

Temperature Dependence of Absorption Cross-section for IR Spectra

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August 5, 2004

Contents

1	Introduction	4
2	Absorption Coefficient Analysis	5
2.1	Line Intensity Calculation	5
2.1.1	Internal Partition Sum $Q(T)$	6
2.2	Temperature Correlation of Line Intensity	8
2.3	Temperature and Pressure Correlation of Line Halfwidth	8
2.4	Pressure Shift of Line Position	8
2.5	Absorption Cross Section	9
2.6	Temperature Dependence of Absorption Cross-Sections	12
2.6.1	Comparison with EPA spectra	15
2.6.2	Temperature Dependence	16
2.6.3	Pressure Dependence	19
2.6.4	Partial Pressure Dependence	19

List of Figures

2.1	Absorption Coefficient of Methane and Ethane at 296 K 1 atm	10
2.2	Absorption Coefficient of Methane and Ethane at 296 K 1 atm	11
2.3	Methane Absorption Coefficient Versus Temperature	13
2.4	Ethane Absorption Coefficient Versus Temperature	14
2.5	Absorbance Spectra of Methane and Ethane	15
2.6	Methane Spectra Comparison, EPA vs. HITRAN	17
2.7	Ethane Spectra Comparison, EPA vs. HITRAN	18
2.8	Temperature Dependence of Methane and Ethane Absorption	19
2.9	Pressure Dependence of Methane and Ethane Absorption . .	20
2.10	Partial Pressure Dependence of Methane and Ethane Absorption	20

List of Tables

- 2.1 Rotational and Vibrational Functions, HITRAN Database 1972 7
- 2.2 Temperature dependence of methane and ethane absorption . 16

Chapter 1

Introduction

This report describes model simulations and calculations of methane and ethane spectra from the HITRAN (High Resolution Transmission) molecular spectroscopic database and associated molecular databases by proper utilization of the JavaHAWKS software package. Methane and ethane absorption cross-sections at near IR region are computed with different temperature and pressure conditions. The computed spectra is compared with experimental spectra data from NIST, EPA, MOTRAN and PNNL. Finally, the computed spectra are used to estimated system performance for a DIAL (Differential Absorption Lidar) instrument on a platform at 500 m altitude under different weather conditions.

Chapter 2

Absorption Coefficient Analysis

The HITRAN Atmospheric Workstation is the latest version in a series of updates and enhancements to the international standard atmospheric molecular spectroscopic database. HITRAN has traditionally supplied the necessary input for the molecular absorption part of the total attenuation in Lambert-Beer's law calculations that are used in various optical performance models, more especially the MOTRAN model.

In order to compute the transmittance due to a given spectral line in the atmosphere it is necessary to describe the absorption coefficient as a function of frequency for each line. The four essential line parameters for each line are the resonant frequency, $\nu_0(cm^{-1})$, the intensity per absorbing molecule, $S(cm^{-1}/molecule \cdot cm^{-2})$, the Lorentz line width parameter, $\alpha_0(cm^{-1}/atm)$, and the energy of the lower state, $E''(cm^{-1})$.

2.1 Line Intensity Calculation

The HITRAN database has used a quantum mechanical model to calculate line intensity. The line intensity S is pressure and temperature dependent and can be calculated from E'' and ν .

Radiative transfer theory for the two states for a vibrational-rotational system defines the spectral line intensity as, [3]

$$S_{\eta\eta'} = \frac{h\nu_{\eta\eta'}}{c} \frac{n_{\eta}}{N} \left(1 - \frac{g_{\eta}}{g_{\eta'}} \frac{n_{\eta'}}{n_{\eta}} \right) B_{\eta\eta'} \quad (2.1)$$

where $B_{\eta\eta'}$ [$cm^3/(ergs s^2)$] is the Einstein coefficient for induced absorp-

tion, n_η and n'_η are the populations of the lower land upper states, respectively, g_η and g'_η are the state statistical weights, and N is the molecular number density. [3] The Einstein Coefficient $B_{\eta\eta'}$ is related to the weighted transition-moment squared $\Re[Debye^2 = 10^{-36} ergs cm^3]$, by

$$\Re_{\eta\eta'} = \frac{3h^2}{8\pi^3} B_{\eta\eta'} \times 10^{36}. \quad (2.2)$$

Assuming local thermodynamic equilibrium (LTE), the populations partition between states is governed by Boltzmann statistics at ambient temperature $T [K]$. Then we have,

$$\begin{aligned} \frac{g_\eta n_{\eta'}}{g_{\eta'} n_\eta} &= \exp(-c_2 \nu_{\eta\eta'} / T) \\ \text{and } \frac{N_\eta}{N} &= \frac{g_\eta \exp(-c_2 E_\eta / T)}{Q(T)} \end{aligned} \quad (2.3)$$

where E_η is the lower state energy [cm^{-1}], and c_2 the second radiation constant = $hc/k = 1.4388 cm K$. The total internal partition sum $Q(T)$ will be discussed later in this chapter.

