Differential Laser Absorption Spectrometry for Global-Scale Monitoring of Atmospheric Carbon Dioxide: Selection of Optimum Sounding Frequencies for High Precision Measurements

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Abstract

The spectroscopic requirements of the transmitter laser wavelengths for a proposed space-borne laser absorption spectrometer are discussed. Results suggest several candidates for lower troposphere carbon dioxide measurements in the (30013 ← 00001), (30012 ← 00001) and (20013 ← 00001) bands.

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Introduction

The United States Global Change Research Program recently established its Carbon Cycle Science (CCS) initiative[1] in order to construct a comprehensive framework for the description and modeling of the global carbon cycle. An important component is the push for high-resolution global-scale measurements of tropospheric carbon dioxide to evaluate sources and sinks.

The laser absorption spectrometry (LAS) approach to global CO_2 measurement utilizes laser illumination of the Earth's surface from orbit with subsequent analysis of the differentially attenuated multi-wavelength coherently detected surface backscatter signature to retrieve target trace gas mixing ratios within the instrumental field-of-view. Preferential weighting of selected altitudes within the total column would be achieved by tuning the transmitter laser across a known, well-characterized CO_2 absorption line. By this means we propose that high accuracy (~0.3% or 1 ppm) profilometry of the tropospheric CO_2 mixing ratio will be feasible with a vertical resolution of 2 km at the lowest altitudes and 3-4 km in the mid- and upper-troposphere, and a horizontal resolution of 100 km.

Early experiments with an airborne coherent LAS instrument have demonstrated the utility of the technique for inferring column-average mixing ratios of ozone[2], while the same instrument has also been applied to the remote discrimination of surface petrology[3]. The principles underlying the tailored weighting function approach to LAS have been outlined previously[4] and form the basis for this study.

The spectroscopic requirements on probe wavelengths were first considered in the range where suitably powerful and compact transmitter lasers are or may become available: the (30012 $\leftarrow$ 00001) band of CO_2 in 1.57 - 1.58 μm range, (30013 $\leftarrow$ 00001) band near 1.6 μm and (20013 $\leftarrow$ 00001) band in the 2.05 - 2.07 μm range. The goal here is to identify CO_2 absorption lines in these ranges whose absorption coefficient is below a certain threshold susceptibility to uncertainties in knowledge of the atmospheric temperature profile. Weighting functions, as prescribed in ref. 4, were calculated at and near the selected frequencies to reveal the targeted altitudes. An iteration process of determining the temperature susceptibility and matching weighting functions peaks to desired altitudes then leads to the final selection of sounding frequencies proposed for the LAS instrument.

Spectroscopic considerations

The HITRAN 96 database[5] was first consulted for various parameters in the CO_2 line listing at the reference temperature of 296 K (T_o): the line frequency (ν_o), molecular line intensity ($S(T_o)$), air-broadened halfwidth ($\gamma(T_o)$), its coefficient of temperature dependence (n), and the lower level energy (E"). The absorption line is predominantly pressure broadened in the troposphere obeying the Lorentzian profile: $g(\nu-\nu_o) = (\gamma(T) / \pi) / [(\nu-\nu_o)^2 + \gamma(T)^2]$, where $\gamma(T) = \gamma(T_o)\,(T_o / T)^n$.

The Beer-Lambert law defines the optical depth for a pathlength L (km) and pressure P_a (atm): $OD = \alpha(\nu)\, P_a\, L$. The linear absorption coefficient per unit atmosphere of gas $\alpha(\nu) = N(T)\, S(T)\, g(\nu-\nu_o)$. Assuming a constant pressure, $\alpha(\nu) = N_L\ S(T_o)\,(T_o/T)\,(\gamma / \pi) / [(\nu-\nu_o)^2 + \gamma^2] \exp(1.439\, E"\, (1/T_o - 1/T))$ (where N_L = Loschmidt's number = 2.479×10^{19} molecules/cm^3-atm) when the transition frequencies satisfy the condition that hcv >> kT (k is the Boltzmann constant)[6]. This condition holds true for the infrared spectral region under consideration here.

Temperature susceptibility analysis

For the present purpose, the temperature susceptibility of an absorption line is used to understand what limits the accuracy of LAS measurements in the context of an Earth orbiting instrument for global-scale measurements. We define this as the equivalent mass mixing ratio change relative to temperature (expressed in the units of ppm/K), which indicates the measurement error expected due to 1 K uncertainty in the temperature knowledge.

Transmission spectra with the resolution of 0.01 cm^{-1} are calculated for different temperatures (at 270, 280 and 290 K) using a commercially available software package[7], assuming constant pressure of 1 atm and CO_2 concentration of 360 ppm (in absence of any other molecule species) for a path of 500 meters. The rate of change in absorption relative to temperature is obtained and subsequently multiplied with a conversion factor of 360 ppm per % absorption (at the temperature of interest, here 280 K) to give the temperature susceptibility. The least temperature susceptible absorption line is identified via numerical comparison. Its E" is then extracted from the HITRAN96 database.

