

Experimental study of the line mixing coefficient for 118.75 GHz oxygen line

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Abstract

The oxygen fine structure line 1– at 118.75 GHz was studied by two spectrometers at low (0.2–3.5 Torr) and high (atmosphere) pressures in air and pure oxygen. Improvement in the spectrometer with BWO and acoustic detector included use of a powerful (more than 40 mW) radiation source. Improvement in the modern resonator spectrometer included exclusion of apparatus function by sample substitution and a wider (110–130 GHz) scanned frequency range. As a result, the 1– oxygen line was observed by both spectrometers with high (up to 450) signal-to-noise ratio which permitted precise measurements of the line parameters. The investigation separated linear- and quadratic-with-pressure displacement of the line center. The line mixing coefficient responsible for apparent quadratic dependence of the center frequency on pressure was measured experimentally for the first time for this line. The line mixing coefficient was measured at 297 K as $-4.62(38) \times 10^{-5} \text{ Torr}^{-1}$ for pure oxygen and $-5.9(29) \times 10^{-5} \text{ Torr}^{-1}$ for air, compared to the previously calculated value $-3.1 \times 10^{-5} \text{ Torr}^{-1}$. Linear dependence of the line center frequency on pressure does not exceed $\pm 20 \text{ kHz/Torr}$ for air and $\pm 10 \text{ kHz/Torr}$ for pure oxygen. Refined values of line broadening were obtained. Integral intensity of the line was measured. A comparison with the previous investigations is presented. Inconsistencies in published data about pressure line shifts of oxygen molecule spectral lines are discussed.

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1. Introduction

The single isolated 118-GHz, $N = 1 -$ line of the oxygen molecule belongs to the fine structure band of magnetic-dipole transitions in which the unpaired electron spin of the $^3\Sigma_g$ electronic ground state changes alignment with respect to rotational angular momentum of the molecule. This line is of great importance for remote sensing of the atmosphere. In particular the line is widely used by airborne and satellite-based instruments for atmosphere temperature profile recovery [1]. The line was also chosen for the search of molecular

oxygen in astronomical objects for the ODIN satellite mission [2]. Measurements from flying instruments are then used for recovery of atmospheric parameters using the spectral parameters obtained in the laboratory. The accuracy of recovered atmospheric parameters directly depends on the accuracy of laboratory measurements of parameters of the line.

Due to high applied importance of the line, its parameters have been extensively studied by a number of investigators in the past [3–5]. The 118-GHz oxygen line has relatively weak strength, which, on the one hand, makes it so attractive for limb sounding instruments since it allows analyzing very long atmospheric paths, but on the other hand, makes laboratory studies difficult. So even such an important parameter of the line as pressure broadening measured by different authors differs within 15%, more than the experimental

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error quoted by authors. The shape of the 118-GHz oxygen line at pressures up to atmospheric was studied earlier in the laboratory in pure oxygen [3]. The results led authors of [3] to the conclusion that the Van Vleck–Weisskopf (VW) profile was inconsistent for fitting their data. The line profile in a real atmosphere was studied in our earlier work [6]. It was shown that the VW profile could be fitted within experimental accuracy to both the line observed in our experiment in air and the line observed in pure oxygen in [3], if the line central frequency was also an adjustable parameter and a constant-with-frequency term was added. In both cases the result of the fit revealed small (–75 MHz in oxygen and –150 MHz in air) negative shifts of the line central frequency in comparison with the central frequency measured at low pressure. We suggested at that time a line shift linear with pressure as interpretation of the effect. However, the shift parameter value seemed to be too big for the magnetic-dipole transition of a non-polar molecule. On the other hand, other authors reported [7] about hundreds of kilohertz per Torr shifts of electronic-rotational-fine structure transitions of oxygen lines; moreover, the shift values revealed essential dependence on the rotational and fine structure quantum numbers. We also did not determine the dependence of the line center displacement on pressure in the work [6] since the study was performed only at one atmosphere pressure. Another effect (line mixing or coupling) leads to a line center displacement that is proportional to the square of pressure. The line mixing was studied for fine structure oxygen lines forming together the 60-GHz oxygen absorption band [8,9], but for the 118-GHz line the mixing parameter was not measured.

Having now the possibility of separate investigation of both effects and in particular experimental measurement of the line mixing coefficient, we initiated this new study of the 118-GHz oxygen line. Results of that study are the subject of the present paper.

