Line strengths and half-widths of CO_2, CO, and N_2O in the near infrared region at room temperature

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ABSTRACT

The absorption spectra of CO_2, CO, and N_2O in the near infrared region were measured with a high-resolution Fourier transform spectrometer at room temperature to examine the uncertainties of the line parameters of the spectroscopic database. The line strengths and half-widths of these molecules were determined by a nonlinear least squares technique. We compared our results with the values compiled in the HITRAN databases. Large differences between the measured line strengths and the compiled ones in the HITRAN databases were found for the weak bands of each molecule. Air-broadened half-widths of CO_2, CO, and N_2O, which were calculated with measured N_2- and O_2-broadened half-widths, were close to the values of the HITRAN96 database. Self-broadened half-widths of CO_2 and N_2O agreed with the HITRAN96 values;while self-broadened half-widths of CO were different from the HITRAN96 values.

1. INTRODUCTION

In order to obtain the vertical profiles and column amounts of trace gases, which are related to the global warming and ozone depletion, solar spectra have been measured with ground-based high-resolution spectrometers by many investigators. Accurate absorption line parameters such as line center positions, line strengths, and half-widths are necessary for the analysis of solar spectra, whereas the uncertainties of the line parameters are still large, especially in the near infrared region. Many absorption lines from the visible to the far infrared region have been compiled in the spectroscopic databases. Among the spectroscopic databases, the HITRAN database(Rothman *et al.*, 1983;Rothman *et al.*, 1987;Rothman *et al.*, 1992;Rothman, 1996) has been mostly used for the radiative transfer calculation of the Earth's atmosphere. The accuracy of absorption line parameters is estimated to be 10%, that is not sufficient to retrieve the vertical profiles of trace gases. To examine the uncertainties of the line parameters of HITRAN, we measured the absorption spectra of trace gases with a high-resolution Fourier transform spectrometer.

2. EXPERIMENT

The absorption spectra were obtained using a Bruker IFS–120HR Fourier transform spectrometer with a KBr beam splitter, a tungsten lamp and an InSb detector. The spectral resolution was set at 0.008–0.02 cm^{-1}, depending on the gas pressure to be measured. We used the several kinds of absorption cells according to the line strengths of trace gases. The purity of the absorbing gases was above 99.9%. The N_2 and O_2 samples of high purity were used for the buffer gases. Pressure measurements were made with MKS Baratron pressure transducers designed for 0–100 torr and 0–1,000 torr ranges. All spectra were measured at room temperature. The variation of the sample gas temperature was controlled within ± 1 K during the measurement. The signal to noise ratio was better than 200 for each measurement.

3. ANALYSIS

The line strengths, self-, N_2-, and O_2-broadened half-widths of CO_2, CO, and N_2O were determined with a nonlinear least squares procedure. An iterative method was used to minimize the sum of the squares of the difference between the measured spectrum and calculated one with the appropriate line parameters. At lower pressures of the sample gas, the Voigt profile was assumed as a line shape.

The line strengths in a vibration-rotation band of the linear molecule are expressed by

$$S(m) = \frac{8\pi^3 N_T}{3hcQ_{rot}}\omega(m)exp\left[-\frac{hcE_{rot}(m)}{kT}\right]g_{J'l'}\left|U^{J'l'}_{J''l''}\right|^2\left|M^{v'J'l'}_{v''J''l''}\right|^2\left[1-exp\left(-\frac{h\omega}{kT}\right)\right], \quad (1)$$

$$N_T = \frac{N_L T_0}{Q_{vib}T}, \quad (2)$$

where $|U^{J'l'}_{J''l''}|$ is the matrix element of the dipole moment of a pure rotational transition, $|M^{v'l'J'}_{v''l''J''}|$ is the matrix element of the dipole moment of the vibrational transition, and the other symbols have their usual meanings. The square of the matrix element of the vibrational transition can be expressed as

$$|M^{v'l'J'}_{v''l''J''}|^2 = |R^{v'l'}_{v''l''}|^2 F(m), \tag{3}$$

where $F(m)$ is the factor that accounts for the vibration-rotation interaction and $|R^{v'l'}_{v''l''}|$ is the matrix element of the pure vibrational transition. For a linear molecule, $F(m)$ may be expressed as function of the running index m by,

$$F(m) = 1 + am + bm^2, \tag{4}$$

where

$$m = \begin{cases} J''+1 & \text{for the R–branch,} \\ -J'' & \text{for the P–branch.} \end{cases} \tag{5}$$

The air-broadened half-widths were calculated from experimental values for N_2-broadened and O_2-broadened half-widths assuming the relation

$$\gamma^0_{\text{abs}-\text{air}} = 0.79\gamma^0_{\text{abs}-\text{N}_2} + 0.21\gamma^0_{\text{abs}-\text{O}_2}. \tag{6}$$

