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# Measurements of the Pressure Shift of the $1_{10}$–$1_{01}$ Water Line at 556 GHz Produced by Mixtures of Gases

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Microwave measurements of pressure shifts by mixtures of gases are reported. Recently in IR measurements a nonlinear dependence of shift vs concentration was found (*J. Mor. Spectrosc.* **153**, 406–418, (1992). Our measurements were carried out on the $1_{10} \leftarrow 1_{01}$ water ($H_2{}^{16}O$) line near 556 GHz using nitrogen, oxygen, and their mixtures as perturbers. The result showed no measurable nonlinearity. Further experiments are discussed. 

## 1. INTRODUCTION

Giesen *et al.* have recently found (*1*) that the shift of two measured IR water lines, $13_{2,12}$–$14_{1,13}$ and $9_{5,5}$–$10_{6,4}$, perturbed by pure air does not agree with the weighted mean of the shifts measured by the collision of pure nitrogen and oxygen, in contrast with the broadening parameters, which do.

Typically, the "additivity" of lineshifts in the case of mixtures is taken as granted. In some papers shifts of lines by air were not measured but rather calculated as a weighted mean from pure gas measurements. It is interesting to examine measurements (in some cases less accurate than those of Ref. (*1*)) analogous to ours. Surprisingly, only three such papers were found, which belonged to another group using FTIR techniques (*2*) to study isotope-substituted water molecules.

Similar behavior was found among the results of Ref. (*2*); some data show differences between measured and calculated shifts well outside three times the standard deviation listed in Ref. (*2*). A statistical analysis of these data clearly shows for all three papers that the deviation of air shifts from the weighted averages of the nitrogen and oxygen shifts does not follow the normal Gaussian distribution, suggesting that these deviations do not originate from statistical errors. Possible explanations of these findings include an experimental error of unknown origin common to different types of spectrometers, and one arising from molecular origins, e.g, "memory of previous partner in collision," which can lead to a concentration cross term in the lineshift.

One source of experimental error found was simply different water concentrations in the different air samples (*3*); when this effect was controlled, dependences on concentrations measured on a $Q(6,3)$ ammonia line were found to be linear.

However, this study has not yet been extended to the aforementioned two water lines; therefore this problem cannot be considered as fully solved. Recently a paper (*4*) concerning ozone broadening and shifts by air, nitrogen, and oxygen has appeared in which the authors note, already knowing the results of Ref. (*1*), that while their measured broadening coefficients consistently follow the linear relationship mentioned, their measured shifts by air do not always correspond to a linear combination of the $N_2$ and $O_2$ shifts.



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This situation makes further study of this problem very desirable, and we in Nizhnii Novgorod Laboratory started investigations of microwave measurements of pressure shifts of the $1_{10} \leftarrow 1_{01}$ water ($H_2{}^{16}O$) line near 556 GHz using nitrogen, oxygen, and their mixtures as perturbers. The present short communication presents the results of these first microwave measurements in this direction.

## 2. EXPERIMENTAL DETAILS

The present investigation of the pressure shift and broadening of the $1_{10} \leftarrow 1_{01}$ water line by collisions with nitrogen, oxygen, and their mixtures as perturbers was carried out using a submillimeter RAD spectrometer (*5*). The method of investigation of the lineshift and line broadening by the RAD spectrometer has been previously described in Ref. (*6*). All measurements were made at room temperature, $T = 297(1)$ K.

Strong water lines were observed each time from water impurities in the sample. But the concentration of water vapor was controlled by the intensity of the line and was kept to less than 0.5% in the nitrogen sample and 0.5% in the oxygen sample. The self-shift parameter for this water line measured by us is equal to $\Delta_{ss} = -2.28(4)$ MHz/Torr. Thus self-shift should not affect the results because its maximal contribution could not be more than a few kHz/Torr.

