



Measurement of the pressure broadening coefficient of the 625 GHz transition of H₂O₂ in the sub-millimeter-wave region

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ABSTRACT

The hydrogen peroxide (H₂O₂) molecule plays an important role in stratospheric ozone chemistry as a reservoir molecule in the HO_x cycle. The Superconducting Sub-Millimeter-Wave Limb Emission Sounder (SMILES) instrument in the Japanese Experiment Module (JEM) on the International Space Station monitors H₂O₂ using the pure rotational J_{K_a,K_c} = 20_{1,19}–19_{2,17} transition at 625.044 GHz in the ground vibronic state. Accurate retrievals of H₂O₂ abundances rely on a knowledge of pressure broadening effects for this transition, and the required nitrogen (N₂) and oxygen (O₂) broadening coefficients are measured here for the first time. Values of the pressure broadening coefficients, $\gamma(\text{N}_2) = 4.03 \pm 0.06$ MHz/Torr and $\gamma(\text{O}_2) = 2.49 \pm 0.04$ MHz/Torr are obtained at room temperature, with statistical 3 σ uncertainties given. The value for air broadening is then derived to be $\gamma(\text{air}) = 3.71 \pm 0.09$ MHz/Torr, where the uncertainty includes possible systematic errors.

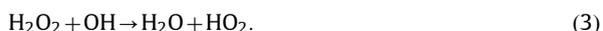
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1. Introduction

Stratospheric chemistry in general and ozone recovery in particular remain as important long-term environmental issues. There are large uncertainties among various models for the recovery period of stratospheric ozone from its recent human-induced depletion [1]. H₂O₂ plays an important role in HO_x chemistry in the upper stratosphere and lower mesosphere [2]. Both OH and HO₂ destroy odd oxygen (O, O₃). H₂O₂ is formed from the self-reaction of HO₂ radicals,



H₂O₂ produces OH and HO₂,



Thus, H₂O₂ is a key species which controls the partitioning of [OH]/[HO₂] in the atmosphere.

The Superconducting Sub-Millimeter-Wave Limb Emission Sounder (SMILES) instrument was designed to be onboard the Japanese Experiment Module (JEM) on the International Space Station (ISS) as a collaborative project of the National Institute of Information and Communications Technology (NICT) and the Japan Aerospace Exploration Agency (JAXA). SMILES was launched on September 11, 2009 by the H-II Transfer Vehicle (HTV) [3].

The SMILES mission has two key purposes: (1) space demonstration of a low noise sub-millimeter-wave receiver, consisting of superconductor–insulator–superconductor (SIS) mixers in a mechanical cooler and (2) space demonstration of super-sensitive observations in the middle atmosphere (8–90 km) using a sub-millimeter-wave mixer for limb emission observations.

Previously there have been three similar instruments in earth orbit, all using conventional Schottky diode receivers. The first millimeter-wave limb-emission sounding was done by the Microwave Limb Sounder (MLS) on the Upper Atmosphere Research Satellite (UARS)

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launched by NASA in September 1991 [4]. The Swedish Space Corporation (SSC) launched the Odin satellite in February 2001 in collaboration with France, Finland, and Canada [5]. The Sub-Millimeter Radiometer (SMR) onboard Odin made the first measurements in the sub-millimeter-wave region. NASA launched the Earth Observing System Microwave Limb Sounder (EOS-MLS) onboard the Aura spacecraft in 2004 [6]. SMILES is expected to perform the most sensitive observations among these four instruments.

One of the science targets of SMILES is to establish a more precise understanding of HO_x chemistry by means of simultaneous observations of O₃, H₂O₂, HO₂, HOCl, and ClO. SMILES will observe the 625.044 GHz transition of H₂O₂, which is the pure rotational transition ($J_{Ka,Kc} = 20_{1,19} - 19_{2,17}$) in the ground vibronic state. The pressure broadening coefficient is a key factor in retrieving the altitude dependence of the H₂O₂ molecular abundance from the observed spectral line shapes. The SMILES mission demands a knowledge of this coefficient, γ , within an accuracy of 3% because of its high signal-to-noise ratio capabilities [7]. This paper presents the first laboratory measurements of this pressure broadening coefficient at the 625.044 GHz transition of H₂O₂.