4. RESULTS AND DISCUSSION

4.1 CO_2

Absorption spectra were measured for the (30011–00001), (30012–00001), (30013-00001), and (30014–00001) bands of CO_2 in the 1.6 μm region. Figure 1 shows the self-broadened half-widths of the (30012–00001) band. The measured half-widths agreed well with the HITRAN92(Rothman *et al.*, 1992) values which were based on the recent high-resolution experiments(Jones, 1987; Dana *et al.*, 1989; Dana *et al.*, 1992). Our results were also in good agreement with the values reported by Margottin-Maclou *et al.*(1988). Self-broadened half-widths of the HITRAN86(Rothman *et al.*, 1987) database were larger than those of the HITRAN92 database and our results for $7 \leq m \leq 46$. Figure 2 shows the N_2-broadened half-widths of the (30012–00001) band. Our results were very close to the values of the recent high-resolution experiments(Johns, 1987; Dana *et al.*, 1989; Margottin-Maclou *et al.*, 1988). Similar results were observed in the other three bands for the self- and N_2-broadened half-widths.

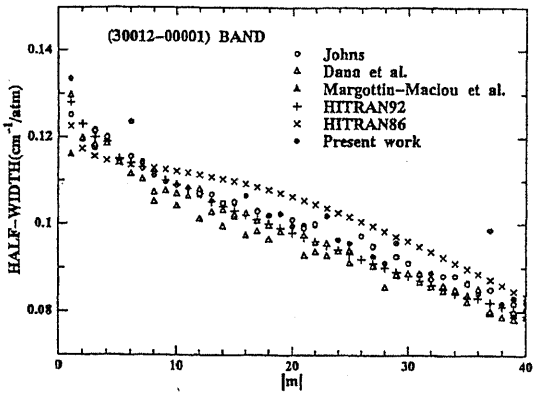

Fig.1 Self-broadened half-widths of the (30012–00001) band of CO_2.

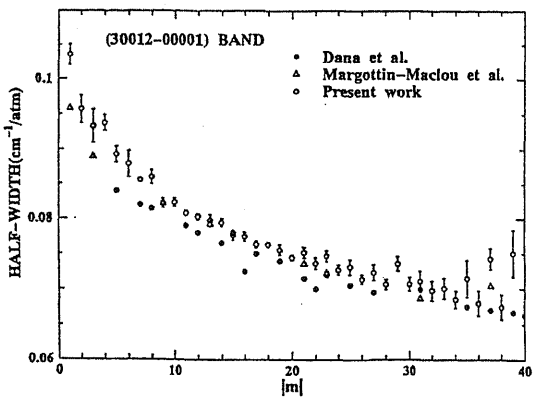

Fig.2 N_2-broadened half-widths of the (30012–00001) band of CO_2.

Figures 3 and 4 show the comparisons of the measured line strengths with the HITRAN values for the (30011–00001) and (30012–00001) bands of CO_2, respectively. The line strengths of the HITRAN92 database for the four bands in the 1.6 μm region are based on the experimental results carried out in the 1970's(Valero and Suarez, 1978; Suarez and Valero, 1978a; Suarez and Valero, 1978b). The line strengths obtained for the (30011–00001) band agreed well with the AFGL82(Rothman *et al.*, 1983) values, but the large difference between our results and the recent HITRAN values was found. For this weak band, the line strengths reported by Valero and Suarez were about 10–15% larger than those obtained by Toth *et al.*(1971). However, for the (30012–00001) band, our results were close to the HITRAN92 values, though the measured strengths of the R-branch were a few percent smaller than those of HITRAN. Similar results were found for

the other weak and strong bands. In the HITRAN96 database(Rothman, 1996), the line strengths of only the (30011–00001) band were revised and agreed with our results.

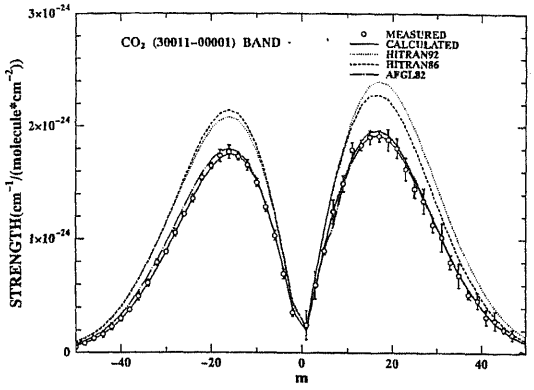

Fig.3 Line strengths of the (30011–00001) band of CO_2.

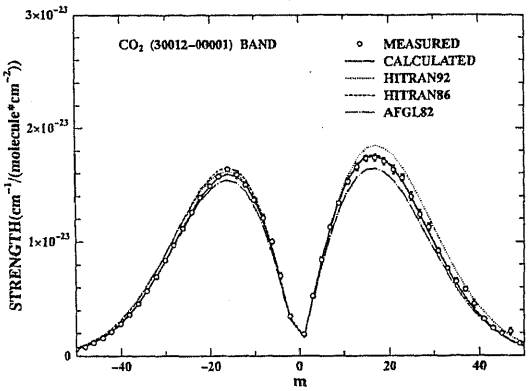

Fig.4 Line strengths of the (30012–00001) band of CO_2.