The pressure dependences of the $1_{10} \leftarrow 1_{01}$ water linecenter frequency on the pressures of nitrogen, oxygen, and two different mixtures of these gases are presented in Fig. 1. These results illustrate the quality of the measurements.

Next we fixed the pressure of the gas in the RAD cell to $P = 1$ Torr and changed only the composition of the gas mixture. The results of these measurements are presented in Fig. 2 and Table I. "Calculated" values correspond to the values obtained as a weighted mean of measured values for the pure perturbers—nitrogen and oxygen.

As can be seen from the data of Table I and Fig. 2, the dependence of lineshift vs concentration can be taken as linear to a good degree of accuracy. Additionally, broad-

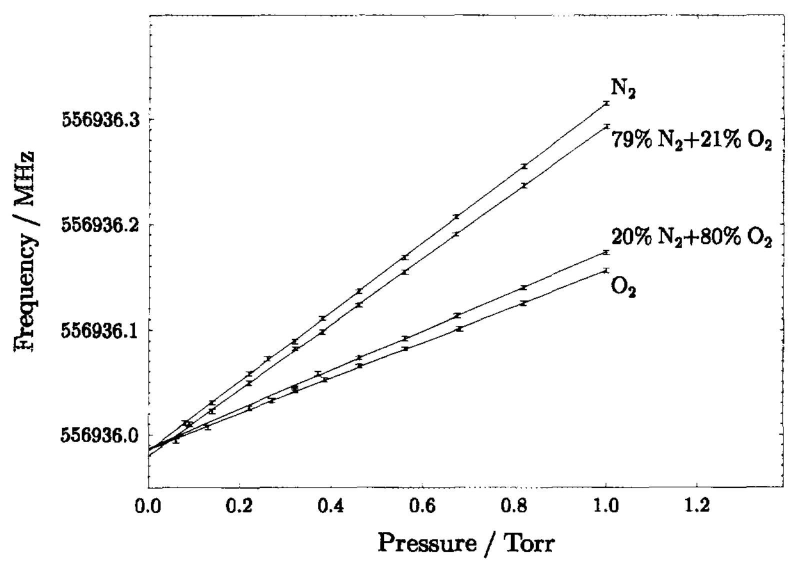


FIG. 1. Center frequency dependence of the $1_{10}$–$1_{01}$ $H_2{}^{16}O$ line on the pressure of nitrogen, oxygen, and their mixtures.

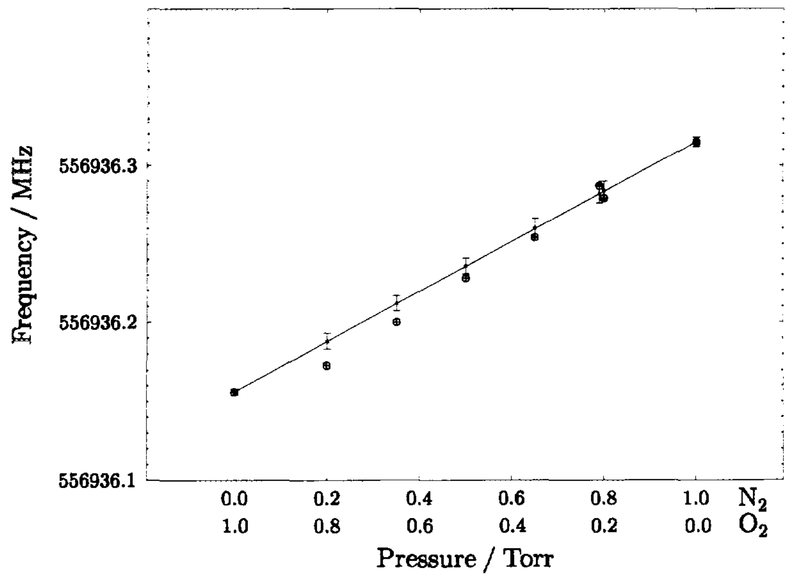


FIG. 2. The dependence of the center frequency of the $1_{10}$–$1_{01}$ $H_2{}^{16}O$ line on mixtures of nitrogen and oxygen. ⊕, experimental points; |, calculated points using $\nu_o$ = 556 935.985(2) MHz and the pressure correction calculated as the weighted mean from measured shift parameters for pure gases. The gas pressure in the RAD cell was kept constant at $P$ = 1 Torr.

