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Simulation of Intensities of High-resolution Lines of Methane in the Region of 1035 cm^{-1}

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Abstract

Absorption lines of methane occur prominently in the near infrared spectra of the giant outer planets. In the earth's atmosphere, methane is the most abundant greenhouse gas in the troposphere after water and CO_2. Wetlands are the most important natural sources of global methane emission. However, more studies are needed about methane and its effect on climate change. In this work, interaction of a 9.6 μm CO_2 laser beam with high-resolution lines of methane in the vicinity of 1035 cm^{-1} is studied with the help of quasi-random model of molecular band absorption. This model can represent any type of distribution of spectral lines accurately in a given frequency interval. Simpson's rule of numerical integration is used to find out the transmittance values for interval 1 cm^{-1} and for different absorber thickness (0.01, 0.1 and 1.0 atm-cm). From the generated absorptance values, we simulate the intensities of these lines.

Keywords: Molecular band absorption, methane, quasi-random model.

Introduction

The knowledge of the transmission of electromagnetic radiation through the earth's atmosphere is very important to many aspects of space sciences. The passage of a laser beam is affected by the atmosphere in many ways. Out of various gases present in the earth's atmosphere, methane is the second most important anthropogenic gases, directly contributing to 0.48 W/m^2 to the total anthropogenic radiative forcing 2.63 W/m^2 by well mixed greenhouse gases [1]. Methane is an attractive reference material because of its dense spectrum, moderately strong lines and availability. Hence, precise knowledge of spectra of CH_4 is imperative for accurate measurements involving the interaction of a laser beam through the atmosphere. Diffusion scattering infrared (IR) spectroscopy was applied to study the absorption and plasma assisted catalytic conversion of methane of the surface of γ-Alumina [2]. Using a 5.6 m long HC-PBF as gas cell, the spectrum of methane at $\nu_2 + 2\nu_3$ band near 1300 nm has been recorded by A. M. Cubillas *et al.* [3]. In this proposed work, interaction of a 9.6 μm CO_2 laser beam with some high resolution lines of methane is studied. The quasi-random model which is one of the elementary model of molecular band absorption, can be used to simulate the intensities of these absorption lines. IR transmittance based on the quasi-random model, have been calculated for H_2O (Stull *et al,* 1964 [4]) and CO_2 (Stull *et al,* 1964 [5]) and results fitted with experimental measurements.

The quasi-random model of molecular band absorption is a variant of one of the methods described by Goody and Yung, 1989 [6]. Using this model interaction of a dye laser beam with the rotational lines of nitrogen in the wavelength region of 5700 Å has been studied [7]. Interaction of 4μm laser beam with the absorption lines of SO_2 is studied by the quasi-random model [8]. The dependence of absorptance on temperature has also been shown by Gohain Barua *et al*,2001[9], taking into account of the relationship between line width and temperature [5].

In this paper, simulation of intensities of methane lines in the vicinity of 1035 cm^1 is studied with the help of the quasi-random model.

Quasi-random model

The quasi-random model can represent any type of distribution of spectral lines accurately in a given frequency interval. It also accurately simulates the distribution including as many of the weaker lines as actually contribute to the absorption. The frequency interval, Ω, over which average transmittance is to be calculated, is divided into a number of smaller intervals δ.The position of any spectral line is localized by the smaller interval δ without introducing any serious errors. The transmittance at a frequency ν, as effected by n_p lines within the interval δ_p is computed from the expression (Green and Wyatt, 1965 [10])

$$\Im(\nu) = \prod_{k=1}^{5} \left\{ \left(\frac{1}{\delta}\right) \int_{\delta p} \exp\left[-\frac{s_k u \alpha / \pi}{(\nu - \nu_k)^2 + \alpha^2} \right]^2 d\nu_k \right\}^{n_k} \tag{1}$$

where n_k represent the number of lines within the intensity range *k*, which itself is characterized by average intensities s_k , α is the half width at half maximum, *u* is the absorber thickness, ν_k refers to the center of the line. It has been found that the top five intensity sectors are sufficient to describe the absorptive properties associated with the lines therein.

