

A-3.4 Advanced study of the spectroscopic line parameters of trace gases for ILAS-II observation in space

Contact person Masashi Fukabori
Senior Researcher
Physical Meteorology Research Department
Meteorological Research Institute
Japan Meteorological Agency
Nagamine1-1, Tsukuba, Ibaraki 305-0052, Japan
Tel:+81-298-53-8715 Fax:+81-298-55-6936
E-mail:fukabori@mri-jma.go.jp

Total Budget for FY1999 - FY2000 12,808,000 Yen (FY2000; 6,404,000 Yen)

Abstract The objective of this study is to determine the accurate absorption line parameters, such as the line position, the line strength, and the half-width, which are required in the data analysis of ILAS-II. The main targets of experiments are the absorption bands of CH₄, N₂O, and CO₂ in the spectral region of CH.2 which is newly installed in ILAS-II. The absorption spectra of CH₄, N₂O, and CO₂ were measured with a high-resolution Fourier transform spectrometer at room temperature. The measurements included several absorption bands: the ν_3 band of CH₄, the $2\nu_1$, $\nu_1+2\nu_2$, and ν_3 bands of N₂O, and the ν_3 band of CO₂. The nonlinear least squares fitting procedure was used to determine the line strengths, N₂- and O₂-broadened half-widths of the above bands. The line strengths and half-widths of CH₄ and N₂O were in good agreement with the latest HITRAN database and the recent high-resolution experiments. N₂- and O₂-broadened half-widths of CO₂ agreed with the high-resolution experiments, whereas the line strengths were close to the HITRAN86 values rather than that of HITRAN96,2K. The coefficient of the Herman-Wallis factor agreed well with both the experiment and theoretical calculation.

Key Words ILAS-II, Absorption spectrum, Line parameter, Line strength, Half-width

1. Introduction

The Improved Limb Atmospheric Spectrometer-II (ILAS-II) is a solar occultation sensor to measure and study the stratospheric ozone layer environment with infrared grating spectrometers and a visible grating spectrometer. ILAS-II observes the transmittance of the solar spectra with three infrared channels which cover the 6.21-11.76 μ m(CH.1), 3.0-5.7 μ m(CH.2), and 12.78-12.85 μ m(CH.3) spectral regions. CH.3 is very narrow band and is mainly restricted to the observation of ClONO₂. The main targets of CH.1 and CH.2 are vertical profiles of O₃ and O₃-related species such as HNO₃, NO₂, N₂O, CH₄, and H₂O. Since CH.2 is newly installed in ILAS-II, it is necessary to consider the spectral features of CH.2 for the retrieval algorithm. There are important absorption bands of CH₄, N₂O, and O₃ in the spectral region of CH.2. Besides these bands, the strong absorption bands of CO₂ exist around 4.3 μ m region. Because the absorption due to CO₂ overlaps the absorption bands of N₂O and O₃, the contributions of the absorption bands of CO₂ should be carefully taken into account for the analysis of these gases. Uncertainties of the line parameters of these gases in the spectral region of CH.2 have not been examined in the ILAS project. Accurate absorption line parameters of CO₂ as well as those of CH₄ and N₂O are required for the data analysis. The purpose of this study is to examine the validity of the currently adopted spectroscopic database.

2. Research Objective

The accuracy of the measurements by ILAS and ILAS-II depends not only on the precision of the instruments employed but also on the reliability of the available spectroscopic database. Accurate absorption line parameters such as the line position, the line strength, and the half-width are necessary for the analysis of solar spectra, whereas the uncertainties of the line parameters still exist even in the infrared region. Indeed the overtone and combination bands of trace gases in the near infrared region have large uncertainties because of their weakness. Several spectroscopic databases are available for the studies of remote sensing and widely used by many investigators. A great number of absorption lines from the visible to the far infrared region have been compiled in the spectroscopic databases (e.g. HITRAN86¹), HITRAN92²), HITRAN96³), and HITRAN2K⁴). The HITRAN database has been employed for the analysis of ILAS. The accuracy of the line parameters of HITRAN is estimated to be 10-20%, that is not sufficient to retrieve the vertical profiles of trace gases. It is necessary to examine the uncertainties of the line parameters of HITRAN in order to improve the accuracy of ILAS-II. The objective of this study is to determine the accurate absorption line parameters required in the data analysis of ILAS-II through the laboratory measurements.

