Research Institute, Department of Physics, University of Stellenbosch, Private Bag X1, Matieland 7602, South Africa; cmsteen@sun.ac.za
[2] CSIR National Laser Centre, P.O. Box 395, Pretoria 0001, South Africa
Received 2010 March 8; accepted 2010 April 7; published 2010 April 20

ABSTRACT

The forbidden singlet–triplet transitions of carbon monoxide (CO) are important in the interpretation of vacuum ultraviolet interstellar absorption spectra and in particular for the measurement of large CO column densities. Twenty rovibronic lines of the $e^3\Sigma^-(\nu' = 5) - X^1\Sigma^+(\nu'' = 0)$ band of $^{12}C^{16}O$ for which laboratory wavelengths were previously unavailable were identified in laser-induced fluorescence excitation spectra. Wavelengths were assigned to five rovibronic transitions to an average accuracy of 0.0028 Å. A further 15 lines could not be fully resolved and average wavelengths were measured for these groups of closely spaced lines. A wavelength difference of 0.011 ± 0.0028 Å between the measured wavelengths and the calculated wavelengths in the atlas of Eidelsberg & Rostas demonstrates the need for more experimental data on CO.

Key words: ISM: molecules – methods: laboratory – molecular data – ultraviolet: general

1. INTRODUCTION

Carbon monoxide (CO) is the second most abundant molecule in outer space. Measurement of its absorption spectrum in the vacuum ultraviolet (VUV) by satellite-based spectrographs finds application in the determination of the column density of CO in interstellar clouds (Morton & Noreau 1994). The forbidden bands of $^{12}C^{16}O$ consisting of rovibronic transitions from the singlet $X^1\Sigma^+(\nu'' = 0)$ ground state to one of the triplet states, such as the $e^3\Sigma^-$ state, are (due to their low oscillator strengths) particularly useful for the measurement of large column densities, avoiding saturation. Calculated wavelength values for the forbidden transitions are available (Eidelsberg & Rostas 2003) but accurate laboratory-measured wavelengths for many of these transitions do not exist. We have developed a setup for high-resolution laser-induced fluorescence (LIF) spectroscopy in the VUV optimized for the investigation of these transitions (Du Plessis et al. 2007). In this Letter, we report laboratory-measured VUV wavelengths for 20 rovibronic transitions in the $e^3\Sigma^-(\nu' = 5) - X^1\Sigma^+(\nu'' = 0)$ band of $^{12}C^{16}O$ and compare them to the calculated values of Eidelsberg & Rostas (2003). We also give a brief description of the experimental parameters that were optimized to make the measurements possible.

2. EXPERIMENTAL METHOD

The experimental setup has been described in detail elsewhere (Steinmann et al. 2003) and only the features important for the detection of the forbidden lines are discussed here. Wavelength tunable, pulsed VUV laser radiation is used to excite CO in a pulsed supersonic jet. The timing of the laser pulse relative to the gas pulse is controlled by a delay generator (Stanford Research Systems, DG535). The LIF emitted by the excited CO molecules is measured as a function of the VUV excitation wavelength using a solar blind photomultiplier tube (Hamamatsu, R937). The signal from the photomultiplier is integrated using a gated boxcar integrator (Stanford Research Systems, SR250) and digitized. Custom software is responsible for control of the setup and data acquisition. Wavelength calibration was done using seven lines of the $A^1\Pi(\nu' = 3) - X^1\Sigma^+(\nu'' = 0)$ band of $^{13}C^{16}O$ (Q(1), Q(2), Q(3), P(2), P(3), P(6), and P(12)). The wavelength values of these $^{13}C^{16}O$ lines have been taken from Morton & Noreau (1994). The accuracy of these wavelengths is determined by the accuracy of the upper state term values used in their calculation, which is stated to be approximately 0.1 cm^{-1} (Haridass & Huber 1994). The standard deviation of the least-squares fit of the calibration is 1×10^{-3} Å or 0.05 cm^{-1} in terms of wavenumbers. Therefore, we consider the accuracy of the calibration to be 2×10^{-3} Å or 0.1 cm^{-1}.