Substituting 2.2 and 2.3 in 2.1, the spectral line intensity is given by

$$S_{\eta\eta'}(T) = \frac{8\pi^3}{3hc} \nu_{\eta\eta'} \frac{g_\eta \exp(-c_2 E_\eta / T)}{Q(T)} [1 - e^{-c_2 \nu_{\eta\eta'} / T}] \Re_{\eta\eta'} \times 10^{-36}. \quad (2.4)$$

This algorithm is used in HITRAN to calculate spectral line intensity. The spectral line intensity profiles at reference temperature for different species are given in HITRAN database.

2.1.1 Internal Partition Sum $Q(T)$

The usual classical approximation for the calculation of Internal Partition Sum is base upon splitting partition function to independent temperature variations of the rotational and vibrational components.

$$Q(T) = Q_v(T) Q_r(T) \quad (2.5)$$

where Q_v and Q_r are the vibrational and rotational partition functions.

Vibrational partition functions

The vibrational partition functions Q_v of methane for the most abundant isotopes of methane are given in Table 2.1. The partition functions for the other isotopes are similar. The data source is from 1972 HITRAN database. There is less than 1% variation within temperature range 175K to 325K. It is shown by Herzberg [1] that the variations of vibrational partition functions are negligible for both methane and ethane under atmospheric temperature conditions.

Rotational partition functions

The formula for the rotational partition functions are different for linear, symmetric, and asymmetric top molecules. Herzberg [1] gives rotational partition functions for both methane and ethane,

$$\begin{aligned} Q_r(\text{methane}) &= 1.02704 \sqrt{\frac{T^3}{B^2 A}} \\ Q_r(\text{ethane}) &= \frac{1}{\sigma} \frac{\pi}{A_1 B} \left(\frac{kT}{hc} \right)^2 \end{aligned} \quad (2.6)$$

Table 2.1: Rotational and Vibrational Functions, HITRAN Database 1972

Molecule	175	200	225	250	275	296	325
CH_4	1.000	1.000	1.001	1.002	1.004	1.007	1.011

In conditions that the temperature is neither very high nor very low, the classical algorithm for partition functions does not give significant error. Therefore, we can use the algorithm described above to calculate the temperature dependence of spectral line intensity.

The HITRAN database has used as improved algorithm to provide a set of internal partition sums with the greatest possible degree of accuracy in the temperature range 70-3000 K [2]. However, it is not necessary here since we are studying the molecule species under atmospheric temperatures in the range 250 K - 325 K in general. Classical approximation is good enough for our calculation.

2.2 Temperature Correlation of Line Intensity

From Equation 2.4, and 2.6, we can use the following expression to calculate the correlation of line intensity. Also, we can calculate $S_{\eta\eta'}(T)$ from the HITRAN quantity $S_{\eta\eta'}(T_{ref})$,

$$\frac{S_{\eta\eta'}(T)}{S_{\eta\eta'}(T_{ref})} = \left(\frac{T_{ref}}{T}\right)^j \frac{e^{-c_2 E_{\eta}/T}}{e^{-c_2 E_{\eta}/T_{ref}}} \frac{(1 - e^{-c_2 \nu_{\eta\eta'}/T})}{(1 - e^{-c_2 \nu_{\eta\eta'}/T_{ref}})} \quad (2.7)$$

$j = 1.5$ for methane, $j = 2$ for ethane.

Since $S_{\eta\eta'}(T_{ref})$, E_{η} and $\nu_{\eta\eta'}$ are given by HITRAN database, $S_{\eta\eta'}(T)$ can be calculated for given temperature T .

2.3 Temperature and Pressure Correlation of Line Halfwidth

The pressure and temperature broadened line halfwidth $\gamma(p, T)$ for a gas at pressure p [atm], temperature T [K], and partial pressure p_s [atm], is given as,

$$\gamma(p, T) = \left(\frac{T_{ref}}{T}\right)^n [\gamma_{air}(p_{ref}, T_{ref})(p - p_s) + \gamma_{self}(p_{ref}, T_{ref})p_s] \quad (2.8)$$

where $\gamma_{air}(p_{ref}, T_{ref})$ and $\gamma_{self}(p_{ref}, T_{ref})$ are the air-broadened and self-broadened halfwidth at half maximum (HWHM) [cm^{-1}/atm] at $T_{ref} = 296 K$ and $p_{ref} = 1 atm$, respectively. The value n is the coefficient of temperature dependence of the air-broadened halfwidth as appearing in the relation,

$$\gamma_{air}(p_{ref}, T) = \gamma_{air}(p_{ref}, T_{ref})(T_{ref}/T)^n \quad (2.9)$$

and p_s is the partial pressure of the gas species mixed in the atmosphere. $\gamma_{air}(p_{ref}, T_{ref})$, $\gamma_{self}(p_{ref}, T_{ref})$ and n are given in HITRAN database, which can be used to calculate Line Halfwidth $\gamma(p, T)$ at certain temperature and pressure.