2. Experimental details

The measurements were carried out using a sub-millimeter-wave spectrometer that employs a backward wave oscillator (BWO) (Istok OB-80-1) as the radiation source. Fig. 1 shows a schematic diagram of the experimental setup. The BWO oscillation frequency was stabilized with a two-step phase lock loop.

frequency (625 GHz) was phase-locked to the seventh harmonic of the output of a Gunn oscillator (J.E. Carlstrom Co.) using a quasi-optical harmonic mixer. The Gunn oscillation frequency (about 100 GHz) was in turn phase-locked to the eighth harmonics of the reference frequency from a synthesized sweeper (HP 83622A) using a harmonic mixer. A liquid helium cooled InSb detector (QMC QFI/2BI) detected the sub-millimeter-wave radiation passing through the absorption cell.

Source frequency modulation at 51 kHz was used with a lock-in amplifier (Stanford SR850) and a 2f detection scheme. In order to get sufficient sensitivity even at higher pressures (larger line widths), the modulation amplitude of the BWO was set to a relatively large value of about 1 MHz. As described below, the resulting artificial modulation broadening effect was accounted for in the analysis by using a convolution method. A personal computer was used to control frequency scanning of the spectrometer and data acquisition. Each spectrum was acquired by averaging 30–50 scans with individual sweep times of 5–10 s and spans of 25–50 MHz.

The H₂O₂ sample was prepared by concentration of a commercially available 30% hydrogen peroxide solution (Wako Chemicals Ltd). As the vapor pressure of H₂O is 10 times higher than that of H₂O₂ at room temperature, this 30% sample was distilled by slow pumping until the total volume was decreased to one-third. By this distillation, any effect of the residual H₂O on the H₂O₂ pressure broadening measurement was minimized. Commercially available N₂ and O₂ (Nippon Sanso) were used as the buffer (broadening) gases in order to derive the air broadening coefficient for the H₂O₂ transition.

The absorption cell used in this experiment was a 2 m long glass cylinder with 7 cm diameter Teflon windows at

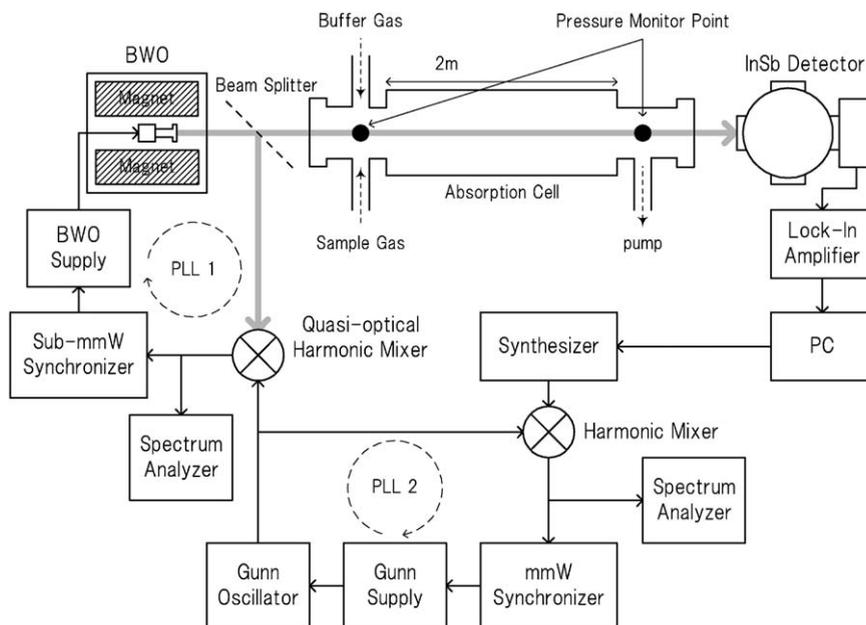


Fig. 1. Block diagram of the experimental setup.

each end. The sample and the buffer gas flowed into the cell from separate inlets at one end of the cell as shown in Fig. 1. The gases were slowly and continuously pumped out from the other end of the cell to avoid unwanted effects from air leakage or hydrogen peroxide decomposition.

