

# The Laboratory Measurement of Pressure Broadening Parameter for Atmospheric Remote Sensing

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The upcoming JEM/SMILES (Superconducting Submillimeter-wave Limb Emission Sounder) and EOS-MLS (Earth Observing System-Microwave Limb Sounder) missions are planned to continually monitor key atmospheric species that play a crucial role in the chemistry of the upper atmosphere. For reliable retrieval of spatial distributions of key species from observational data, various types of spectroscopic parameters should be known very accurately. In this investigation, the pressure broadening parameters and their temperature dependences of BrO and O<sub>3</sub> have been critically examined.

## Keywords

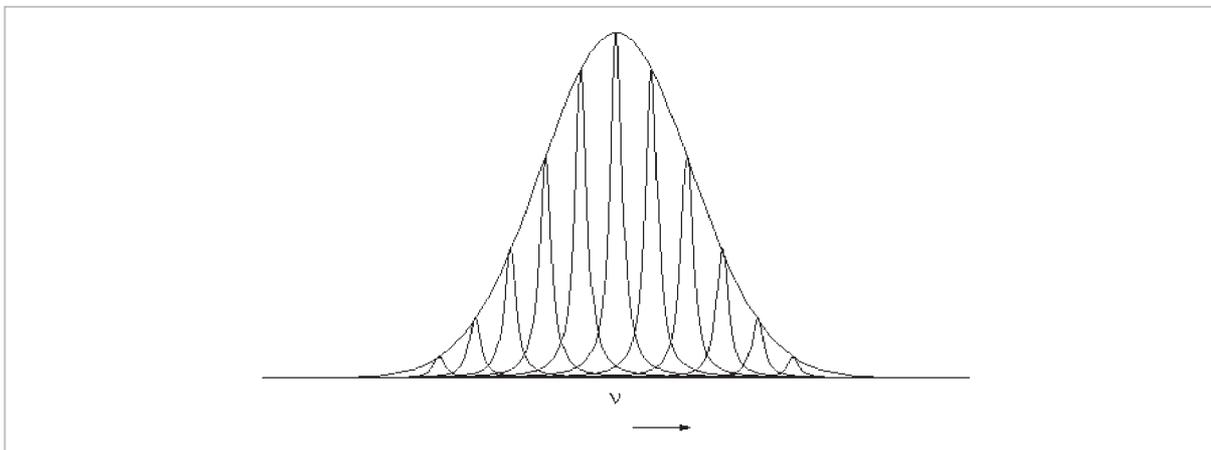
Pressure broadening parameter, BWO, Submillimeter-wave, SMILES

## 1 Observation of pressure broadening of molecular spectra

Spectral line broadening of molecules in the gas phase in the submillimeter wavelength region is mainly caused by the Doppler effect, due to the translational motion of the molecules themselves, and by collisions with other

molecules. In many laboratory spectroscopy experiments in the submillimeter wave region, the observed lineshape is described by the Voigt profile (Fig. 1), which is a convolution of the Gaussian and Lorentzian functions.

Since the velocity of gas-phase molecules follows the Maxwell-Boltzmann distribution, the spectral line profile due to the Doppler effect (Doppler width) will be given by the



**Fig. 1** If the Lorentzian broadening is smaller than the Gaussian broadening, the spectral line profile can be expressed by a superposition of the Lorentzian profiles of the peak intensity given by the normal distribution, leading to the Voigt function

Gaussian function (normal distribution), and will become larger as temperature increases.

On the other hand, the spectral line broadening due to collisions with other molecules is caused by disruptions of quantum states of the molecules, and the lineshape becomes Lorentzian. In this case, the line broadening increases with the gas pressure, and thus it is also called pressure broadening. Since molecular collisions discussed here are involved with various interactions between molecules (from hard collisions that alter the quantum states of both molecules to relatively soft collisions that only cause phase fluctuations), it is extremely difficult to make a precise theoretical prediction of pressure broadening parameters; as a result, experimental observations are essential in determining the parameters.