Two experiments were performed by use of two experimental setups. The first one used a high-resolution spectrometer with BWO based frequency synthesizer and radio-acoustic detection (RAD) [10] under low (0.5–3.5 Torr) pressure, with the goal to determine (or to set limits on) the value of linear-with-pressure line center shift. The other one, under atmospheric pressure, used a resonator spectrometer with fast digital frequency scanning [11], but using spectrometer baseline subtraction, which gave us better signal-to-noise ratio of the observed line in comparison with [6] and therefore better accuracy of the line parameters in atmospheric air. Pure oxygen was also used in this experiment, which increased the line signal by a factor of 5. The main features of these two experimental methods were described in [12,13] correspondingly. The new improvements are described in the present paper.

2. Theory

It was shown in [8] that the shape of the 118-GHz line should be affected by line mixing (or coupling) at near atmospheric pressures because the line belongs to the group of afore-mentioned transitions, most of which are located around 60 GHz. Considering only first-order effects of line mixing, the absorption coefficient from a group of coupled lines can be calculated as a sum of terms, each associated with a line, like this:

$$\gamma_{line}(v) = a \cdot v^2 \cdot \left(\frac{\Delta v + Y \cdot (v - v_0)}{\Delta v^2 + (v - v_0)^2} + \frac{\Delta v - Y \cdot (v + v_0)}{\Delta v^2 + (v + v_0)^2} \right), \quad (1)$$

where a is the line amplitude, Δv is the line half width at half maximum, v_0 is the line central frequency, and Y is the line mixing parameter. The line mixing parameters are related theoretically to off-diagonal elements of a relaxation matrix \mathbf{M} , which is determined by the process in which the gas molecules approach equilibrium through collisions after a perturbation, by

$$Y_i = \frac{2}{\mu_i} \cdot \sum_{j \neq i} \frac{\mu_j \cdot \mathbf{M}_{ji}}{v_i - v_j}, \quad (2)$$

where μ_i is the dipole-moment matrix element for the line with frequency v_i , and the summation in (2) includes negative-frequency resonances (which are written explicitly in (1) as the second term), the zero-frequency or non-resonant absorption, as well as the positive resonances. The terms in (2) may add or cancel, depending on the arrangement of lines in the spectrum as well as the sign of elements of \mathbf{M} . The numerators of terms in (2) are first-order in gas pressure, while the denominators are first-order in frequency spacings of the lines. Thus, even for a separated line like 118 GHz, there are small but potentially observable departures from the VW profile. We are concerned here with experimental determination of Y .

Fig. 1 presents a comparison of function (1) with the VW profile for the 118-GHz oxygen line at room temperature, atmospheric pressure, and the line parameters taken from [9], in the working range of our spectrometer. For making the comparison we calculated a set of frequency-amplitude points using function (1) and then fitted the VW line shape to the set, varying amplitude, width and central frequency. Linear- and constant-with-frequency variable terms were also added to the VW profile as is usually done in treating experimental data to include possible apparatus function or other factors influencing the observed line shape. The deviation of points corresponding to the difference of these two profiles is about ± 0.03 (in the same arbitrary units as the line), thus the difference between these two models can be observed only in the case that experimental signal-to-noise ratio exceeds 120. This defines the

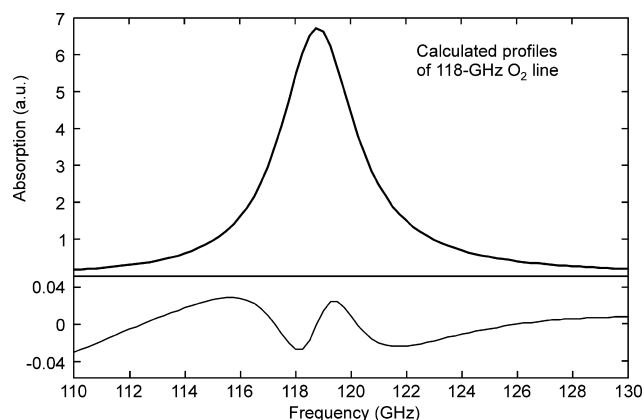


Fig. 1. Theoretical comparison of the function (1) with VVW profile calculated for the 118-GHz oxygen line under pressure 750 Torr, temperature 300 K and the line parameters taken from work [9]. Upper trace presents both the function (1) and VVW profiles overlapping with each other to the thickness of the line. Lower trace is zoomed in difference of the two upper profiles.

sensitivity required of the spectral apparatus devoted to the study of this effect.