3. RESULTS AND DISCUSSION

3.1. Experimental Conditions for the Detection of Forbidden Transitions

The spectral lines of the forbidden singlet–triplet rovibronic transitions that were investigated lie among lines of the allowed $A^1\Pi(\nu' = 3) - X^1\Sigma^+(\nu'' = 0)$ band of $^{13}C^{16}O$ which normally dominate the spectra and tend to obscure the weak forbidden lines. It is possible to suppress the detection of the allowed transitions by optimizing the integration gate of the boxcar integrator to exploit the longer fluorescence lifetime of the singlet–triplet transitions (Du Plessis et al. 2007). By delaying the start of the integration by a few hundred nanoseconds and lengthening the integration period, the fluorescence intensities of the singlet–triplet lines are of the same order of magnitude as that of the allowed transitions. A typical spectrum is shown in Figure 1. The second method to enhance the forbidden lines and suppress the allowed lines is to optimize the delay between the VUV pulse and the gas pulse. As can be seen from Figure 2, at a pulse delay of 0.5 ms the singlet–triplet signal is at ∼60% of its maximum whereas the singlet–singlet signal is only at 10%, giving a ratio of ∼1:1 between the two signals. At a delay of 0.8 ms, which would have been the optimized setting for the singlet–singlet fluorescence, the ratio between the two signals would be 1:13. The best signal-to-noise ratio was obtained by operating the supersonic jet with one bar of CO gas.

3.2. Results on Forbidden Transitions of CO

A total of 20 rovibronic transitions for which laboratory wavelengths were previously unavailable were identified in our

[3] Current address: Laser Centre Vrije Universiteit, de Boelelaan 1081, 1081 HV, Amsterdam, The Netherlands.

Table 1
Transitions of the $e^3\Sigma^- - X^1\Sigma^+$ (5 0) Band that could be Resolved Individually and Compared to Calculated Wavelengths of Eidelsberg & Rostas (2003)

Line	Calculated Wavelength (Å)	Measured Wavelength (Å)	Wavelength Uncertainty[a] (Å)	Number of Times Observed	m-c (Å)	m-c (cm^{-1})
$R(0)F_1$	1449.538	1449.552	4.6×10^{-3}	15	1.4×10^{-2}	−0.67
$R(0)F_3$	1449.394	1449.405	2.3×10^{-3}	16	1.1×10^{-2}	−0.52
$R(1)F_3$	1449.324	1449.333	1.9×10^{-3}	16	9×10^{-3}	−0.43
$R(6)F_3$	1449.441	1449.452	2.5×10^{-3}	8	1.1×10^{-2}	−0.52
$P(2)F_1$	1449.781	1449.793	1.2×10^{-2}	3	1.2×10^{-2}	−0.57
Ave	...	...	2.8×10^{-3}	...	1.1×10^{-2}	−0.54

Note. [a] The wavelength uncertainty is the standard deviation of the wavelength values obtained from different independent observations. The average of this column is based on the first four lines where the number of observations allows statistical analysis.

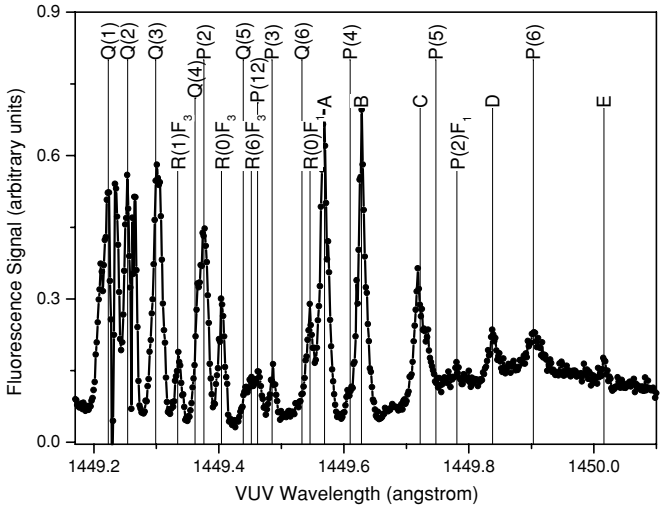

Figure 1. Spectrum showing the forbidden triplet lines of the $e^3\Sigma^- - X^1\Sigma^+$ (5 0) band of $^{12}C^{16}O$ labeled by the lower set of labels and A–E for the partially resolved bands. The upper labels are the singlet–singlet transitions of the $A^1\Pi - X^1\Sigma^+$(3 0) band used for calibration of the spectra.

