



PRESSURE BROADENING OF THE 83.869 cm^{-1} ROTATIONAL LINES OF OH BY N_2 , O_2 , H_2 , AND He

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Abstract—We present pressure broadening coefficients of the 83.869 cm^{-1} (2.514 THz) F_1 , $5/2^- \leftarrow F_1$, $3/2^+$ rotational lines of OH by N_2 , O_2 , H_2 , and He at 293 and 192 K. We also remeasured the position of the manifold of lines, with results that are in excellent agreement with a previous accurate determination. The frequency of the strongest component of the transition ($F = 2 \leftarrow 3$) and its 2σ uncertainty is $2,514,316.37(3)\text{ MHz}$.

INTRODUCTION

The central role of the OH radical in ozone layer photochemistry and the need for quantitative measurements of its concentration vs altitude and solar time has been discussed extensively in the literature. An abridged discussion of this role, with further references to atmospheric measurement techniques, is given by Chance et al.¹ The high level of OH line saturation in the atmospheric absorption spectrum makes the retrieval accuracies strongly dependent on the accuracy of the pressure broadening coefficients. The present work is an extension of our measurements of the pressure broadening of OH to provide the quantitative basis for the evaluation of atmospheric measurements of OH. The manifold of OH lines at 83.869 cm^{-1} is an important set for the measurement of OH using Fourier transform spectroscopy² and has been suggested as a primary candidate for the measurement of OH from a satellite platform using heterodyne spectroscopy.³

EXPERIMENTAL DETAILS

The absorption spectrum of OH was measured using a tunable far infrared radiation (TuFIR) source.^{4,5} The present measurement was made with the source in a three-wave mixing arrangement, with radiation from two frequency stabilized CO_2 lasers and a microwave synthesizer were mixed in a metal-insulator-metal diode. The nonlinear mixing at the diode results in two sidebands, one above and one below the difference frequency of the two lasers. The frequency offset of these sidebands can be tuned by varying the microwave frequency. The frequency of the resulting TuFIR radiation is known with an accuracy of $\sim 10\text{ kHz}$ and has about equivalent spectral purity.⁶

Measurements were made using a Pyrex absorption cell 50 cm long and 2.5 cm dia, with high density polyethylene windows 1.6 mm thick. The cell walls were coated with halocarbon wax to reduce wall losses of OH. The cell was immersed in a temperature bath of ethanol and dry ice used to cool the cell walls to $192 \pm 2\text{ K}$. The pressure was measured at the center of the cell using a capacitance manometer of 0.15% accuracy. Flow rates of all gases introduced into the cell are measured using mass flow meters. These flow rates were used in the regression analysis below to determine partial pressures for each gas.

OH was produced in the absorption cell from the reaction of H atoms with NO_2 . H atoms were generated in a side arm from a d.c. discharge in a He- H_2 mixture. NO_2 and the broadening gas

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were introduced separately into the absorption cell immediately adjacent to the discharge side arm and the reacting gas mixture is pumped through the absorption cell. NO_2 partial pressures were negligibly small compared with those of other gases. A rapid degradation of the signal-to-noise ratio due to broadening limited the range of pressures in our measurements, forcing us to keep the total pressures below 1000 Pa.

Linewidths are determined by fitting synthetic spectral lineshapes to the measured spectra using a nonlinear least-squares routine.¹ The synthetic lineshapes are generated using fixed values of the Gaussian line shapes and the instrumental and measurement parameters. Lorentzian widths, line positions, intensities, and baseline corrections are varied in the fitting. Figure 1 shows two representative spectra and the fitting results.

The OH transition is split by the proton hyperfine interaction into three lines. These three lines, in the order of increasing frequency, correspond to $F = 2 \leftarrow 2$, $F = 3 \leftarrow 2$ and $F = 2 \leftarrow 1$. Their relative intensities should be 1:14:9, based on angular momentum coupling.⁷ The frequency separations are determined from the analysis of microwave resonance data more accurately than from the present measurements.⁸ They are 18.337(9) MHz ($F = 2 \leftarrow 3 - F = 2 \leftarrow 2$) and 36.791(9) MHz ($F = 1 \leftarrow 2 - F = 2 \leftarrow 3$). In the analysis the positions, widths and intensities of the two smaller hyperfine components are locked to those of $F = 2 \leftarrow 3$. Selected comparison between the results obtained using this procedure and those obtained by varying parameters for the two larger hyperfine components independently show no significant differences.

Since OH is generated in a He- H_2 discharge, the broadening by these gases is measured along with the broadening by O_2 and N_2 . Pressure broadening coefficients for each cell temperature are obtained from the fitted widths using three-component linear regression analysis. The results of these analyses are summarized in Table 1. Air broadening is calculated as $\gamma_{\text{air}} = 0.79 \gamma_{\text{N}_2} + 0.21 \gamma_{\text{O}_2}$.