4.2 CO

Absorption spectra were measured for the (2-0) band of CO. Figure 5 shows the N_2- and O_2-broadened half-widths of the (2-0) band. O_2-broadened half-widths were very close to the values obtained by Nakazawa and Tanaka(1982), though N_2-broadened half-widths were slightly different from their results around m=10. N_2-broadened half-widths measured by the recent high-resolution experiments(Anselm *et al.*, 1993;Hamdouni *et al.*, 1993) agreed quite well with our results. Self-broadened half-widths were 5-8% smaller than the HITRAN96 values.

The measured line strengths agreed well with the values of HITRAN92 and HITRAN96 within the experimental error shown in Fig.6. The vibration-rotation coupling function obtained in this study was

$$F(m) = 1 + 5.08 \times 10^{-3} m + 3.52 \times 10^{-5} m^2. \quad (7)$$

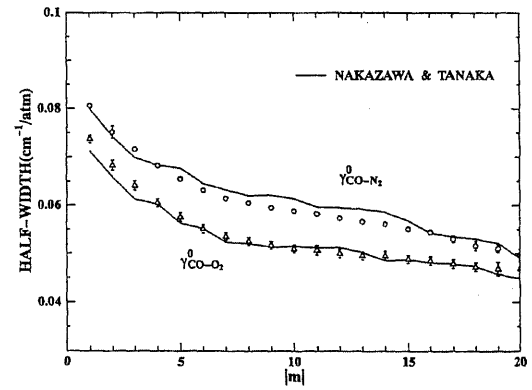

Fig.5 N_2- and O_2-broadened half-widths of the (2-0) band of CO.

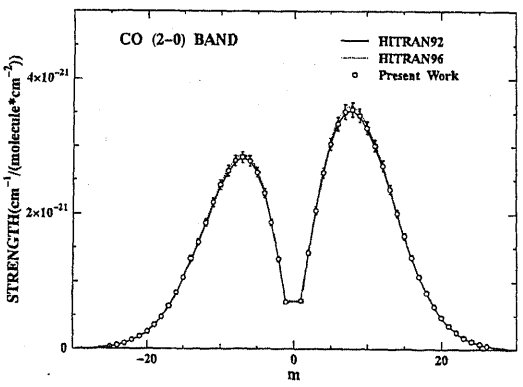

Fig.6 Line strengths of the (2-0) band of CO.

4.3 N_2O

Absorption spectra were measured for several bands of N_2O in the 2.0, 2.1, 2.3, 2.5, 2.6, and 2.9 μm regions. Since all lines of the R-branch in the (0002-0000) band do not blend with lines of other bands, the R-branch of this band is the appropriate region to determine the half-widths. Self-, N_2-, and O_2-broadened half-widths of N_2O were obtained for lines of this R-branch. Figure 7 shows the comparison of the measured self-broadened half-widths with the values obtained by other workers(Toth, 1971;Margolis, 1972;Lacome *et al.*, 1984;Toth, 1993) and of HITRAN92. Our results were close to the values obtained by Lacome *et al.*(1984) and Toth(1993) for the self-broadened half-widths. The values reported in the 1970's, which were obtained by the low-resolution spectra using a grating spectrometer, were about 25% larger than our values around m=16.

Figure 8 shows the comparison of the measured line strengths with the HITRAN values for the (4000-0000) band in the 2.3 μm region. The measured line strengths agreed well with the HITRAN96 values in the

R-branch, but the measured line strengths were about 5% less than the HITRAN96 values in the P-branch. Similar to the (4000-0000) band, the measured line strengths of the other bands were slightly different from the HITRAN96 values.

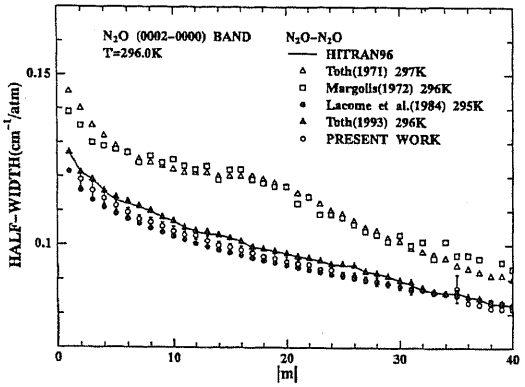

Fig.7 Self-broadened half-widths of the (0002-0000) band of N_2O.

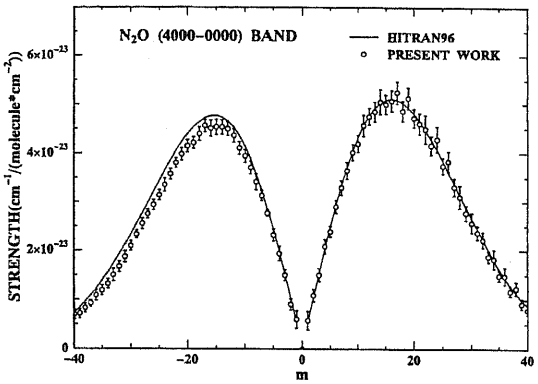

Fig.8 Line strengths of the (4000-0000) band of N_2O.

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