Pressure broadening increases linearly with the collision frequency (number of collisions per unit time), and therefore it increases with the pressure. At high pressures exceeding 1 atm, the frequency of multiple collisions (involving more than two molecules) becomes no longer negligible, so the functions above will not be applicable. However, as the pressure in the atmospheric regions above the stratosphere will never reach such a high pressure, the pressure broadening  $\Delta\nu$  (half width at half maximum) may be expressed in terms of the pressure broadening coefficient  $\Gamma$  and the gas pressure  $p$ .

$$\Delta\nu = \Gamma \cdot p \quad (1)$$

The pressure-broadening parameter depends also on temperature, and will increase with a decrease in temperature. This may be relatively easily understood, considering that, while the number of molecules per unit volume is inversely proportional to temperature, the velocity of molecular motion is proportional to the square root of temperature. In other words, as the line width is proportional to  $Nu\sigma$ , where  $N$  is the number of molecules per unit volume,  $u$  the average velocity of the molecules, and  $\sigma$  the collisional cross-section, respectively, the following relationship can be

derived.

$$\Delta\nu \propto Nu\sigma \propto \frac{1}{\sqrt{T}} \quad (2)$$

However, as the cross section  $\sigma$  in fact depends on the molecular velocity, the relationship above is not quite correct; as a result, a more straightforward path to obtaining the precise pressure-broadening parameter is by laboratory observations. Taking  $\Gamma_0$  as the pressure-broadening parameter at 296 K, the parameter at temperature  $T$  may be expressed as

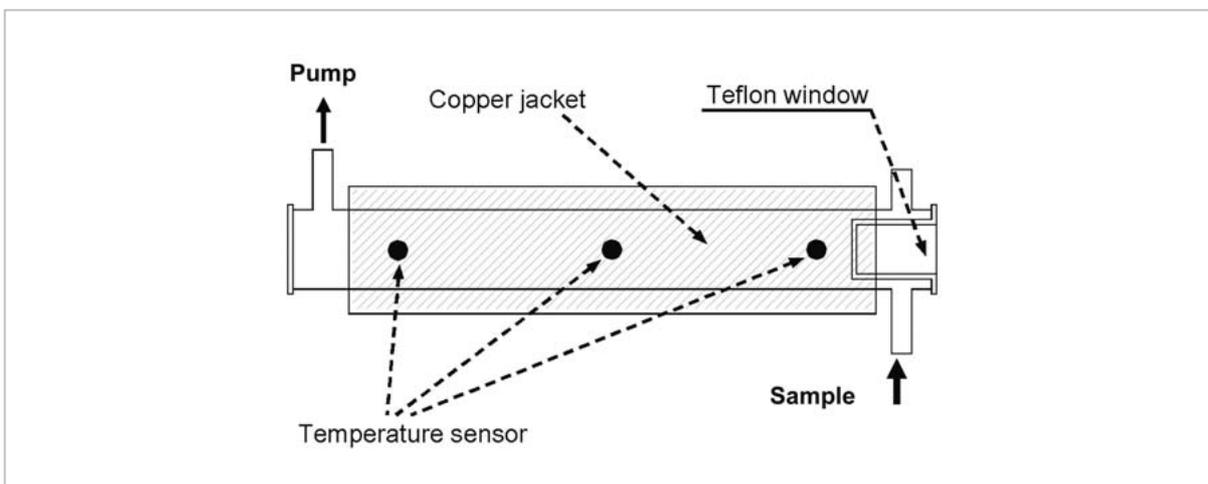
$$\Gamma = \Gamma_0 \left( \frac{T}{296} \right)^n \quad (3)$$

where  $n$  is the temperature exponent for the pressure broadening.