2.4 Pressure Shift of Line Position

The pressure shift of line position is given by,

$$\nu_{\eta\eta'}^* = \nu_{\eta\eta'} + \delta p \quad (2.10)$$

where δ [cm^{-1}/atm] is the air-broadened pressure shift at $T_{ref} = 296 K$ and $p_{ref} = 1 atm$, of the line transition frequency $\nu_{\eta\eta'}$. δ is also given by HITRAN database for each line transition frequency.

2.5 Absorption Cross Section

Calculation of the absorption coefficient from line intensity and halfwidth functions, at normal temperature and pressure, uses the line shapes of the broadened transition lines following the Lorentz shape,

$$f(\nu, \nu_{\eta\eta'}, T, p) = \frac{\gamma(p, T)}{\pi\gamma(p, T)^2 + \pi[\nu - \nu_{\eta\eta'}^*p]^2} \quad (2.11)$$

The absorption cross-section $\sigma(\nu, p, T)$ [$cm^2/molecule$] is given by

$$\sigma(\nu, p, T) = S_{\eta\eta'}(T)f(\nu, \nu_{\eta\eta'}, T, p) \quad (2.12)$$

Figure 2.1 and 2.2 show the calculated spectra on wavenumber and wavelength scales, respectively.

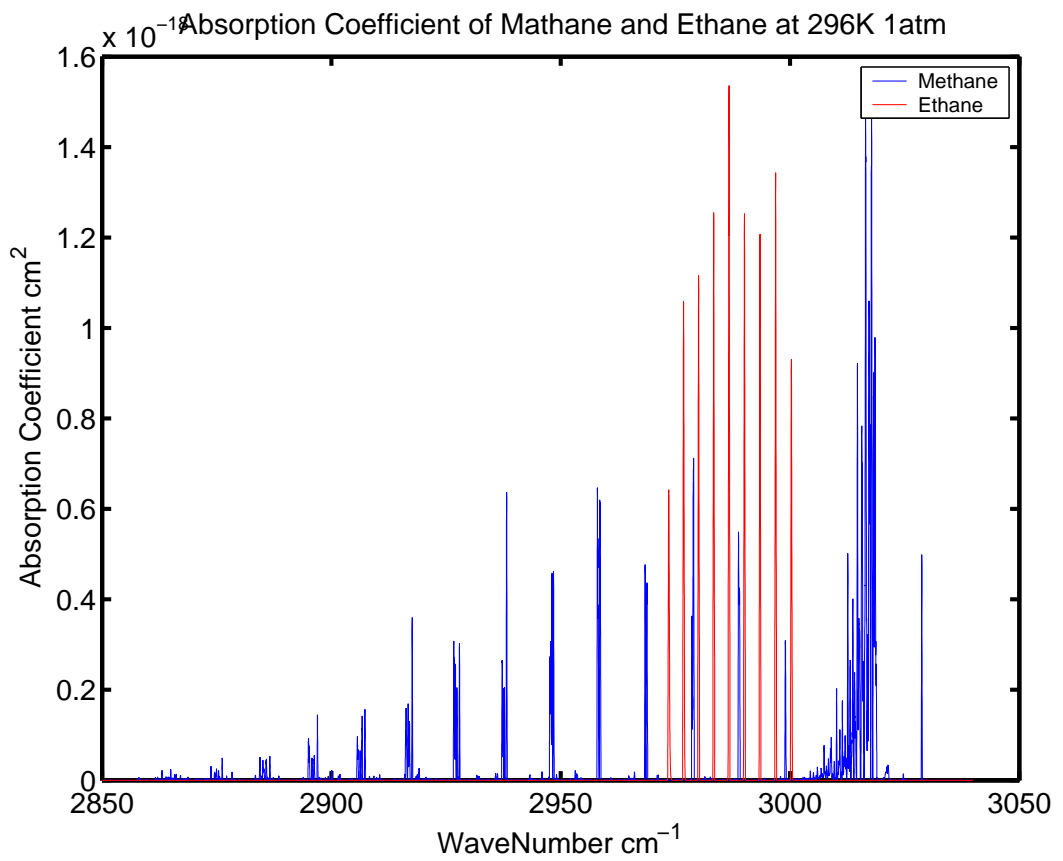


Figure 2.1: Absorption Coefficient of Methane and Ethane at 296 K 1 atm

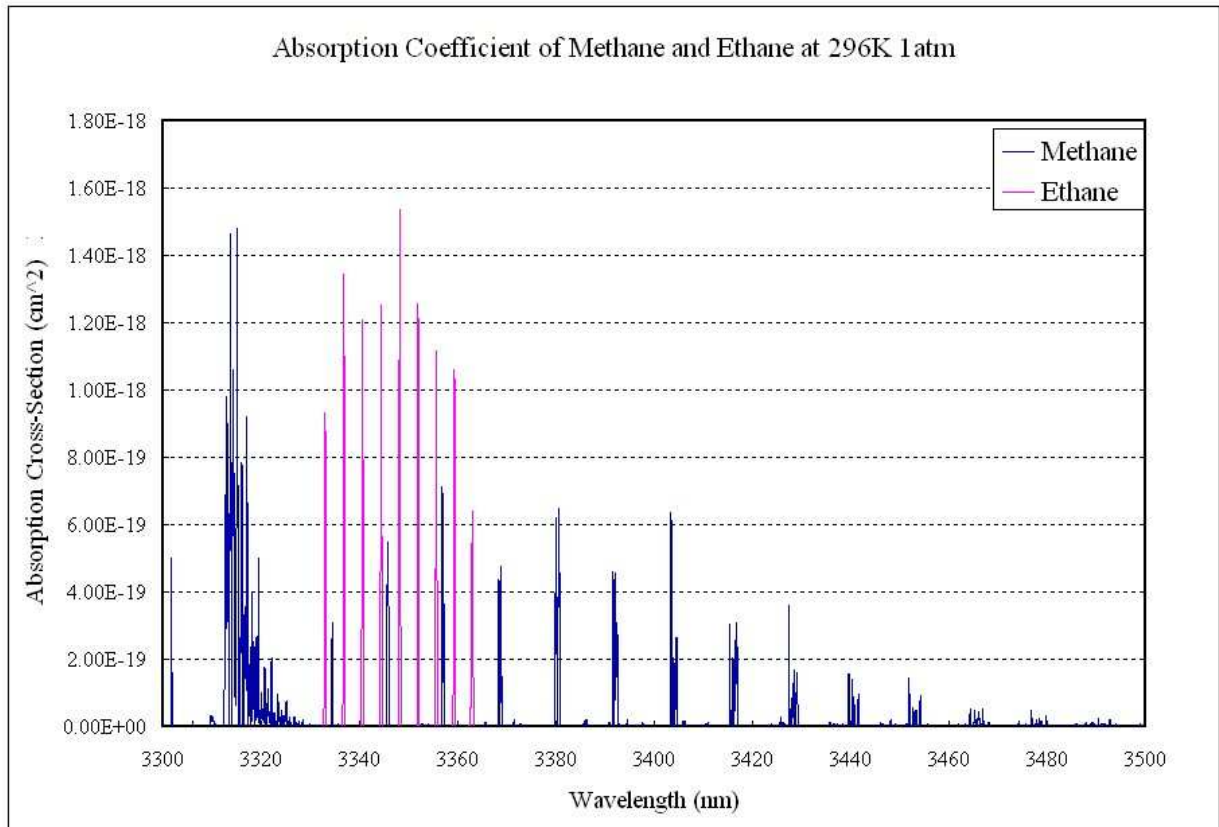


Figure 2.2: Absorption Coefficient of Methane and Ethane at 296 K 1 atm

2.6 Temperature Dependence of Absorption Cross-Sections

From Equations 2.7, 2.8, 2.9, 2.10, and 2.11, we can calculate the absorption cross-sections corresponding to a particular temperature conditions.

Figure 2.3 shows the methane absorption coefficients at a chosen wavelength (3429 nm) for different temperature conditions. We can see significant changes of the magnitude of absorption coefficients with the changes of temperature. The results presented in the figures show that the absorption coefficient increases with the increase of temperature. Figure 2.4 shows the ethane absorption coefficients at a chosen absorption wavelength (3429 nm) corresponding to different temperature conditions. However, the ethane absorption coefficient decreases with the increase of temperature.