In spite of such a small difference in the shapes there is at least one principal thing that should be taken into consideration even if the line is observed with S/N ratio smaller than 120. The line peak frequency calculated using the function (1) appears to be shifted in comparison with the line center ν_0 observed at low pressures. The value of this apparent shift increases as the square of the pressure because of linear increase with pressure of both the line mixing parameter Y and the line half width $\Delta\nu$. Dependence of the apparent shift value vs. pressure for

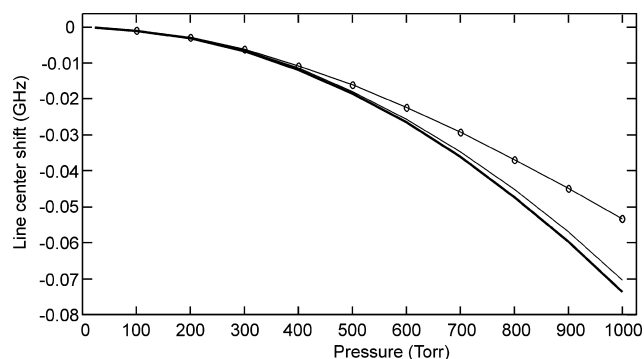


Fig. 2. Value of the apparent shift of the 118-GHz oxygen line central frequency vs. pressure (P) calculated assuming the function (1) with the following line parameters: $\nu_0 = 118.750343$ GHz; $\Delta\nu = \Delta\nu_p \cdot P$, $\Delta\nu_p = 2.17$ MHz/Torr, $Y = Y_p \cdot P$, $Y_p = 3.1 \times 10^{-5}$ 1/Torr (parameters were taken from MPM-93 [9]). Lower thick solid trace was obtained when the line central frequency was determined as the frequency of the function maximum. For the intermediate trace the central frequency was determined from fitting the VVW profile to the function (1) in a wide enough frequency range so its further increase did not affect the result. The upper trace with circles was obtained in the same way as the intermediate one but limiting the frequency range to that shown in Fig. 1.

the 118-GHz oxygen line at room temperature, calculated by three different ways, is given in Fig. 2.

Thus the 118-GHz oxygen line center frequencies determined from fitting the function (1) and the VVW profile to experimental data would be different. The value of this shift rises to about -50 MHz at atmospheric pressure and thus can constitute an essential part of the effect observed in [6] and interpreted at that time as a linear-with-pressure shift. On the other hand, the calculated value of this apparent quadratic-with-pressure shift is only about -1 kHz at 3.5 Torr and so can be neglected, being below the modern level of measurement accuracy, although the linear pressure shift of the line estimated in [6] as -190 ± 80 kHz/Torr could be observed.

3. Experiment with RAD spectrometer at low pressure

The gas cell of the spectrometer was isolated from external magnetic field by double permalloy shielding to prevent Zeeman line broadening. The spectrometer employs amplitude modulation of radiation and synchronous detection of the signal. Pure (99.998 Vol.%) oxygen and nitrogen samples for the low-pressure experiment were bought from Messer MG Company. Gas pressure in the RAD cell was measured by an MKS Baratron gauge of type of 122AAX-00010ADS, having 0.15% accuracy declared by the manufacturer. The experiment was carried out at room temperature, which was controlled by a Hg based laboratory thermometer with 1°C accuracy.

It was shown earlier in our works that the spectrometer is very well suited for study of line pressure shifting and broadening because of its principle of absorption signal detection. In opposition to conventional video-spectrometers where the useful signal is observed in the presence of a large uninformative background, the output signal S in RAD spectrometer appears only if there is radiation absorption inside the cell. Although, some shortcomings still persist. Let's analyze here some possible sources of RAD spectrometer observed line shape distortion. If P is incident radiation power, then the signal S , which is related to power loss in the gas cell, can be expressed using the Beer–Lambert law through absorption coefficient γ of the sample as: $S = P \cdot \gamma L$ (for $\gamma L \ll 1$), where L is the cell length. Thus the spectrometer sensitivity is in direct proportion to radiation power P , which is another advantage of the spectrometer. But power P always has frequency dependence because of both the radiation source amplitude-frequency characteristic and radiation interference in spectrometer waveguide parts, so it should be taken into account as a multiplicative term to the line shape function. Moreover the high power of the BWO (more than 40 mW) used in the present study leads to appearance of noticeable parasitic signals coming from absorption of the radiation