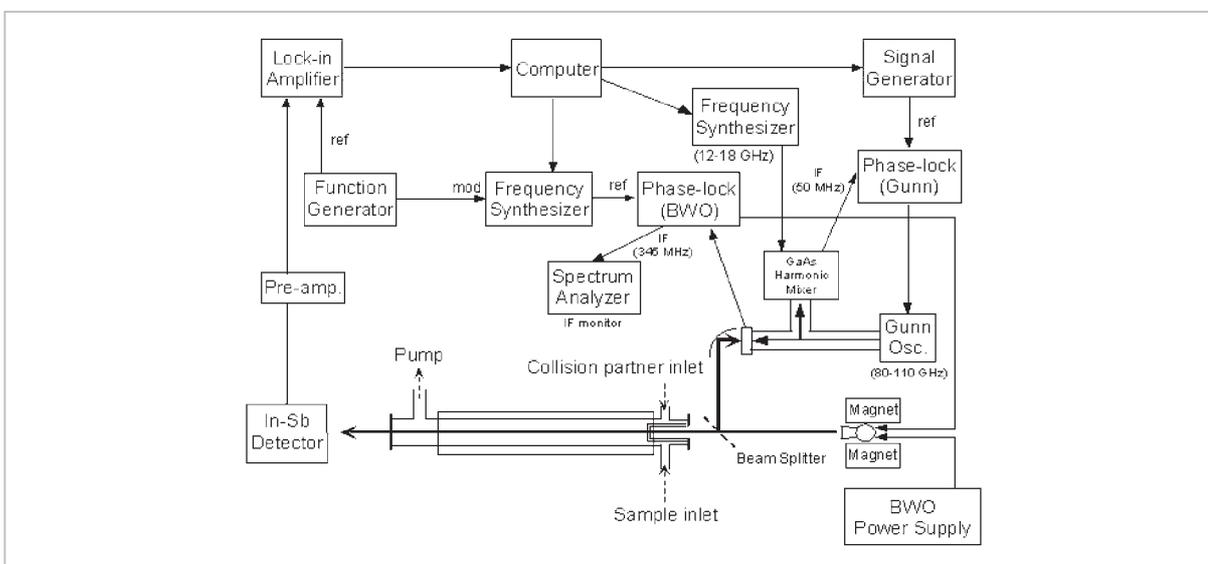
## 2 Experimental apparatus and analysis method

Among the molecules planned to be observed in the JEM/SMILES project, unstable species such as BrO and O<sub>3</sub> must be generated in the absorption cell or immediately before the cell. BrO was generated by a DC discharge in a gas mixture of bromine and oxygen, while O<sub>3</sub> was generated by flowing oxygen gas through an ozonizer. The generated ozone together with the parent gas was continuously pumped through the absorption cell from the inlet (Fig. 2). By maintaining the cell temperature and the ozone pressure that serves as a reference sample, the O<sub>2</sub> or N<sub>2</sub> buffer gas was introduced in the absorption cell, making "high pressure" measurements possible.

The gas kinetic temperature was assumed to be the same as the cell temperature, as the time needed for achieving equilibrium should be much shorter than the gas traversal time through the cell. The glass cell is covered with a pair of copper jackets connected to a refrigerated liquid circulator, which allows the temperature to be controlled from -70 to +20°C. The glass cell is 180 cm long, and the central portion of 150 cm in length is covered with the copper jackets. Since the molecules residing in



**Fig.2** Schematic diagram of the glass cell used in the present experiment. The sample generated externally is drawn into the cell by a vacuum pump. The cell temperature is measured at three points, and the average value is used to represent the sample temperature. To remove the effects of the uncovered areas from the observation data, a recessed top-hat shaped Teflon window is placed at the sample inlet side.