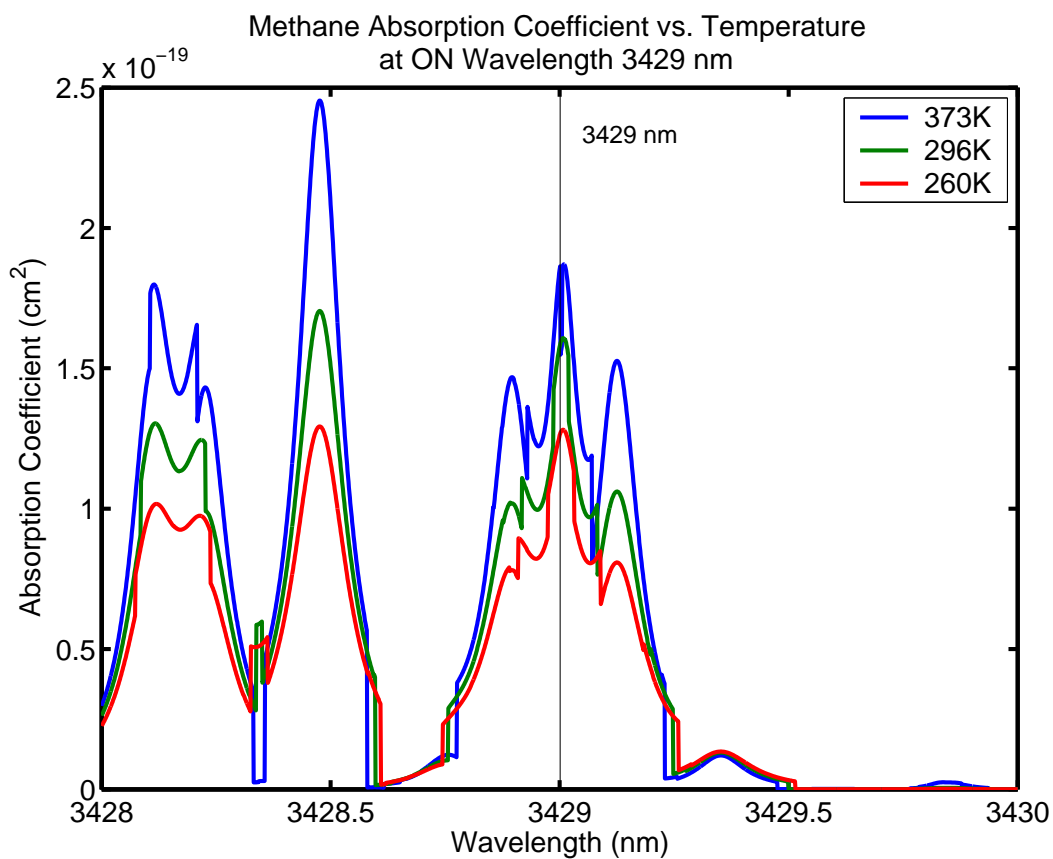


Figure 2.3: Methane Absorption Coefficient Versus Temperature

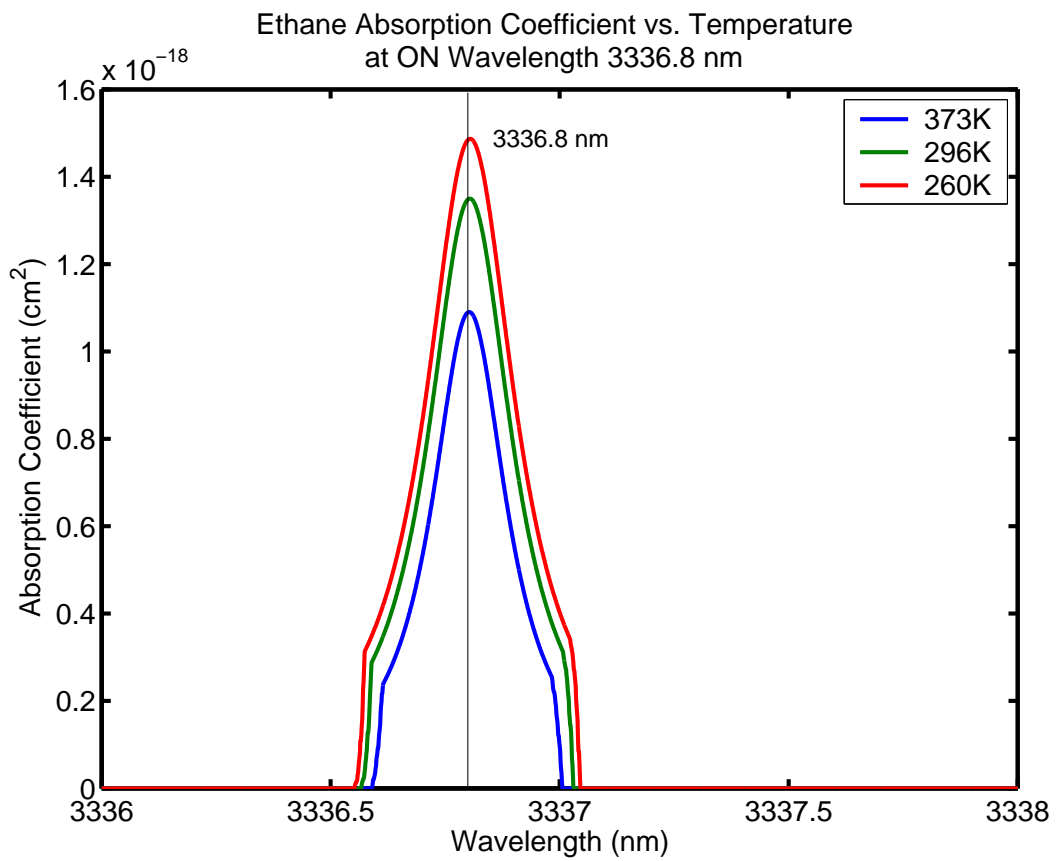


Figure 2.4: Ethane Absorption Coefficient Versus Temperature

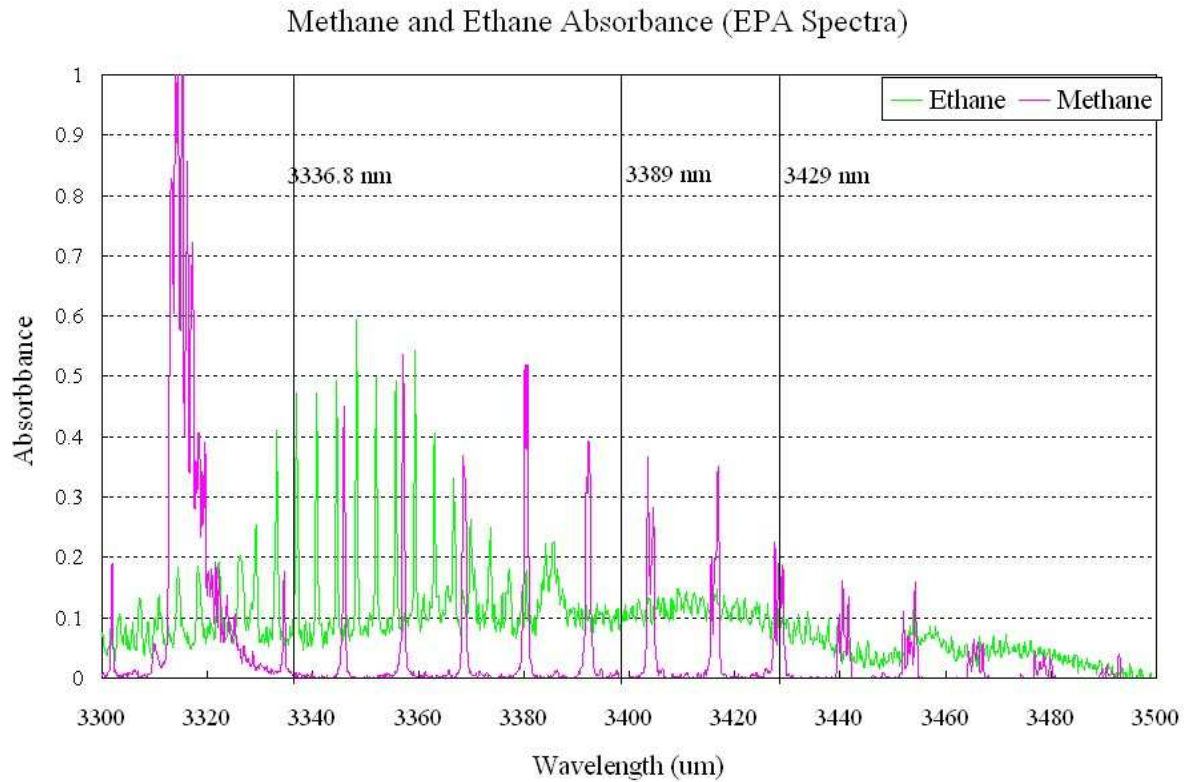


Figure 2.5: Absorbance Spectra of Methane and Ethane

2.6.1 Comparison with EPA spectra

Figure 2.5 shows absorbance spectra of methane and ethane from EPA. These are spectra taken under laboratory conditions with 0.25 cm^{-1} resolution. Methane is measured at 100 C° with 400.5 ppm concentration along 4.5 m path. Ethane is measured at 100 C° with 83 ppm concentration along 11.5 m path.

An expression for absorbance by transmission intensity is given by,

$$A = \log_{10}\left(\frac{I_0}{I}\right) \quad (2.13)$$

where I is the intensity. we have

$$I = I_0 e^{kn_s l} \quad (2.14)$$

where k [$cm^2/molecule$] is the absorption coefficient , n_s [$1/cm^3$] is the mixed gas partial number density, l [cm] is the transmission path.

From 2.13 and 2.14, we can relate the absorption coefficient to the absorbance,

$$k = \ln(10) \frac{A}{n_s l} \quad (2.15)$$

where the number density n_s is calculated using gas density law $n_{molecule} = p/kT$, and n_s is the mixed gas partial concentration.

The comparison of HITRAN spectra with EPA spectra is shown in Figures 2.6 and 2.7, where the absorption cross-section is shown in log scale. The results from the two data sets of methane show good agreement. However, there are some difference in the comparison of ethane data that is not understand at present.

2.6.2 Temperature Dependence

The calculation results of the temperature dependence of methane at 3429 nm and ethane at 3336.8 nm is listed in Table 2.2 and plotted in Figure 2.8.