in the RAD gas cell windows. A combination of constant-, linear- and quadratic-with-frequency terms additive to the lineshape function was found sufficient to account for this signal. Thus, the total line shape function to be used for fitting to RAD spectrometer experimental data should look like

$$\gamma_{\text{RAD}}(\nu) = A_0 \cdot (1 + A_1(\nu - \nu_0)) \cdot \gamma(\nu) + A_2 + A_3(\nu - \nu_0) + A_4(\nu - \nu_0)^2, \quad (3)$$

where A_i are adjustable coefficients and $\gamma(\nu)$ is the normalized line profile function. For this function we used a Lorentz profile as most practical for the pressure range of this RAD experiment

$$\gamma(\nu) = \frac{1}{\pi} \cdot \left(\frac{\Delta\nu}{\Delta\nu^2 + (\nu - \nu_0)^2} \right). \quad (4)$$

It should be noted that use of an improper line shape function in conditions of radiation power-frequency dependencies and low S/N ratio of the observed line may lead to measurement of false line center frequency shift arising from the line shape distortion, which usually has a quadratic dependence on pressure, instead of linear-with-pressure shift of the line.

To minimize the line shape distortion due to aforementioned factors, it was found practical to fill the spectrometer cell with non-absorbing gas under the same pressure as the studied sample and to subtract the apparatus function obtained in this way from the line record as shown in Fig. 3. The upper part of the figure is a record of the 118-GHz line in pure oxygen

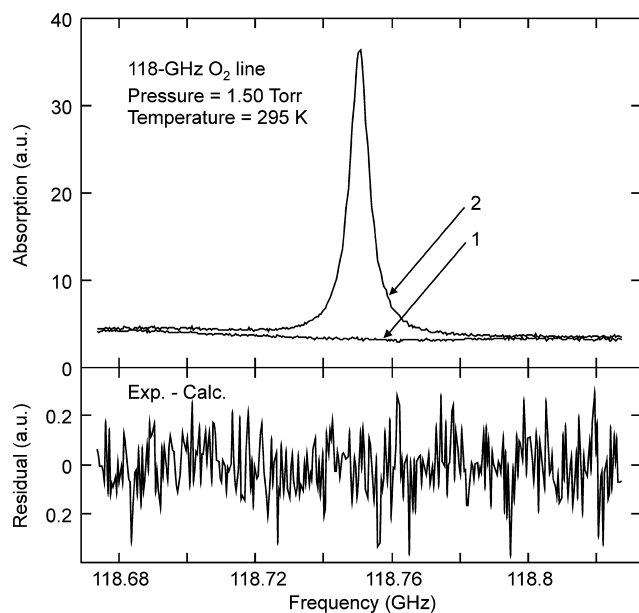


Fig. 3. Typical RAD spectrometer record of the 118-GHz line in pure oxygen (trace 2) and the apparatus function (trace 1) recorded with the cell filled by non-absorbing gas (pure nitrogen) at the same pressure, 1.50 Torr. Lower part of the figure presents residual of the fit of function (3) to difference of traces 2 and 1.

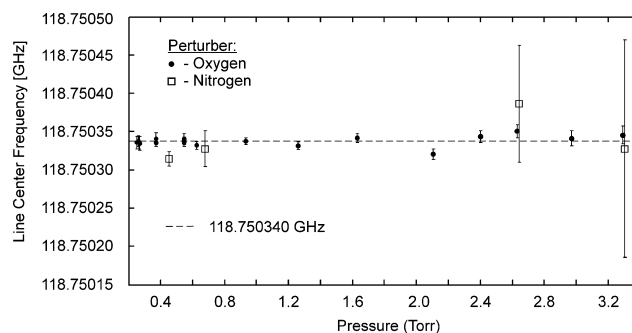


Fig. 4. Typical dependences of measured line center frequency of the 118-GHz oxygen vs. pressure. Two sets of experimental points denoted by circles and squares correspond to observation of the line in pure oxygen and nitrogen respectively. Vertical bars correspond to standard error of the line center determination from function (3) fitted to the observed line. Dashed line corresponds to the “zero pressure” position of the line center determined from our experiment [16] as 118.750340(7) GHz.