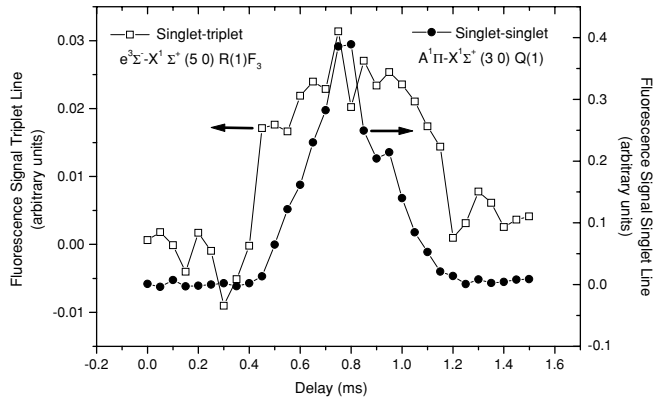

Figure 2. Comparison between the fluorescence signal of a singlet–singlet transition and a singlet–triplet transition as a function of the delay between the VUV and gas pulse.

spectra as shown in Figure 1. The lines recorded in the spectra are from the $e^3\Sigma^- - X^1\Sigma^+$ (5 0) band. Five of these transitions, $R(0)F_1$, $R(0)F_3$, $R(1)F_3$, $R(6)F_3$, and $P(2)F_1$, were resolved individually.[4] In Table 1, measured wavelengths obtained for these transitions are listed and compared to calculated values of

[4] The lines are labeled according to the scheme used in the tables of Eidelsberg & Rostas (2003).

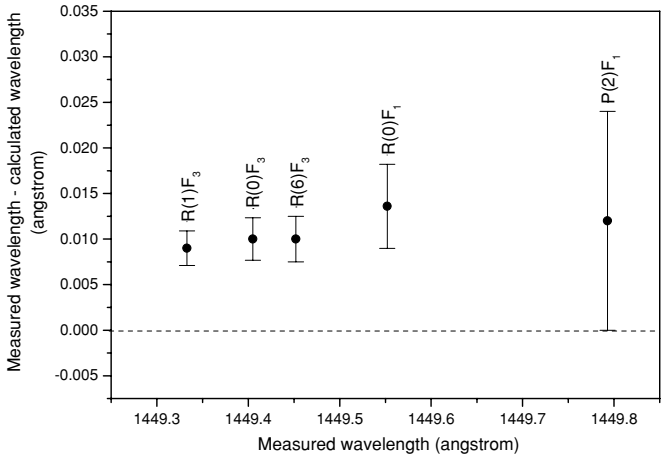

Figure 3. Difference between the average of the measured wavelengths for each transition and the calculated wavelengths of Eidelsberg & Rostas (2003). The wavelength uncertainties of the measurements are plotted as error bars.

Eidelsberg & Rostas (2003). Each measured wavelength value given in Table 1 is the mean of the measured wavelength values obtained from a number of independent observations of the particular transition. The standard deviation of the data for each transition is considered the experimental uncertainty, as given in Table 1. The standard deviation values confirm an average experimental uncertainty of 2.8×10^{-3} Å. It was not possible to resolve the other 15 lines individually and therefore average wavelengths were obtained for each group of closely spaced transitions labeled A–E in Figure 1. These wavelengths are listed and compared to calculated wavelengths in Table 2.

For the five transitions that could be resolved, a systematic difference between the measured wavelengths and the wavelengths calculated by Eidelsberg & Rostas (2003) exists. In Figure 3, the difference between the measured wavelength values and the calculated wavelengths are plotted with the standard deviations of the measured wavelengths as error bars. With the exception of the $P(2)F_1$ line, which was rather weak and detected in only three of the recorded spectra, it is clear that the wavelength difference between the measured wavelengths and the calculated values of Eidelsberg & Rostas (2003) is significantly larger than the uncertainty in the measurement. The average difference from the calculated wavelengths for the five transitions is 0.01(1) Å or 0.5(4) cm^{-1}, with the calculated line blueshifted relative to the measured line. In the case of the 15 lines that could not be resolved fully there is a trend toward a blueshift of the calculated line relative to the measured line, although the shift cannot

Table 2
Transitions of the $e^3\Sigma^- - X^1\Sigma^+$ (5 0) Band that could not be Resolved Individually Compared to Calculated Wavelengths of Eidelsberg & Rostas (2003)