ening parameters for the $1_{10} \leftarrow 1_{01}$ transition of water were measured for broadening by pure nitrogen and oxygen. They were found to be equal to $\Delta_{bn}$ = 5.40(6) MHz/Torr and $\Delta_{bo}$ = 3.10(6) MHz/Torr for nitrogen and oxygen, respectively.

## 3. DISCUSSION

These new microwave measurements of shifts in the $1_{10} \leftarrow 1_{01}$ water line near 556 GHz produced by using nitrogen, oxygen, and their mixture as perturbers did not show measurable nonlinearity due to concentration.

TABLE I

Summary of Results of Measurements of the $1_{10} \leftarrow 1_{01}$ $H_2{}^{16}O$ Lineshift Produced by Nitrogen, Oxygen, and Their Mixtures at Constant Pressure in the Cell ($P$ = 1 Torr, $\nu_o$ = 556 935.985(2) MHz)

| Mixture P = 1.00 Torr $N_2$ | $O_2$ | Calc. Shift par. MHz/Torr | Exp. Shift par. MHz/Torr | Calc. Frequency MHz | Exp. Frequency MHz |
|---|---|---|---|---|---|
| 1.00 | 0.00 | ——— | 0.330(4) | 556936.315(3) | 556936.315(2) |
| 0.79 | 0.21 | 0.296(5) | 0.307(4) | 556936.282(6) | 556936.287(2) |
| 0.80 | 0.20 | 0.298(5) | ——— | 556936.284(6) | 556936.279(2) |
| 0.65 | 0.35 | 0.274(5) | ——— | 556936.260(6) | 556936.254(2) |
| 0.50 | 0.50 | 0.250(4) | ——— | 556936.236(5) | 556936.228(2) |
| 0.35 | 0.65 | 0.226(4) | ——— | 556936.212(5) | 556936.200(2) |
| 0.20 | 0.80 | 0.202(4) | 0.187(5) | 556936.188(5) | 556936.173(2) |
| 0.00 | 1.00 | ——— | 0.170(3) | 556936.156(2) | 556936.156(2) |

But, e.g, in Ref. (2), approximately one-tenth of more than 400 measured lines showed anomalous behavior; therefore, due to the lack of experimental data and any criteria for choosing the proper lines for investigation, the authors plan to continue the course of these measurements.

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## REFERENCES

1. T. GIESEN, R. SCHIEDER, G. WINNEWISSER, AND K. M. T. YAMADA, *J. Mol. Spectrosc.* **153,** 406–418 (1992).
2. C. P. RINSLAND, M. A. H. SMITH, AND V. MALATHY DEVI, *J. Mol. Spectrosc.* **150,** 173–183 (1991); **150,** 640–646 (1991); **156,** 507–511 (1992).
3. M. FABIAN, private communication.
4. M. A. H. SMITH, C. P. RINSLAND, V. MALATHY DEVI, AND E. S. PROCHASKA, *J. Mol. Spectrosc.* **164,** 239–259 (1994).
5. A. F. KRUPNOV, *Vestn. Akad. Nauk SSSR* **7,** 18–29 (1978); A. F. KRUPNOV, *in* "Modern Aspects of Microwave Spectroscopy" (G. W. CHANTRY, Ed.), pp. 217–256, Academic Press, New York, 1979.
6. S. P. BELOV, A. F. KRUPNOV, V. N. MARKOV, V. A. SKVORTSOV, AND M. YU. TRETYAKOV, *Opt. Spektrosk.* **56,** 828–832 (1984).