Weighting function analysis

A line-by-line atmospheric radiative transfer model (GENLN2)[8] is used to calculate the transmittance profiles for a range of frequencies across a CO_2 absorption line from the Earth's surface to 30 km altitude, assuming absorption due to CO_2 molecules only and a surface temperature of 296 K, in the 1976 US standard, mid-latitude summer and mid-latitude winter atmospheres[9]. The transmittance profiles are first converted to optical depth profiles, and the weighting functions are obtained by taking the derivative of optical depth with respect to pressure[4]. Appropriate sounding frequencies are identified by matching the weighting function peaks to altitudes of interest in the troposphere.

Results

The initial consideration of temperature susceptibility at absorption line center suggests that E" of the least temperature susceptible line is 106.1 cm^{-1}. The weighting functions at line centers, however, peak at altitudes higher than the troposphere. It was determined that for a molecular line intensity on the order of 10^{-23} cm/molecule in the (30013 $\leftarrow$ 00001) and (30012 $\leftarrow$ 00001) bands or 10^{-22} cm/molecule in the (20013 $\leftarrow$ 00001) band, weighting functions would peak in the lower troposphere at frequencies at least one half-width from the line centers. However, the total transmittance is much less for sounding frequencies in the (20013 $\leftarrow$ 00001) than in the (30013 $\leftarrow$ 00001) and (30012 $\leftarrow$ 00001) bands. To improve it, these frequencies should be tuned to 2 or 3 half-widths from the absorption line centers.

Listed in table 1 is the final selection of the proposed transmitter frequencies obtained from considering temperature susceptibility at frequencies one half-width from the line centers in the (30013 $\leftarrow$ 00001) and (30012 $\leftarrow$ 00001) bands and three half-widths from the line centers in the (20013 $\leftarrow$ 00001) band. In the (30013 $\leftarrow$ 00001) band, the associated temperature susceptibility for 6207.2461 cm^{-1} (1.6115 μm) was not calculated because it is outside the frequency range of present interest. In the (20013 $\leftarrow$ 00001) band, the temperature susceptibility at three half-widths from 4828.4299 cm^{-1} was relatively higher due to interference from neighboring absorption lines in the weaker (40002 $\leftarrow$ 01101) band.

Shown in figures 1-3 are the absorption stick plots in the regions of interest. In contrast to the absorption spectra for the (30013 $\leftarrow$ 00001) and (30012 $\leftarrow$ 00001) bands, interference becomes a concern in the final selection of transmitter frequencies due to the close spacing between lines in the (20013 $\leftarrow$ 00001) band and thus limits the choices to the two proposed transmitter frequencies. Figures 4 and 5 are the representative plots of the transmittance profiles and weighting functions for the proposed transmitter frequencies from the three CO_2 absorption bands.

This work was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration.

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	Absorption line center (cm^{-1})	Molecular line intensity (cm/molec)	Half-width (cm^{-1})	E" (cm^{-1})	Branch assignment	Proposed transmitter frequency (cm^{-1})	Temperature susceptibility at 280 K (ppm/K)
(30013 ← 00001)	6207.2461	1.320E-23	.0701	234.0833	P24	--	--
	6245.1237	1.514E-23	.0698		R24	6245.06, 6245.2	0.055
(30012 ← 00001)	6327.0614	1.317E-23	.0701	234.0833	P24	6326.99, 6327.13	0.041
	6364.9225	1.517E-23	.0698		R24	6364.85, 6364.99	0.055
(20013 ← 00001)	4828.4299	1.513E-22	.0686	362.7882	P30	4828.22	0.13
	4875.7490	1.741E-22	.0684		R30	4875.54	0.057

Table 1 Temperature susceptibilities and spectroscopic parameters at the proposed transmitter frequencies for LAS.

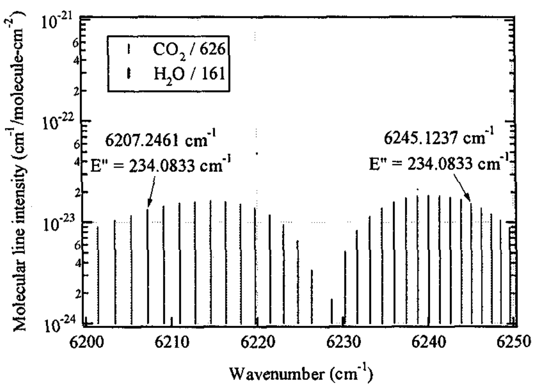


Figure 1 Absorption stick plot from 6200 cm^{-1} to 6250 cm^{-1} in the (30013 ← 00001) band.