(trace 2) and signal from the cell when the oxygen was replaced in the cell by pure nitrogen under the same pressure (trace 1). The lower part of the figure presents the residual of the fit of function (3) to difference of traces 2 and 1. The figure demonstrates good S/N ratio (about 300) of the observed line. The noise-like residual demonstrates adequacy of the fitted line shape function to the experimental data.

Measurements of position of the 118-GHz line center (ν_0) determined from fitting the function (3) to the line record at oxygen pressure in the cell, varying by steps from 0.2 to 3.5 Torr, were repeated several times for different positions of the gas cell shifted along the radiation beam to reveal any possible effect of interference. A similar experiment was performed with the gas cell filled by nitrogen at various pressures, keeping the partial pressure of oxygen in the cell within 0.5–1 Torr. Typical dependences are shown in Fig. 4.

RAD experiments did not reveal any clearly indicated repeatable dependence of the line center frequency vs. pressure. Nevertheless, this experiment allows us to set an upper limit for the 118-GHz line pressure-shifting parameter. Analysis of all experimental data leads us to the conclusion that the linear-with-pressure shifting parameter can not exceed ± 10 kHz/Torr for oxygen and ± 20 kHz/Torr for nitrogen pressure.

Thus, the 118-GHz oxygen line center in air at atmospheric pressure could be found shifted within about ± 15 MHz from its position measured at low pressure due to linear-with-pressure shift.

4. Experiment with resonator spectrometer at atmospheric pressure

In the course of the experiment the 118-GHz line was recorded in the range 110–130 GHz—four times in pure

oxygen, two times in laboratory air and one time in dry air, all with unchanged spectrometer configuration and thus with the same apparatus function. Then the experiment was repeated once again after readjustment of the spectrometer (with different apparatus function) and the line in laboratory air was recorded four times more with a two-day interval between records. Repetition of records and experiments allowed us to estimate possible systematic errors in the oxygen line parameters determination. The experiment consumed large amount of sample gases to fill the resonator and to maintain permanent sample conditions during the experiment. So instead of pure Messer MG Company gases, inexpensive commercially available cylinders with technical grade nitrogen and oxygen from a local supplier were used. Declared gas purity was better than 98 Vol.%. Dry air for the experiment was prepared from the atmosphere by freezing and filtering out water. Residual relative humidity of the air constituted about 2%.

As shown in [13], the sample absorption coefficient γ measured by our resonator spectrometer at frequency points corresponding to eigen-frequencies of the resonator can be expressed (assuming $\gamma L \ll 1$, which corresponds to our case) as

$$\gamma = (2\pi/c) \cdot (\Delta f - \Delta f_0), \quad (5)$$

where Δf and Δf_0 are, respectively, widths of the Fabry-Perot resonance with and without sample (or filled by non-absorbing substance), directly measured in the experiment as described in [13], c is the speed of light and L is the resonator length. Then the sample absorption coefficient γ can be divided into two parts

$$\gamma = \gamma_0 + \Delta\gamma, \quad (6)$$

where γ_0 corresponds to the absorption coefficient at permanent conditions of the sample (T_0 , temperature; P_0 , pressure; and H_0 , humidity) and $\Delta\gamma$ includes all variations of γ due to variations of aforementioned parameters in the course of the experiment. The sample humidity and temperature monitoring during the experiment was performed by “TESTO-645” [14] equipped by a highly accurate humidity/temperature probe. Guaranteed accuracy of the relative humidity measurement was $\pm 1\%$ (10–90% RH, from +15 to +30 °C) and $\pm 2\%$ in the remaining range. Accuracy of the temperature measurement was ± 0.2 °C. A pressure meter (600–800 mmHg range), calibrated with accuracy ± 0.5 mmHg by the state metrology service was used for the sample pressure measurement. The variable part of the sample absorption coefficient ($\Delta\gamma$) was then calculated using the MPM-93 program [9,15] including its recent updates as:

$$\Delta\gamma(T, P, H, \nu) = \text{MPM}(T, P, H, \nu) - \text{MPM}(T_0, P_0, H_0, \nu). \quad (7)$$

The constant part of the sample absorption coefficient (γ_0) can be expressed as

$$\gamma_0 = \gamma_{\text{line}} + \gamma_{\text{non-resonant}}, \quad (8)$$

where γ_{line} is resonant absorption in the 118-GHz oxygen line as if it is a single isolated line and $\gamma_{\text{non-resonant}}$ is the sum of absorption in far wings of spectral lines and continuum absorption in the range of this oxygen line. The non-resonant part of the absorption coefficient ($\gamma_{\text{non-resonant}}$) was also calculated using MPM-93 by decreasing the 118-GHz line intensity parameter in the program by ten orders of magnitude. Thus the absorption in the line itself (γ_{line}) was extracted from experimental data and then used for further treatment. Constant- and linear-with-frequency terms were added to the function (1) to take into account possible small inaccuracies of the MPM-93 model as well as uncontrolled day-to-day variations of our radiation source spectral line width.