We do not observe statistically significant pressure-induced line position shifts. Determinations of the $F = 2 \leftarrow 3$ line position at the lowest pressure for helium broadening (and thus the lowest total line width) and its 2σ uncertainty are 2,514,316.345(36) MHz at 296 K and 2,514,316.433(52) MHz at 192 K, giving a weighted average position of 2,514,316.37(3) MHz.

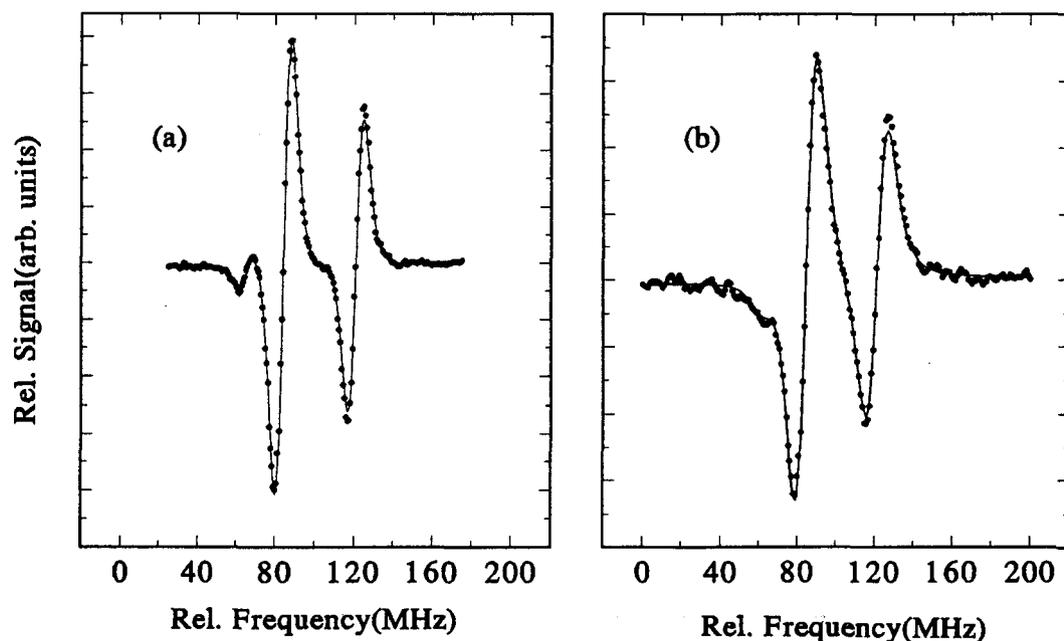


Fig. 1. Representative absorption spectra of OH broadened by H_2 , He and N_2 . The nonlinear least-squares fits to the spectra are shown as solid lines. Spectra shown are taken at 296 K with broadening gas partial pressures of: (a) 12 Pa of H_2 + 113 Pa of He; (b) 9 Pa of H_2 + 92 Pa of He + 157 Pa of N_2 . The figures in the abscissas are frequencies in MHz offset by 2,514,232.358 MHz. The ordinates are in arbitrary linear intensity scales.

Table 1. Pressure broadening coefficients ($10^{-7} \text{ cm}^{-1} \text{ Pa}^{-1}$, HWHM) for the 83.868 cm^{-1} Lines of OH†.

Broadening gas	Temperature	
	$296 \pm 3 \text{ K}$	$192 \pm 2 \text{ K}$
H ₂	9.63 (50)	16.56 (1.20)
He	2.00 (06)	2.20 (14)
N ₂	9.58 (30)	14.84 (56)
O ₂	6.61 (44)	8.38 (30)
Air‡	8.96 (26)	13.48 (44)

† 2σ uncertainties shown.

‡ $\gamma_{\text{air}} = 0.79\gamma_{\text{N}_2} + 0.21\gamma_{\text{O}_2}$.

DISCUSSION

The room temperature He broadening coefficient for this OH line has been measured by Burrows et al.⁹ Their value of $2.21 \times 10^{-7} \text{ cm}^{-1} \text{ Pa}^{-1}$ agrees with our value of 2.00 within the quoted uncertainties. Buffa et al.¹⁰ have calculated N₂ broadening of OH lines. Their values at 300 K and 200 K (in $10^{-7} \text{ cm}^{-1} \text{ Pa}^{-1}$) are 11.1 and 14.8, compared with our values of 9.58 and 14.84. Their theoretical predictions are estimated to be good to 10–20%. Our measurements, particularly the temperature dependence, are in excellent agreement with their calculations. They also predict pressure-induced line position shifts on the order of $10^{-8} \text{ cm}^{-1} \text{ Pa}^{-1}$, which is quite consistent with our null results. Brown et al.¹¹ have measured the positions of several low-lying rotational transitions of OH. Their value of 2,514,316.34(7)(1 σ) MHz for this line is in agreement with our slightly more accurate value of 2,514,316.37(3) (2 σ) MHz.

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