Out of different models of molecular band absorption like the Elsasser model, the Statistical model, the Random Elsasser model, the quasi-random model is characterized by the effect of “wing absorption” [11]. The effect in which the lines in a given frequency interval may substantially contribute to the absorptance in the adjacent frequency interval is termed as the “wing effect”. The wing absorption is there in the Elsasser model, yet it is not possible to demarcate it as all the lines are of equal intensity.

Method of calculation

The high resolution near-infrared absorption spectrum of methane is considered in the vicinity of 1035 cm^{-1} from the GEISA database [12]. The maximum relative intensity is normalized to unity and other values of intensities are taken relative to this one. There are 81 lines present in the studied region. The lines are assumed to be homogenous as the rotational lines are observed to be very fine. The entire spectrum in the range 1035 – 1042 cm^{-1} is divided into frequency interval $\Omega = 1$ cm^{-1} wide. Ω is further divided into smaller interval $\delta = 0.5$ cm^{-1}. These intervals are chosen small enough so that the lines falling into any one of them may be considered to lie at random, without introducing any serious errors. Taking α (half width) as 0.015 cm^{-1} the transmittance values are calculated at the center of the intervals for three different masses per unit area, u = 0.01, 0.1 and 1.0 atm-cm with the help of computer program using Simpson's rule of numerical integration. The transmittance by the wings of the lines at the left and right adjacent intervals is also included. The transmittance at the centre of an interval is finally obtained as (Stull *et al.* 1964 [5])

$$\Im = \Im_j \prod_{k \neq j} \Im_k \tag{2}$$

Results and Conclusions

Influence of the 81 lines are worked out for 0.01, 0.1, and 1.0 atm-cm thickness of methane. The computational results for the propagation of a 9.6 μm CO_2 laser beam through these three path lengths of the absorber are given in Table-I and shown in Fig. 1, 2 and 3 respectively which agree well with the experimental data taken for this work. This verifies that the quasi-random model for simulating the intensity distribution by grouping the line in a given frequency interval works reasonably well. A close look at the figures reveals that the larger the amount of the absorber the more marked is the variation. This is, perhaps, expected, as with smaller amounts of the absorber the absorptance values tend to saturate. All the 81 lines mentioned earlier contribute to the absorptance values.

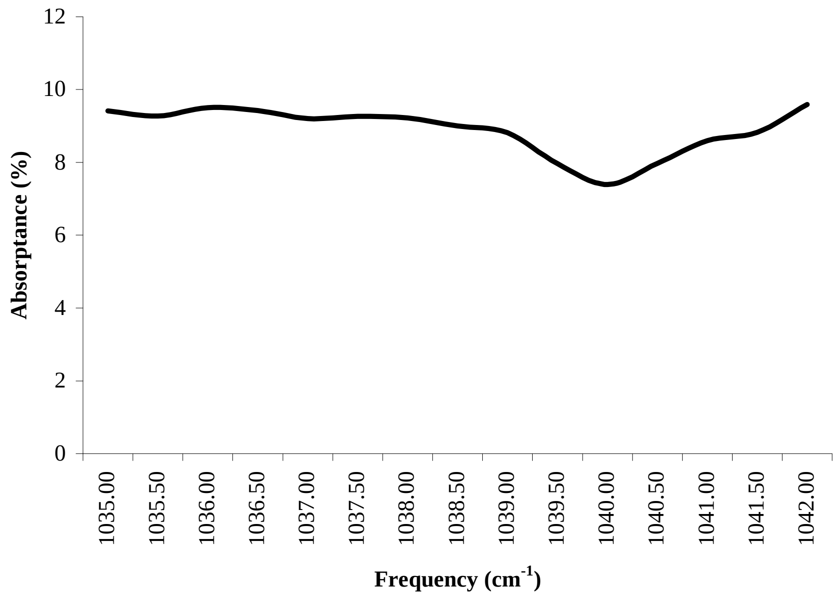

Figure 1: Absorptance of a 9.6 µm CO_2 laser beam for a 0.01 atm-cm path length of methane.

Table I: Absorptance for a CO_2 laser beam of wavelength 9.6 µm by Methane for three different amounts absorber thickness.