Examples of the 118-GHz line record in pure oxygen, dry air, and laboratory air experimentally obtained by use of our resonator spectrometer are given in the upper part of Fig. 5. The laboratory air trace (squares) goes slightly higher than dry air trace (diamonds) due to radiation absorption in atmospheric water. The lower part of Fig. 5 presents a comparison of experimental results with theoretical models. Traces A and B are residuals of fitting the function (1) and VVW respectively to the experimental line in pure oxygen. The curved shape of the trace B corresponds to the theoretical difference shown in the lower part of Fig. 1 and confirms inadequacy of the VVW model, in opposition to function (1), which fits the experimental data to the noise level (Trace A). Trace C is the difference between our laboratory air experimental data and calculation of the absorption using MPM-93 at conditions of the experiment. The average negative displacement (~ 0.02 dB/km) of the difference can be explained in principle by inaccuracy of our humidity measurement within the declared meter accuracy. But the shape of small systematic deviations exceeding the experimental noise level on the trace C, and constituting on average about 4% of the oxygen line amplitude, reveals a lower position of the experimental line center compared to the calculated one. Part D presents residuals of the fit of function (1) (thick line) and VVW profile (thin line) to laboratory air experimental data. The difference between these two residuals is not so obvious as in the case of pure oxygen but still has the same character and is clearly distinguishable.

Analysis of the experimental data showed that repeated experimental traces coincide within experimental noise (~ 0.02 dB/km). Traces corresponding to absorption in laboratory air coincide with traces corresponding to absorption in dry air after subtraction of calculated absorption by water, as described above. Traces corresponding to absorption in pure oxygen multiplied by a factor of 0.21 agree well with the traces corresponding to absorption in dry air. Even rearranging the experimental

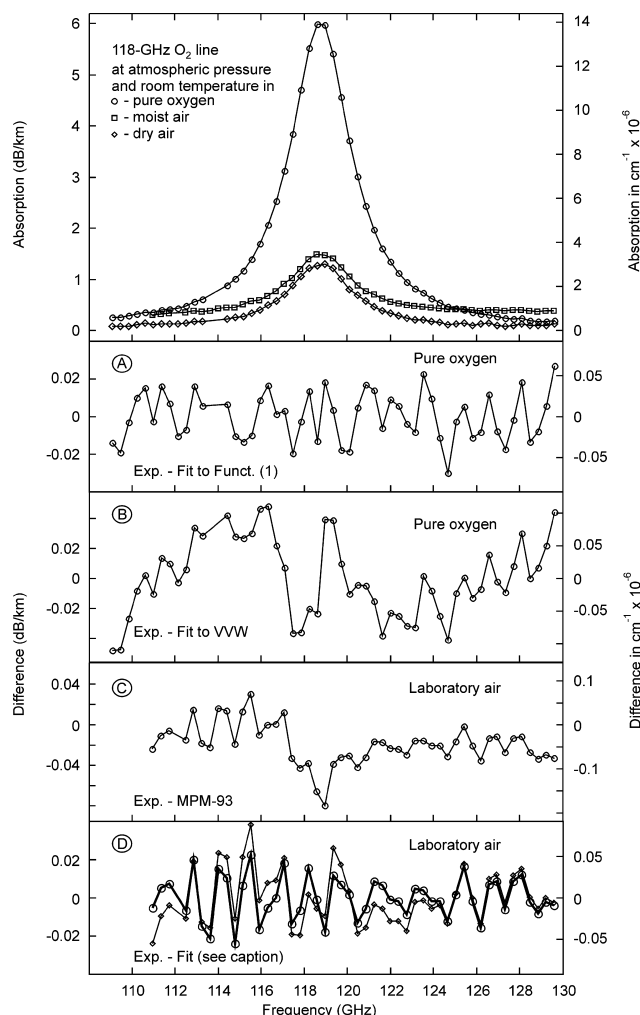


Fig. 5. Resonator spectrometer records of the 118-GHz oxygen line (upper figure) in pure oxygen (circles) at pressure 766 mmHg, temperature 22 °C, laboratory air (squares) at 739 mmHg, 24 °C, humidity 6.3 g/m³, and dry air (diamonds) at 770 mmHg, 20 °C and result of comparison of the data with calculations (lower figures): Traces A and B are residuals of fitting function (1) and VVW, respectively, to the experimental line in pure oxygen. Trace C is the difference between the experiment and MPM-93 calculated absorption at experimental conditions for the line in laboratory air. Trace D presents residuals of fitting function (1) (thick line) and VVW profile (thin line) to the laboratory air experiment.