A mass flow meter (STEC SEC-400MK3) controlled the flow rate and the buffer gas pressure (p_{buffer}). The cell pressure was monitored by capacitor manometers (MKS) set at its front and back ends. The pumping speed was adjusted so that the pressure gradient between the ends of the cell due to the gas flow was less than 1–2%. The total pressure (p_{total}) was defined by averaging the two pressure measurements. The partial pressure of the sample gas (p_{sample}) was adjusted to be approximately constant during measurements. The buffer gas pressure was defined as $p_{\text{buffer}} = p_{\text{total}} - p_{\text{sample}}$. All the measurements were performed at room temperature (296 K in this case).

3. Results and analysis

The observed spectral line shapes were analyzed using a convolution method originally proposed by Pickett in 1980 [8], as used in this field, for example, for measurements of the pressure broadening of O_3 [9,10] and BrO [11]. We used the analysis program originally written by H. Habara as described in Ref. [11]. First, a low pressure self-broadened spectrum was measured as a reference, with only the sample gas (H_2O_2) flowing in the cell. Then a pressure broadening spectrum, with the buffer gas (N_2 or O_2) also flowing, was measured and fitted to a line profile consisting of the convolution of the reference spectrum with a Lorentzian function. There are two advantages to this method. First, other contributions to the line shape, such as Doppler and modulation broadening, are automatically included since they can be assumed to be independent of buffer gas pressure. Second,

the absolute values of the line intensity become less important in the experiment.

The line profile, $F(i)$, is described by

$$F(i) = A \sum_{k=1}^N R(k) \frac{\Delta\nu^2}{\Delta\nu^2 + [(i-k)f + s]^2} + a_0 + a_1i + a_2i^2 + a_3i^3 + a_4i^4, \quad i = 1, 2, \dots, N, \quad (4)$$

where $R(k)$ is the line profile of the reference signal, A the amplitude of the signal, $\Delta\nu$ the line width (HWHM), f the frequency scan step size, s the pressure shift and N the number of points in each scan. A fourth order polynomial function is added to account for the shape of the spectral baseline. Three parameters of the Lorentzian function, $\Delta\nu$, A , and s , are determined from a least-squares analysis, along with any required baseline parameters.

As an example, Fig. 2 shows the result of such a least-squares analysis. Line shapes appear as second derivative functions due to the source frequency modulation with 2f detection scheme used. In this figure, “ref” is the reference spectrum taken for an H_2O_2 pressure of 35 mTorr, “exp” is the experimental one, broadened by O_2 at 1.45 Torr and “fit” is the fitted spectrum, composed of the reference convolved with a Lorentzian function with a 3.70 MHz width. The residual curve, “exp” minus “fit”, is labelled “dif”. To make the figure visually clear, the intensity of “ref” is divided by 50, that of “dif” is multiplied by 10, and the traces are offset by equal amounts.

Fig. 3 shows the derived Lorentzian broadening halfwidths ($\Delta\nu$) for the respective buffer gases (N_2 and O_2) as a function of the buffer gas pressure. Error bars indicate 3σ uncertainty limits, where σ is the standard deviation from the individual least-squares fitting of the Lorentzian function. Broadening coefficients, γ , were determined by fitting these points by least-squares to linear functions with zero intercepts.

γ for H_2O_2 at 625.044 GHz broadened by N_2 is determined to be 4.03 ± 0.06 MHz/Torr. For broadening