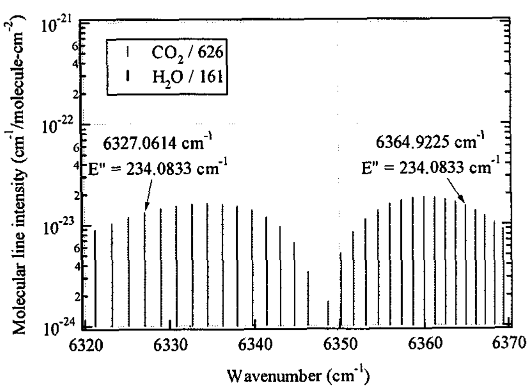


Figure 2 Absorption stick plot from 6320 cm^{-1} to 6320 cm^{-1} in the (30012 ← 00001) band.

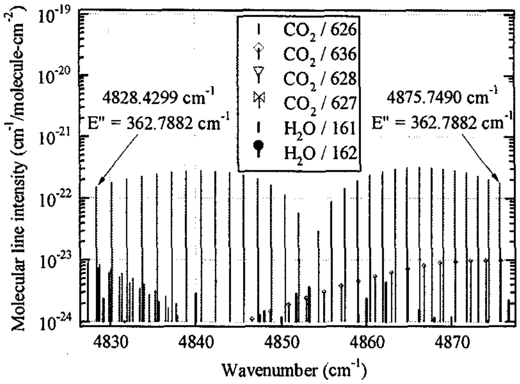
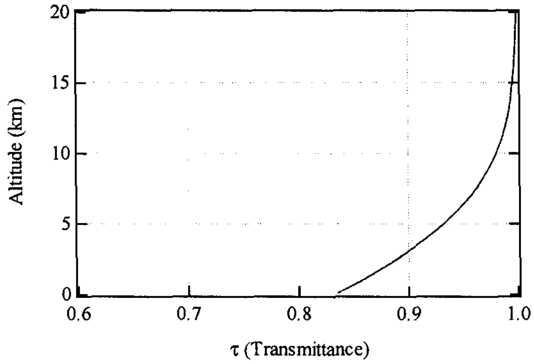


Figure 3 Absorption spectrum from 4827 cm^{-1} to 4877 cm^{-1} in the (20013 ← 00001) band.

(a)



(b)

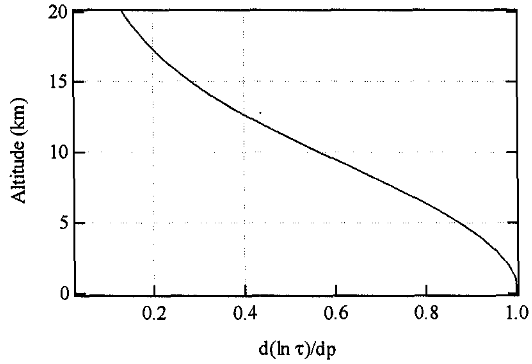
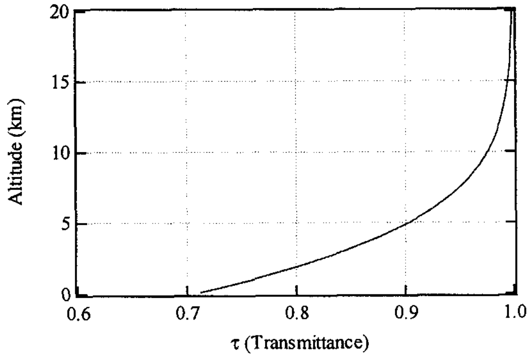


Figure 4 (a) Transmittance profile
(b) weighting function at one half-width from the line center in the (30013 ← 00001) band at 6245.1938 cm^{-1} (0.0701 cm^{-1} offset from 6245.1237 cm^{-1}).

(a)



(b)

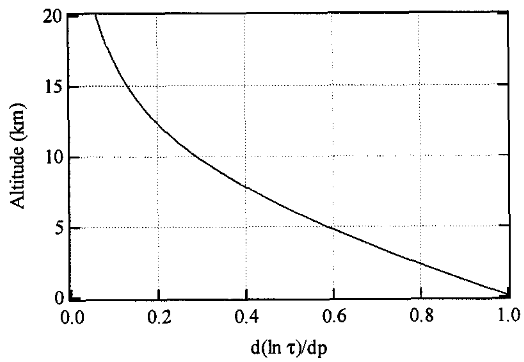


Figure 5 (a) Transmittance profile
(b) weighting function at three half-widths from the line center in the (20013 ← 00001) band at 4875.5440 cm^{-1} (0.2050 cm^{-1} offset from 4875.749 cm^{-1}).