Line	Peak Label	Calculated Wavelength (Å)	Measured Wavelength (Å)	Number of Times Observed	m-c (Å)	m-c (cm^{-1})
$R(1)F_1$	A	1449.570	1449.574	15	4×10^{-3}	−0.19
$Q(1)F_2$	A	1449.562	1449.574	15	1.2×10^{-2}	−0.57
$R(7)F_3$	A	1449.562	1449.574	15	1.2×10^{-2}	−0.57
$Q(2)F_2$	B	1449.623	1449.637	15	1.4×10^{-2}	−0.67
$P(2)F_3$	B	1449.637	1449.637	15	0	0
$R(2)F_1$	B	1449.633	1449.637	15	4×10^{-3}	−0.19
$R(3)F_1$	C	1449.725	1449.734	13	8×10^{-3}	−0.43
$P(3)F_3$	C	1449.728	1449.734	13	6×10^{-3}	−0.29
$Q(3)F_2$	C	1449.716	1449.734	13	1.7×10^{-2}	−0.86
$R(8)F_3$	C	1449.709	1449.734	13	2.4×10^{-2}	−1.19
$Q(4)F_2$	D	1449.839	1449.838	1	-1×10^{-3}	0.05
$R(4)F_1$	D	1449.849	1449.838	1	-1.1×10^{-2}	0.52
$P(4)F_3$	D	1449.851	1449.838	1	-1.3×10^{-2}	0.62
$R(5)F_1$	E	1450.003	1450.016	1	1.3×10^{-2}	−0.62
$P(5)F_3$	E	1450.005	1450.016	1	1.1×10^{-2}	0.62

Note. For J higher than 6, the MOLAT database was consulted (Eidelsberg & Rostas 2006).

be quantified from our data. We recommend that the calculated wavelengths of these lines could be refined by the addition of 0.01(1) Å. The differences between our measured wavelengths and the calculations for the $e^3\Sigma^-(v' = 5) - X^1\Sigma^+(v'' = 0)$ are significant for the following reasons. First, the average wavelength difference is larger than our average experimental uncertainty with a factor of approximately 4. Second, the magnitudes of the differences are relatively large when compared to the data on the other vibronic bands given in the paper of Eidelsberg & Rostas (2003). Of the 187 lines of the $e^3\Sigma^-(v') - X^1\Sigma^+(v'' = 0)$ system for which measured wavelengths are given, only ∼7.5% show differences larger than 0.4 cm^{-1}. We do not currently have an explanation for the difference between measured and calculated wavelengths. Our measured spectra essentially enforce comparison of the experimental $A^1\Pi(v' = 3) - X^1\Sigma^+(v'' = 0)$ $^{13}C^{16}O$ data of Haridass & Huber (1994) and the model of the $e^3\Sigma^-(v' = 5) - X^1\Sigma^+(v'' = 0)$ $^{12}C^{16}O$ band by Eidelsberg & Rostas (2003) a revision of either, together with further spectroscopic investigation of the forbidden $^{12}C^{16}O$ transitions may be needed to resolve the question.

4. CONCLUDING REMARKS

In summary, we have obtained experimentally measured wavelengths for the first time for five transitions in the $e^3\Sigma^-(v' = 5) - X^1\Sigma^+(v'' = 0)$ band and average wavelengths for 15 partially resolved lines. A reduction in the VUV bandwidth will be necessary in order to fully resolve the remaining 15 lines. As illustrated in Figure 3, the significant differences between our measured wavelengths and those calculated by Eidelsberg & Rostas (2003) are obtained. The calculated wavelengths are blueshifted relative to our measurements by 0.011 ± 0.0028 Å, where the error is our experimental uncertainty. Applied to the interpretation of astronomical observations the magnitude of these differences will yield errors of more than 100% in the calculation of non-relativistic heliocentric velocities, such as that of CO in interstellar medium toward X Persei (Sheffer et al. 2002). This demonstrates the need for further spectroscopic investigation of the forbidden singlet–triplet transitions of $^{12}C^{16}O$ in order to understand these differences between model and experiment and improve the data available to the astrophysics community.

G.D.D. acknowledges the Harry Crossley Foundation, the National Research Foundation of South Africa, the CSIR National Laser Centre, and the University of Stellenbosch for financial assistance. G.D.D. is grateful for the fruitful discussions with fellow colleagues Mr. G. W. Bosman, Dr. P. H. Neethling, and Mr. A. Heidt, as well as all the technical assistance received from Mr. U. Deutchlander, Mr. E. Shields, and Mr. J. Germishuizen.

REFERENCES

Du Plessis, A., Rohwer, E., & Steenkamp, C. 2007, J. Mol. Spectrosc., 243, 124
Eidelsberg, M., & Rostas, F. 2003, ApJS, 145, 89
Eidelsberg, M., & Rostas, F. 2006, Atlas of Intersystem Transistions of CO, Molat, l' Observatoire de Paris, http://molat.obspm.fr/index.php?page=pages/Molecules/CO-Michele/CO.php
Haridass, C., & Huber, K. 1994, ApJ, 420, 433
Morton, D., & Noreau, L. 1994, ApJS, 95, 301
Sheffer, Y., Lambert, D., & Federman, S. 2002, ApJ, 574, L171
Steinmann, C., Rohwer, E., & Stafast, H. 2003, ApJ, 590, L123