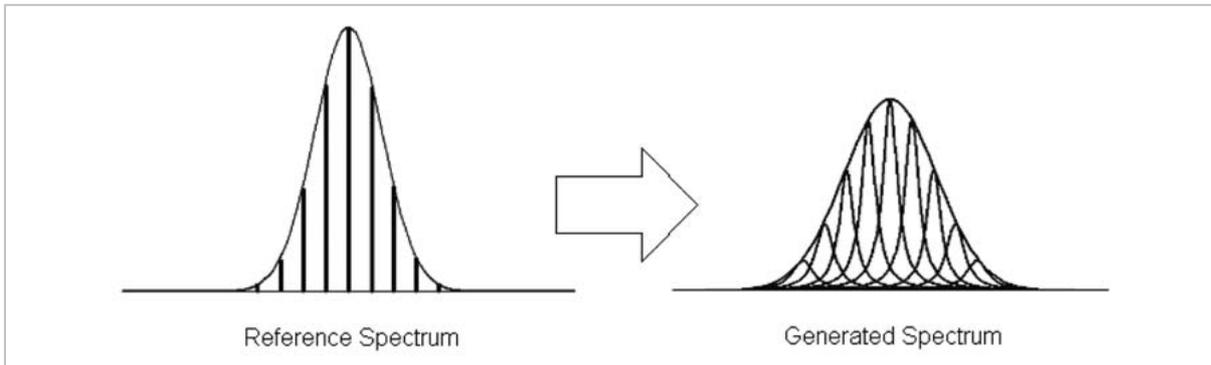
**Fig.3** Block diagram of the submillimeter-wave absorption spectrometer. The BWO (Backward Wave Oscillator) is phase-locked to a Gunn oscillator by a GaAs harmonic mixer.

the uncovered portions at each end should not be observed for measurements, a top-hat shaped window was placed at the radiation and sample inlet side, as shown in Fig. 2. A similar window is not used in the sample outlet side, because radical species such as BrO are largely decomposed before they reach the outlet. In observations of molecules such as O<sub>3</sub>, a similar window has to be used at the outlet side in a similar way as the inlet side. Alternatively, an appropriate calibration of the

gas temperature is needed to remove the influence that is caused by the uncovered portion of the absorption cell.

A BWO (Backward Wave Oscillator) phase-locked to harmonics from a Gunn oscillator was used as a submillimeter-wave source, and the transmitted radiation was detected by using a liquid-He-cooled InSb bolometer (Fig. 3).

The convolution method proposed by Pickett[1] was adopted for analysis of the



**Fig.4** The pressure-broadening (Lorentzian) can be derived simply as the difference from that of the reference spectrum, as the reference line profile is a measured low-pressure line

**Table 1** Pressure broadening parameters for BrO (from Reference [2]); values in parentheses represent one standard deviation

Line / Gas	624.768 GHz ( $J = 23.5 \leftarrow 22.5$ )		650.178 GHz ( $J = 24.5 \leftarrow 23.5$ )	
	$\Gamma_0$ [MHz / Torr]	$n$	$\Gamma_0$ [MHz / Torr]	$N$
N <sub>2</sub>	3.24 (5)	-0.76 (5)	3.20 (7)	-0.84 (7)
O <sub>2</sub>	2.33 (6)	-0.93 (7)	2.41 (6)	-0.70 (7)
Air	3.05 (5)	-0.80 (5)	3.03 (7)	-0.81 (7)

observed line profile. This method employs a spectrum recorded at low pressure as a reference line profile, and a line profile recorded at higher pressure is expressed as a convolution of this reference line with a Voigt profile with the Lorentzian line width and the base line functions as variable parameters. These parameters can be least-squares fitted (Fig. 4). An advantage of this method is that the reference profile is an actually observed spectral line profile, and therefore the effects of instrument induced broadening and of the Doppler broadening can be eliminated in the derivation of the pressure-broadening parameter.

### 3 Results

Laboratory measurements on the 624.77 GHz ( $J = 23.5 \leftarrow 22.5$ ) and 650.18 GHz ( $J = 25.5 \leftarrow 24.5$ ) transitions within the observing bands for SMILES were performed jointly with the JPL group in 2003 [2]. Although the

hyperfine splitting due to the nuclear spin of Br was evident in the BrO spectrum, no additional parameters were required in fitting with the convolution method [1]. It was not possible to detect the difference in pressure broadening among different hyperfine components, and it was assumed with good approximation that such differences may be ignored. The results of the present experiment for the pressure-broadening observations with N<sub>2</sub> and O<sub>2</sub> as buffer gases are presented in Table 1. In the table, the values for the pressure broadening parameters by air were calculated using the experimental results and the composition of the terrestrial atmosphere given by

$$\Gamma_{\text{air}} = 0.79\Gamma_{\text{N}_2} + 0.21\Gamma_{\text{O}_2} \quad (4)$$

where  $\Gamma_{\text{N}_2}$  and  $\Gamma_{\text{O}_2}$  are the pressure-broadening parameters for nitrogen and oxygen, respectively. The JPL group, with whom we carried out the joint research, used a different