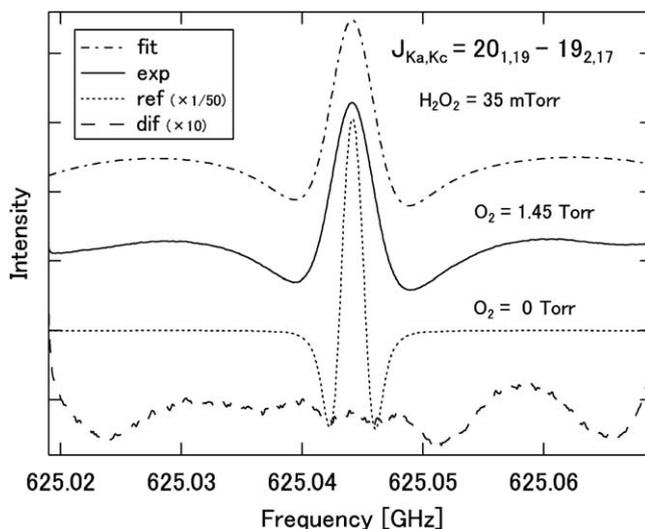


Fig. 2. H_2O_2 spectrum at 625.044 GHz (“ref”: reference spectrum, “exp”: experimental spectrum, “fit”: convolved with Lorentzian, “dif”: the difference between “exp” and “fit”).

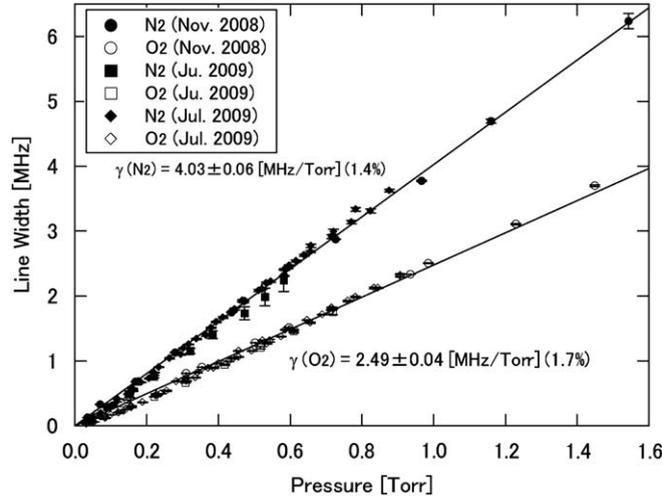


Fig. 3. Pressure broadening of H_2O_2 line (Buffer gases are N_2 and O_2).

Table 1

Comparison to other works.

Frequency	Rotational transition $J_{K_a',K_c'} - J_{K_a'',K_c''}$	Vibrational state	$\gamma(\text{air})$ (MHz/Torr)	Reference
625.044 GHz	$20_{1,19} - 19_{2,17}$	Ground state	3.71 ± 0.06	This work
223.101 GHz	$8_{0,8} - 7_{1,6}$	Ground state	4.45 ± 0.12	Goyette et al. [12]
229.786 GHz	$15_{1,15} - 14_{2,13}$	Ground state	3.92 ± 0.07	Goyette et al. [12]
1257.482 cm^{-1}	$9_{3,6} - 10_{3,7}$	ν_6 band	3.64 ± 0.02	Devi et al. [13]
1290.264 cm^{-1}	$16_{0,16} - 15_{0,15}$	ν_6 band	4.56 ± 0.07	Devi et al. [13]

by O_2 , γ is determined to be 2.49 ± 0.04 MHz/Torr. These errors represent 3σ from the statistics of the linear function fitting. The reliability of the measurement was confirmed by repeating experiments from November 2008 to July 2009. Absolute uncertainties including possible systematic factors are considered below.

4. Discussion

The standard air broadening parameter, $\gamma(\text{air})$, for the 625.044 GHz H_2O_2 transition can be estimated from $\gamma(\text{N}_2)$ and $\gamma(\text{O}_2)$ as

$$\gamma(\text{air}) = \gamma(\text{N}_2) \times 0.79 + \gamma(\text{O}_2) \times 0.21 = 3.71 \pm 0.06 \text{ MHz/Torr}, \quad (5)$$

where 0.79 and 0.21 are the fractions of N_2 and O_2 in air. Table 1 shows a comparison of the present pressure broadening coefficient with those measured previously for different transitions of H_2O_2 in the millimeter [12] and IR [13] regions. In general, higher J transition has smaller γ value for the linear molecule. It was also confirmed that higher J or K transition had smaller γ in general for water vapor molecule [14]. Table 1 shows the series of pure rotational transitions, $\Delta J = +1$, $\Delta K_a = -1$, $\Delta K_c = +2$, and larger J, K has smaller γ value. The J, K trend of these transitions is similar with previous studies. Eighteen H_2O_2 lines have been measured in IR region, and Table 1 shows

the extreme maximum and minimum γ value of those lines.