3. Research Method

The absorption spectra of CH₄, N₂O, and CO₂ were measured using a Bruker IFS-120HR Fourier transform spectrometer. The spectral resolution was set at 0.01 cm⁻¹. We used two kinds of absorption cells whose path lengths are 1.016 and 0.522 cm. The self-, N₂-, and O₂-broadening experiments were carried out at room temperature.

The line strengths, self-, N₂-, and O₂-broadened half-widths of CH₄, N₂O, and CO₂ were determined with a nonlinear least squares fitting procedure. An iterative method is used to minimize the sum of the squares of the difference between the measured spectrum and the calculated one with the appropriate line parameters. The Voigt profile is assumed as a line shape. The Herman-Wallis factor, which represents the vibration-rotation interaction in a molecule, of CO₂ was also analyzed.

4. Results

(1) CH₄

Figure 1 shows the comparison between the measured spectrum and the calculated one using the line parameters from the nonlinear least squares fit for the R(0) line in the ν_3 band of CH₄. The measured spectrum was in excellent agreement with the calculated one. Almost similar result was obtained for the R(1) line. Measured line strengths of the R(0) and R(1) agreed well with the HITRAN2K values within 1-2%. N₂- and O₂-broadened half-widths of the R(0) and R(1) were in good agreement with the values of the recent high-resolution experiments by Benner et al.⁵) and Malathy Devi et al.⁶) Ratios of N₂-broadened half-widths to O₂-broadened ones were 1.05 and 1.07, respectively, for the R(0) and R(1) lines in this study. These values agreed quite well with both the experimental values reported by Benner et al.⁵) and the theoretical values calculated by Tejwani et al.⁷) Figure 2 shows the measured spectrum and the calculated one with the line parameters of HITRAN2K for the Q-branch lines. Though the measured spectrum almost agreed with the calculated one, some different features from the calculated spectrum were found in the line wings.

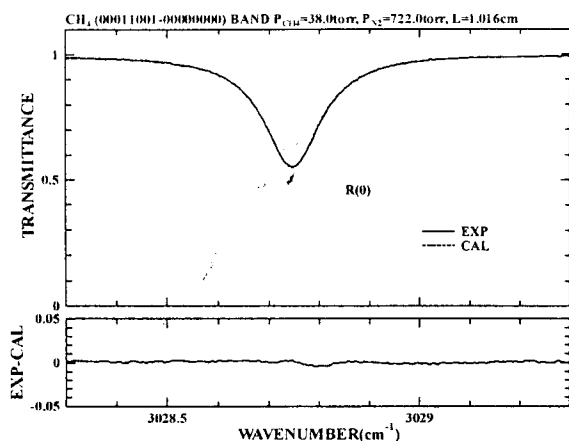


Fig.1 Comparison between the measured spectrum and the calculated one using the line parameters from the nonlinear least squares fit for the R(0) line.

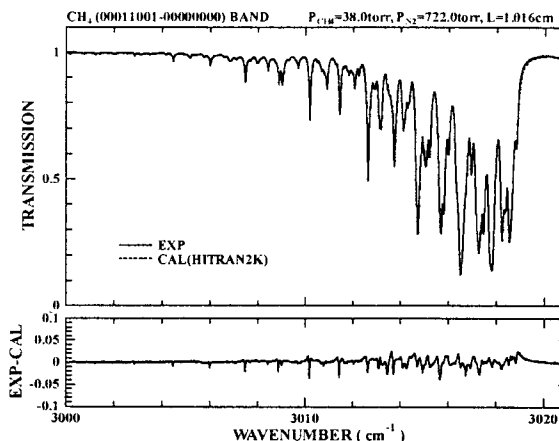


Fig.2 Comparison of the measured spectrum with the calculated one using the line parameters of HITRAN2K in the Q-branch region.