**Table 2** Pressure-broadening parameters of ozone in the laboratory (from Reference[3]); values in parentheses represent one standard deviation

Line/Gas	$^{16}\text{O}^{16}\text{O}^{16}\text{O}$				$^{16}\text{O}^{18}\text{O}^{16}\text{O}$
	544.8575 GHz		625.371 GHz		647.691 GHz
	$\Gamma_{296\text{K}}$	$n$	$\Gamma_{296\text{K}}$	$n$	$\Gamma_{294\text{K}}$
N <sub>2</sub>	3.239(05)	-0.821 (07)	2.934 (08)	-0.930 (13)	3.29 (4)
O <sub>2</sub>	2.806(05)	-0.855 (10)	2.448 (07)	-0.983 (16)	2.39 (4)
Air	3.148 (05)	-0.828 (08)	2.832 (08)	-0.941 (14)	3.10 (4)

instrument to determine the parameters, and their results agree very well with ours.

Pressure-broadening observations for O<sub>3</sub> were subsequently carried out[3]; the results are listed in Table 2. The observed transitions were  $3_3 1 \leftarrow 2_2 0$  (544.8575 GHz) and  $15_6 10 \leftarrow 16_5 11$  (625.371 GHz) for  $^{16}\text{O}^{16}\text{O}^{16}\text{O}$  and  $27_{1 27} \leftarrow 26_{0 26}$  (647.691 GHz) of the symmetric isotope  $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ . The  $3_3 1 \leftarrow 2_2 0$  (544.8575 GHz) transition had been observed in the Odin mission, and an estimated pressure broadening parameter had been used in analysis of the atmospheric data. However, an actual measured value is now available as a result of the present study. It has been found to be significantly different from the estimated value previously used. Thus, the present result has undoubtedly exerted a significant impact on the atmospheric study. Further, although the natural abundance of  $^{18}\text{O}$  is only 0.2%, and the spectrum of the  $^{16}\text{O}^{18}\text{O}^{16}\text{O}$  isotope is considerably weaker compared to the normal O<sub>3</sub>, repeated measurements with long integration time made with our high-sensitivity spectrometer has allowed us to determine the pressure-broadening parameters of even this weak line of ozone isotopic species. The air-broadened parameters in Table 2 have been calculated by using Eq. (1). The 625.371-GHz transition was observed also by Drouin et al.[4], and their results were compared with ours. These two sets of data differ beyond the error limits. The cause of the discrepancies is not well understood at this stage. The repeated experi-

ments were carried out at intervals of several months, and the results always remained the same.

## 4 Conclusions

In our investigations, we observed pressure broadening of BrO,  $^{16}\text{O}^{16}\text{O}^{16}\text{O}$ , and  $^{16}\text{O}^{18}\text{O}^{16}\text{O}$  in the submillimeter-wave region and obtained pressure broadening parameters with 1~3% accuracy. In addition, the temperature dependence exponents were determined for each transition.

However, some discrepancies were found between the results obtained by us and by the JPL group for the same transition of ozone. These problems must be resolved in future investigation. It may be possible that the gas-temperature monitoring included some degree of inaccuracy; accordingly, more stringent temperature control and a more direct temperature measurement system should be implemented. Temperature and pressure control of gases in the cell and their long term stability all affect the accuracy of the pressure broadening parameters. Therefore it is important to pursue further improvement in the experimental method in future, in addition to accumulating more experimental data.

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