Here we discuss the absolute accuracy of this experiment in the light of possible systematic errors. The total error can be derived by summation of (1) the error of least-squares fitting, (2) the error from the temperature fluctuation, and (3) the uncertainty of the pressure measurement in the cell. Other random components are small enough to be neglected. As already shown, the error from least-squares analysis was ± 0.06 MHz/Torr. The error from temperature fluctuation is estimated as follows: the temperature dependence of γ is usually described in terms of the exponent, n , in a power function

$$\gamma(T) = \gamma_0 \left(\frac{T}{T_0} \right)^n, \quad (6)$$

where γ_0 is the pressure broadening coefficient at T_0 (usually taken as room temperature). For the present experiments, the temperature fluctuation (ΔT) in the laboratory over the measurement period was estimated to be a maximum of 2 K. Using a Taylor expansion of Eq. (6) and neglecting terms above second order, the error of γ arising from temperature ($\Delta\gamma_T$) can be estimated as

$$\Delta\gamma_T = \frac{n\gamma_0}{T_0} \Delta T. \quad (7)$$

Substituting $\Delta T = 2$ K, $n = 0.5$ (HITRAN04 value), $\gamma_0 = 3.71$ MHz/Torr and $T_0 = 296$ K, $\Delta\gamma_T = 0.01$ MHz/Torr.

The uncertainty of the pressure measurement in the cell is estimated as follows: pressure uncertainty arises mainly from the capacitor manometers, which have a specified error of 2% (± 0.01 Torr). If we take the maximum specified error, and every pressure measurement 0.01 Torr higher or lower, then $\gamma(\text{air})$ would be changed to 3.64 ± 0.06 or 3.76 ± 0.05 MHz/Torr, respectively. The effect of pressure fluctuation, $\Delta\gamma_p$, is thus estimated as ± 0.06 MHz/Torr, almost the same as the statistical error from our least-squares analysis ($\Delta\gamma_{\text{Analysis}}$).

The total experimental accuracy ($\Delta\gamma_{\text{exp}}$) is then given by

$$\Delta\gamma_{\text{exp}} = \sqrt{\Delta\gamma_{\text{Analysis}}^2 + \Delta\gamma_T^2 + \Delta\gamma_p^2}, \quad (8)$$

where $\Delta\gamma_{\text{Analysis}} = 0.06$ MHz/Torr, $\Delta\gamma_T = 0.01$ MHz/Torr, and $\Delta\gamma_p = 0.06$ MHz/Torr as we estimated. The total absolute accuracy of this experiment, $\Delta\gamma_{\text{exp}}$, is estimated from Eq. (8) to be 0.09 MHz/Torr.

We can assume that the error from least-squares analysis ($\Delta\gamma_{\text{Analysis}}$) includes also some of the effect of temperature and pressure fluctuation. As the error from pressure is six times larger than that from temperature, the accuracy and reliability of the pressure measurement is dominant. In order to measure more accurate pressure broadening coefficients, it will be necessary to perform more accurate pressure measurements. The total uncertainty of the present result ($\Delta\gamma_{\text{exp}}$) is estimated as 2.4% of the value of the air broadening coefficient, $\gamma(\text{air})$, which is within the requirement (3%) of the SMILES space mission.

5. Summary

Foreign gas pressure broadening coefficients γ were measured for the 625.044 GHz pure rotational transition ($J_{K_a, K_c} = 20_{1,19} - 19_{2,17}$) of H_2O_2 in the vibronic ground state by absorption spectroscopy using a backward wave oscillator sub-millimeter radiation source. The results were

- $\gamma(\text{N}_2) = 4.03 \pm 0.06$ MHz/Torr (1.4%).
- $\gamma(\text{O}_2) = 2.49 \pm 0.04$ MHz/Torr (1.7%).

The total experimental error was evaluated to be 2.4%, well within the requirements of the SMILES atmospheric observation mission.

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