(2) N₂O

Figure 3 shows the comparison of the measured line strengths with the values compiled in HITRAN96,2K for the ν_3 band of N₂O. Measured line strengths agreed quite well with the HITRAN values, which are based on the high-resolution experiment by Toth.⁸⁾ As shown in Fig.4, N₂-broadened half-widths of the ν_3 band were very close to the recent results reported by Lacomme et al.⁹⁾ and Toth.¹⁰⁾ O₂-broadened half-widths were also in good agreement with those of Lacomme et al.⁹⁾ Almost similar results were obtained for the $2\nu_1$ and $\nu_1+2\nu_2$ bands.

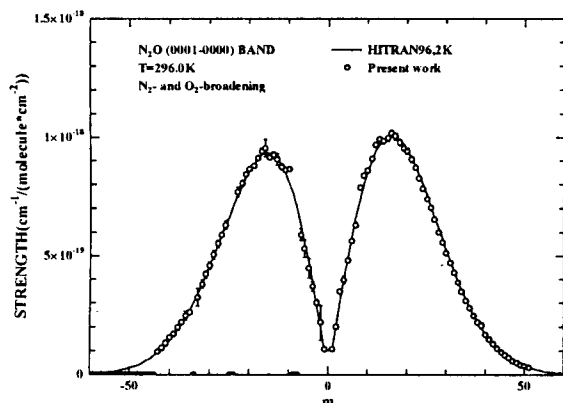


Fig.3 Comparison of the measured line strengths with the values compiled in HITRAN96,2K for the ν_3 band of N₂O.

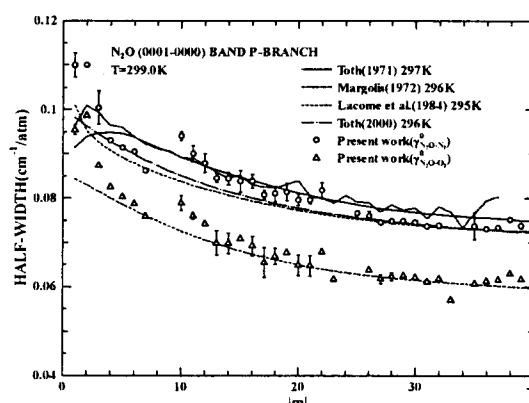


Fig.4 Comparison of the N₂- and O₂-broadened half-widths in the ν_3 band of N₂O.

(3) CO₂

Figure 5 shows the comparison of the measured line strengths with the values compiled in HITRAN86 and HITRAN92,96,2K in the ν_3 band of CO₂. Measured line strengths agreed well with the values of the HITRAN86 database rather than those of HITRAN92,96,2K, which are based on the high-resolution experiment by Johns.^{11,12)} N₂- and O₂-broadened half-widths of the ν_3 band were very close to the results reported by Johns.¹¹⁾, Margottin-Maclou et al.¹³⁾, and Dana et al.¹⁴⁾ (Fig.6). The coefficient of the Herman-Wallis factor was in excellent agreement with both the experimental value¹²⁾ and the theoretical calculation of Watson.¹⁵⁾

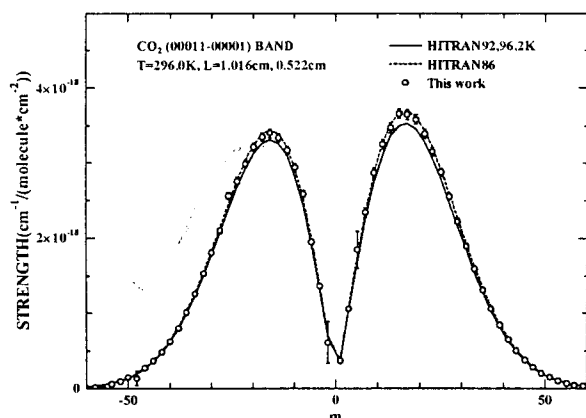


Fig.5 Comparison of the measured strengths with the values compiled in the HITRAN databases in the ν_3 band of CO_2 .