Table 2.2: Temperature dependence of methane and ethane absorption

Temperature (K)	260	270	280	290	296	310	320	373
$CH_4 \cdot 10^{-18} cm^2$	0.1262	0.1350	0.1442	0.1529	0.1577	0.1694	0.1769	0.1852
$C_2H_6 \cdot 10^{-18} cm^2$	1.484	1.445	1.407	1.370	1.348	1.299	1.264	1.090

Methane Spectra. Comparison of HITRAN and EPA data

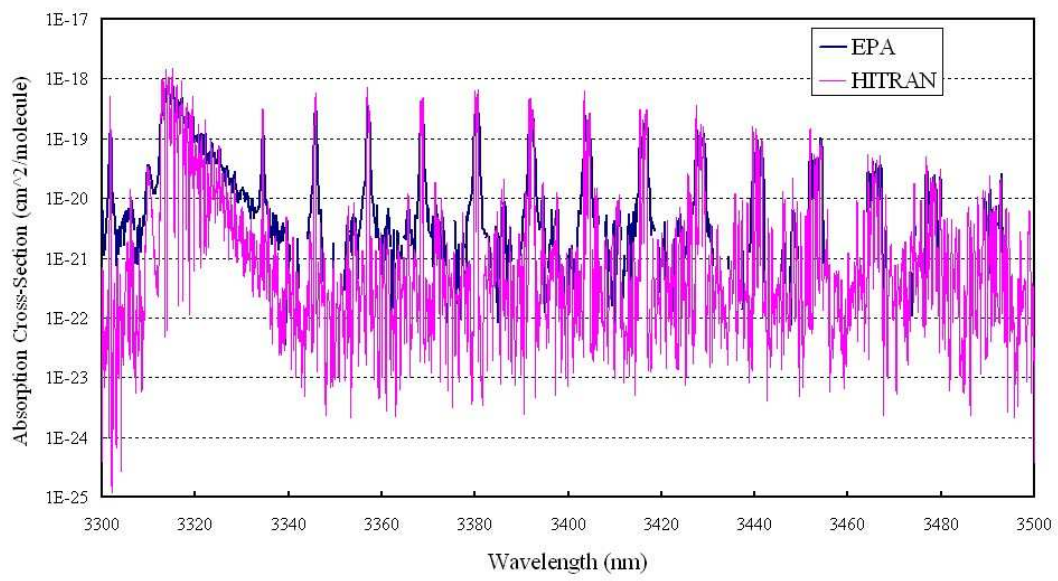


Figure 2.6: Methane Spectra Comparison, EPA vs. HITRAN

Ethane Spectra. Comparison of HITRAN and EPA data

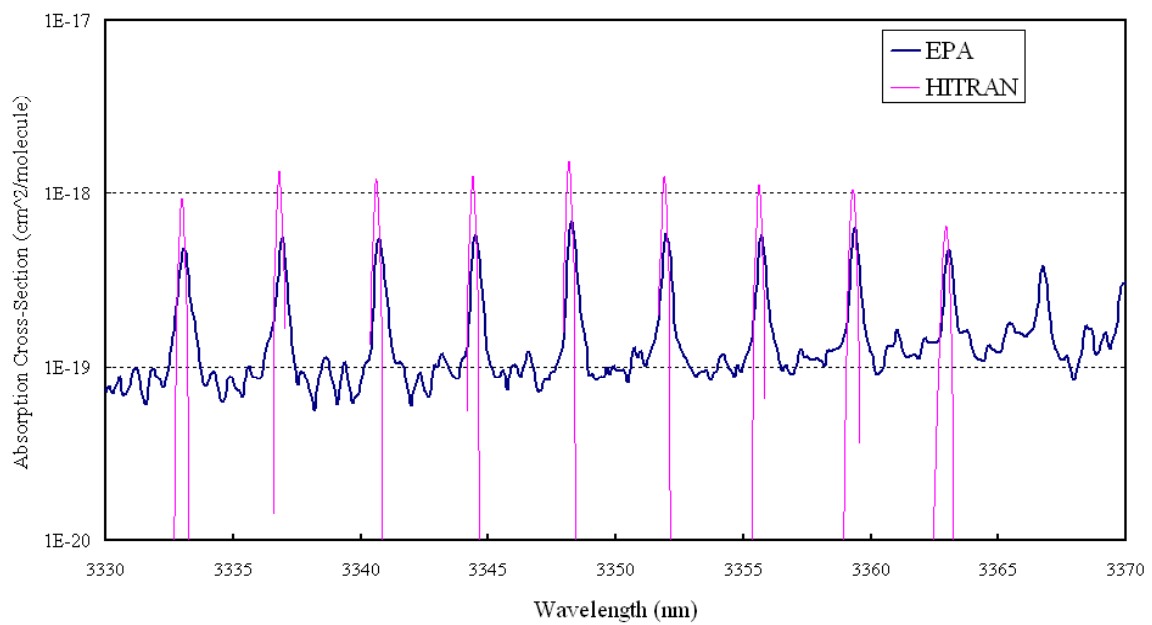


Figure 2.7: Ethane Spectra Comparison, EPA vs. HITRAN

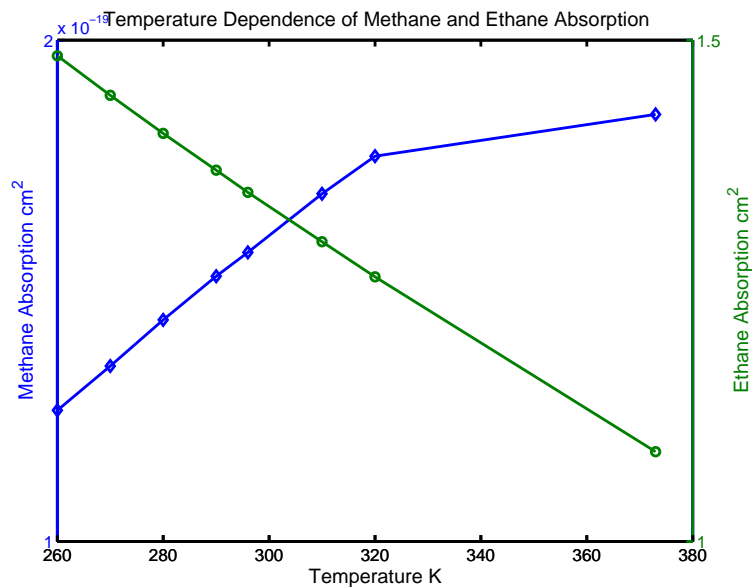


Figure 2.8: Temperature Dependence of Methane and Ethane Absorption

2.6.3 Pressure Dependence