Frequency (cm^{-1})	Variation of *u* (atm-cm)		
	***u* = 0.01**	***u* = 0.1**	***u* = 1.0**
1035.00	9.4113	7.0314	5.115
1035.50	9.2684	6.1763	3.4477
1036.00	9.5012	6.8596	3.5884
1036.50	9.4227	6.391	2.5806
1037.00	9.2059	5.0456	1.2133
1037.50	9.2596	5.3605	1.6822
1038.00	9.2156	5.3671	1.6927
1038.50	8.996	4.2956	0.6814
1039.00	8.8142	3.8556	0.7343
1039.50	7.9613	1.9748	0.2864
1040.00	7.3924	1.2193	0.104
1040.50	7.9711	2.0857	0.2913
1041.00	8.5939	3.3432	0.6945
1041.50	8.8239	3.8806	0.8796
1042.00	9.5857	7.048	3.5954

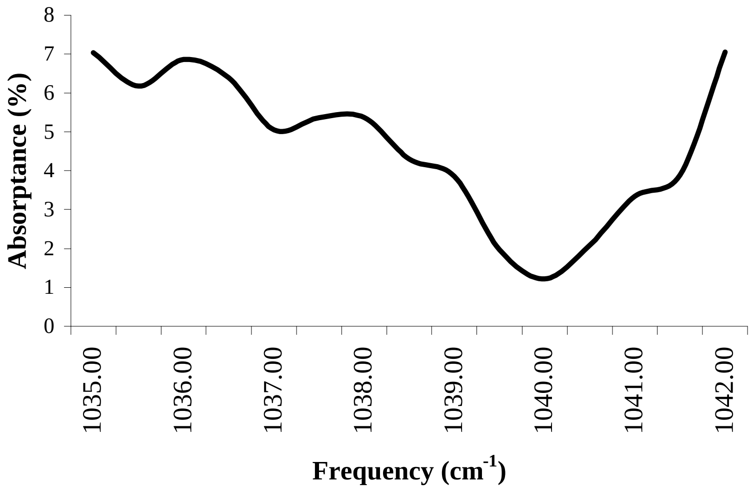

Figure 2: Absorptance of a 9.6 μm CO_2 laser beam for a 0.1 atm-cm path length of methane.

Till now, a large number of high resolution absorption spectra of other diatomic and polyatomic molecules have been reported; the present work can easily be extended to these spectra. Temperature and pressure dependence of the line width, and consequently of the absorptance, is the aspect that calls for further research.

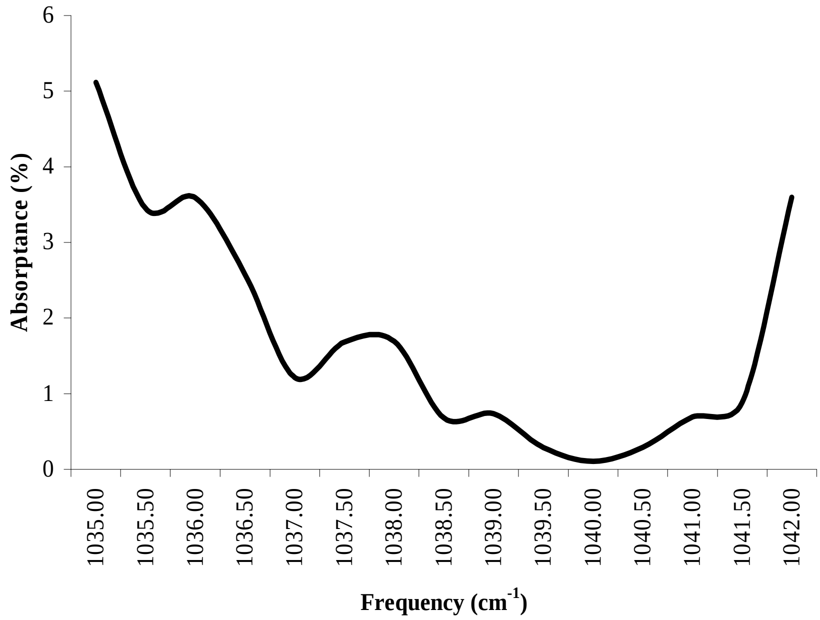

Figure 3: Absorptance of a 9.6 μm CO_2 laser beam for a 1.0 atm-cm path length of methane.

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