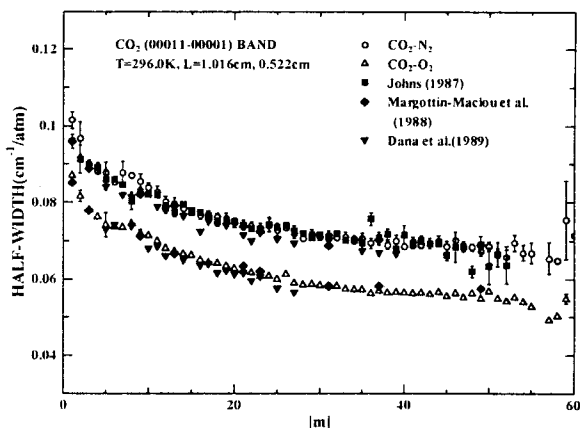


Fig.6 Comparison of N_2 - and O_2 -broadened half-widths in the ν_3 band of CO_2 .

5. Discussion

The line strengths and half-widths of CH_4 , N_2O , and CO_2 were determined accurately and the validity of the HITRAN database was examined. Measurements of the absorption spectra were restricted at room temperature. To improve the accuracy of the retrieval of trace gases, the temperature dependence of the line parameters are essential. Since the temperature dependence of the line parameters is the urgent problem in the ILAS-II project, the experiment at low temperatures will be the subsequent objective. Our results will entail the further understanding of the absorption properties of trace gases.

References

- 1) Rothman, L.S., R.R.Gamache, A.Goldman, L.R.Brown, R.A.Toth, H.M.Pickett, R.L.Poynter, J.-M.Flaud, C.Camy-Peyret, A.Barbe, N.Husson, C.P. Rinsland, and M. A. H. Smith, *Appl.Opt.* 26, 4058-4097, 1987.
- 2) Rothman, L.S., R.R.Gamache, R.H.Tipping, C.P.Rinsland, M.A.H.Smith, D.Chris Benner, V. Malathy Devi, J.-M.Flaud, C.Camy-Peyret, A.Perrin, A.Goldman, S.T.Massie, L.R.Brown, and R.A.Toth, *J.Quant.Spectrosc.Radiat.Transfer* 48, 469-507, 1992.
- 3) Rothman, L.S., C.P.Rinsland, A.Goldman, S.T.Massie, D.P.Edwards, J.-M.Flaud, A.Perrin, C.Camy-Peyret, V.Dana, J.-Y.Mandin, J.Schroeder, A.Mccann, R.R.Gamache, R.B.Wattson, K.Yoshino, K.V.Chance, K.W.Jucks, L.R.Brown, V.Nemtchinov, and P.Varanasi, *J.Quant.Spectrosc.Radiat.Transfer* 60, 665-710, 1998.
- 4) HP address, <http://www.HITRAN.com>
- 5) Benner, D.C., V.Malathy Devi, M.A.H.Smith, and C.P.Rinsland, *J.Quant.Spectrosc. Radiat.Transfer* 50, 65-89, 1993.
- 6) Malathy Devi, V., D.C.Benner, M.A.H.Smith, and C.P.Rinsland, *Appl.Opt.* 30, 287-304, 1991.
- 7) Tejwani, G.D.T. and P.Varanasi, *J.Quant.Spectrosc.Radiat.Transfer* 15, 243-254, 1975.
- 8) Toth, R.A., *Appl.Opt.* 32, 7326-7365, 1993.
- 9) Lacome, N., A.Levy, and G.Guelachvili, *Appl.Opt.* 23, 425-435, 1984.
- 10) Toth, R.A., *J.Quant.Spectrosc.Radiat.Transfer* 66, 285-304, 2000.
- 11) Johns, J.W.C., *J.Mol.Spectrosc.* 125, 442-464, 1987.
- 12) Johns, J.W.C., *J.Mol.Spectrosc.* 134, 433-439, 1989.
- 13) Margottin-Maclou, M., P.Dahoo, A.Henry, A.Valentin, and L.Henry, *J.Mol.Spectrosc.* 131, 21-35, 1988.
- 14) Dana, V., J.-Y.Mandin, G.Guelachvili, Q.Kou, M.Morlillon-Chapey, R.B.Wattson, and

L.S.Rothman, *J.Mol.Spectrosc.* 152, 328-341, 1992.
15) Watson, J.K.G., *J.Mol.Spectrosc.* 125, 428-441, 1987.