The pressure dependence for the absorption at the selected methane and ethane lines is shown in Figure 2.9. The variation of absorption cross-section due to atmospheric pressure is less than 1%.

2.6.4 Partial Pressure Dependence

Figure 2.10 shows the partial pressure dependence of methane and ethane. Several cases were considered with the concentrations of methane and ethane that vary from 1 ppm to 10000 ppm. The results show that the variation of absorption cross-section due to partial pressure is much less than 1%.

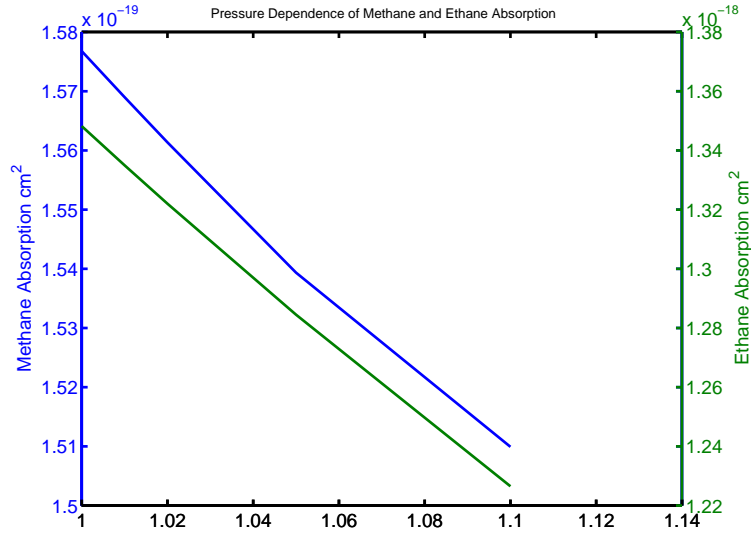


Figure 2.9: Pressure Dependence of Methane and Ethane Absorption

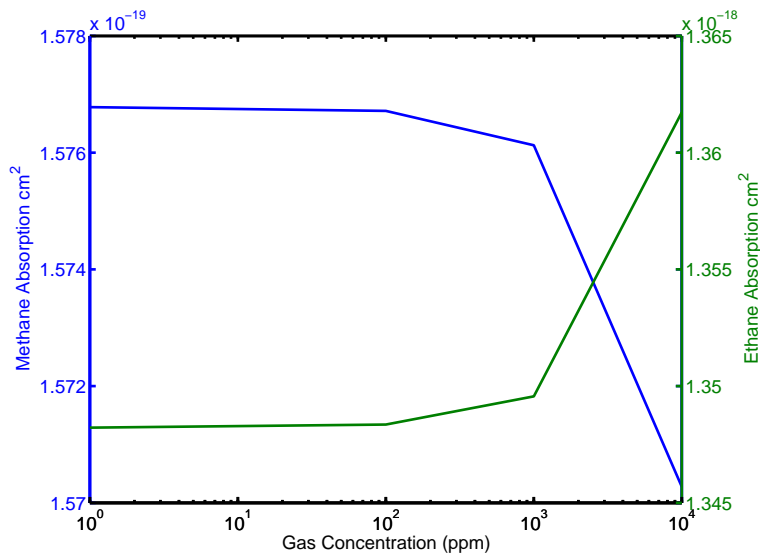


Figure 2.10: Partial Pressure Dependence of Methane and Ethane Absorption

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