setup and recording the 118-GHz line with an essentially different apparatus function gave data in good agreement with previous records. All of this confirms consistency of the experiment and correctness of water

absorption calculation by MPM-93 in this range. Nevertheless, the line parameters obtained from fitting the line shape function to experimental data vary from trace to trace, which gives an idea about possible systematic errors.

The summary of the 118-GHz line parameters obtained from fitting function (1) to experimental data and averaged over all experiments is given in Table 1. For the line dry air broadening parameter calculation we used the partial pressure of water, calculated using the sample humidity and temperature, and the broadening parameter of the 118-GHz oxygen line by pure water vapor of 2.52 MHz/Torr [16]. All experiments were carried out at room temperature varying from 19.7 up to 24 °C. The temperature exponent value 0.8 [9] was used for recalculation of mixing and broadening parameters to uniform temperature 24 °C. Values of corrections obtained from recalculations constituted about 1% of the broadening parameter value. The line integral intensity was calculated as the line amplitude (the line absorption coefficient at the line maximum) multiplied by π times the line half width and divided by oxygen-molecules concentration in the sample ($\gamma_{\text{line}}(v_0) \cdot \pi \cdot \Delta v/n$). The molecular concentration was calculated as $n = P \cdot f_1 \cdot f_2/k \cdot T$ where f_1 is the ¹⁶O¹⁶O isotope natural abundance, f_2 is the oxygen concentration (0.2095 in air and 1 in pure oxygen) and $k = 1.380662 \times 10^{-23}$ J/K is the Boltzmann's constant. For averaging integral intensity over all air experiments at uniform pressure and temperature we recalculated our data before the line shape fitting using the MPM program (formula (7)).

The resonator spectrometer experiment did not reveal the presence of any essential linear-with-pressure line shift. The values for linear shift parameter, shown in Table 1 as experimental results, also coincide with RAD spectrometer results and can be considered as zeros within experimental accuracy. After concluding that the line center has no linear pressure shift we tried fitting the function (1) to our data with the line center frequency as a fixed parameter. This essentially decreased the standard deviation of the line mixing parameter in both cases. The parameter value remained practically the same for pure oxygen data $-4.60(17) \times 10^{-5}$ Torr⁻¹, but for air data we got $-4.8(13) \times 10^{-5}$ Torr⁻¹, which became very close to the mixing parameter in pure oxygen in spite of a still quite high error of the parameter determination.

Table 1

Parameters of the 118-GHz line obtained from the resonator spectrometer experiment and recalculated to 24 °C

| Sample | Mixing parameter (1/Torr) | Broadening parameter (MHz/Torr) | Linear shift parameter (kHz/Torr) | Integral Intensity (cm mol ⁻¹) |
|---------|------------------------------|------------------------------------|--------------------------------------|---|
| Oxygen | $-4.62(38) \times 10^{-5}$ | 2.24(1) | +0.6(60) | $9.77(20) \times 10^{-26}$ |
| Dry air | $-5.9(29) \times 10^{-5}$ | 2.25(3) | +21(45) | $10.10(29) \times 10^{-26}$ |

Error values in the table correspond to standard deviations of the parameters based on information obtained from the fit.

It should be mentioned that fitting the VVW function to these experimental data gives practically the same values of the line broadening parameter and the line intensity (differences are essentially less than standard deviations of parameters) but reveals apparent shift of the line center: $-50(4)$ MHz in oxygen and $-55(16)$ MHz in dry air, as expected.

The line broadening parameters obtained from the experiment coincide very well with the values of these parameters measured by us using RAD spectrometer at lower pressures (2.23(1) for oxygen, and 2.24(2) MHz/Torr for air). Comparison of the line broadening parameters obtained by different authors is given in [16].

5. Discussion and comparisons with other work

The experiment allowed determining the line-mixing parameters for the 118-GHz oxygen line broadened by pure oxygen and by air, presented in table 1 as *Y/P*. As far as we know this is the first direct measurement of this parameter for this oxygen line. For comparison, the value of the mixing parameter in [9] is -3.1×10^{-5} Torr $^{-1}$ for the 118 GHz-line in air. However, those mixing parameters were derived from measurements in the range of 49–67 GHz, and the value for the 1+ line resulted from the fitted value at the 1+ line and assumptions regarding similarity of *M* in the two branches of the fine-structure spectrum. An earlier version of MPM [15] obtained -5.9×10^{-5} Torr $^{-1}$ by a different method. A theoretical value of -7.77×10^{-6} Torr $^{-1}$ (pure oxygen) was calculated in [19], but those calculations disregarded coupling to the non-resonant and negative-resonant lines, and made many other approximations. We must also note that no treatment thus far has included the contribution of coupling between the line at 118 GHz and those at higher frequencies, such as 368, 425, and 487 GHz. Those are transitions between the *N* = 3 and the *N* = 1 triplets of states, so they might have significant off-diagonal elements of *M* coupling to 118 GHz.

For a consistency check we compared the line integral intensity obtained from our experiment with the calculated one given in the GEISA databank [17]. The databank gives 9.956×10^{-26} cm mol $^{-1}$ for the 118-GHz oxygen line intensity at 296 K. Thus we got about 2% less than the tabulated value for pure oxygen, which probably corresponds to purity of the technical grade sample used in this experiment and which gave, by the way, the biggest contribution to the intensity error for the oxygen experiment, exceeding other sources of error by about a factor of 5. For air, our intensity value is a bit higher than tabulated, but in both cases the measured line intensity practically coincides with the GEISA value within experimental errors.

The study confirmed the negative displacement of the 118-GHz line center at atmospheric pressure experimentally observed in [6] and also obtained by re-treating data from [3]. Refined values of the displacement in oxygen and in dry air are obtained. It was shown that the displacement is mostly determined by the line mixing. It should be noted, however, that the problem of linear-with-pressure shifts of oxygen molecule lines is not fully solved at the moment. Pressure shifts of oxygen lines were investigated in [7,18]. Shifts of the electron-rotational-fine structure transitions (*A*-band), investigated in the papers mentioned, showed, by agreement in the sign and order of magnitude, about two times difference in absolute values of the shift parameters, and different relations of self- and nitrogen-shifts in these papers. Values of the shift parameters in these papers varied from 0.11 to 0.32 MHz/Torr depending on rotational and fine structure quantum numbers in [18], and from 0.28 to 0.67 MHz/Torr (also depending on quantum numbers) for self-shift and from 0.63 to 0.83 MHz/Torr for N $_2$ -shift in [7]. Strong dependencies on rotational-fine structure quantum numbers of the shifts found in the papers cited give some grounds to expect pressure shifts of other lines of oxygen. But combination differences for the rotational lines investigated in the papers [12] give expected magnitude of pressure-shift parameters of 0.05–0.1 MHz/Torr, which is somewhat close to the estimated accuracy of line-shift measurements in these papers. So for unambiguous solution of the problem of other oxygen line-shifts, further increase of accuracy and careful investigation are needed.

6. Conclusions

Improvements of the experimental technique achieved in [11,13] permitted accurate analysis of the 118-GHz oxygen line shape in laboratory air as well as in pure oxygen at atmospheric pressure and room temperature. Direct measurement of the apparatus function in the experiment and subtracting it from the observed absorption signal allowed an increase of several times in signal-to-noise ratio of the observed atmospheric oxygen line, as compared to our previous measurements [6]. It was found that the observed line fits the function (1), including first-order effects of line mixing, to the experimental accuracy level. The VVW line shape function fitted to the data gives practically the same values of the line width and amplitude as function (1) but reveals an apparent shift of the line center, which is in fact the influence of the collisional line shape distortion due to mixing of the line with other lines belonging to the 60-GHz oxygen band. The experiment did not reveal any linear-with-pressure shift of the line center. Measured values of the line intensity and central frequency coincide very well with modern tabulated data. The value of

the line-mixing parameter was experimentally determined from the experiment as well as a refined value of the line pressure-broadening parameters by air and oxygen. Spectroscopic parameters of the 118-GHz oxygen line obtained in this work can be used for atmosphere remote sensing and for refinement of existing atmospheric radiation transfer models.

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