

Note

Temperature dependence of pressure broadening
of the $N = 1$ – fine structure oxygen line at 118.75 GHzM.Yu. Tretyakov^{*}, M.A. Koshelev, I.A. Koval, V.V. Parshin, L.M. Kukin,
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Abstract

The absorption profile of the $N = 1$ – fine structure line of oxygen was recorded by a resonator spectrometer at a frequency range of 110–130 GHz at atmospheric pressure and different temperatures ranging from -21 °C up to $+22$ °C. Analysis of the observed line shape allowed determination of the temperature dependence of the line pressure broadening. The measured value of the temperature exponent is $n = 0.74(5)$ for self-broadening. Consistency of the measurements is supported by simultaneous measurements of the line intensity, the line mixing parameter and the line center frequency, and by comparison of obtained values with previously known data.

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1. Introduction

The single isolated 118-GHz, $N = 1$ – line of the oxygen molecule is of great importance for remote sensing of the Earth's atmosphere. In particular the line is widely used by airborne and satellite-based instruments for atmosphere temperature and pressure profile recovery. Accuracy and reliability of recovered information directly depends on accuracy of the line parameters, which can be obtained only in precise laboratory experiments.

Spectroscopic parameters of the 118-GHz oxygen line were studied earlier by different authors using different methods of microwave spectroscopy (see e.g. our recent paper [1] and references therein). However, data available to date on the temperature dependence of the line pressure-broadening parameter are somewhat uncertain. Measurements of the 9+ oxygen line width in pure O_2 at four temperatures were reported in [2]; using the data and com-

monly accepted formula for the pressure broadening temperature dependence (Eq. (2) below) one can get the inverse-temperature exponent $n = 0.84(4)$. However, in an early version of the widely accepted Millimeter-Wave Propagation Model (MPM) [3] this value was rounded to 0.9 and used for air broadening of all oxygen fine-structure lines. In later MPM versions (see e.g. [4]) the value was reduced to 0.8. In Ref. [5] the 118-GHz line width was studied at four temperature points for O_2 -broadening and at three points for N_2 -broadening. Corresponding n -values can be obtained from the reported data as 1.04(11) for O_2 and 0.61(10) for N_2 . Using the data one can get $n = 0.72(11)$ for air broadening assuming air composition as 21% O_2 and 79% N_2 . The authors of [5] mentioned that the line width measurements were preliminary but for some reason the study was not continued and to the best of our knowledge no subsequent experimental studies of temperature dependences of oxygen line broadening were undertaken until now.

The present work continues the series of our papers devoted to study of the rotational spectrum of oxygen (see [1] and references therein). We report here the results

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of laboratory measurements of the 118-GHz oxygen line broadening temperature dependence.

2. Experimental details

For the study we used the BWO-based resonator spectrometer [6] and measurement method described in detail in [7]. The 118-GHz oxygen line absorption profile in pure oxygen was measured at ~ 100 frequencies of eigen-modes of the Fabry–Perot resonator in the 110–130 GHz frequency range at a few temperatures ranging from -21°C up to $+10^\circ\text{C}$. Absolute accuracy of the absorption measurements was about 0.1 dB/km. For the low temperature measurements the resonator was placed on the roof of our institute to use the cold winter atmosphere for natural cooling. Technical grade oxygen from a local supplier with declared purity better than 98% was used as the studied sample. The apparatus function of the spectrometer was recorded in pure nitrogen obtained by slow evaporation from the liquid phase. Both gases were slowly blown through the resonator volume in the course of the measurements. Temperature and residual moisture inside the resonator were monitored by “TESTO-645” [8] equipped by a highly accurate humidity/temperature probe. Guaranteed accuracy of the humidity measurements was $\pm 2\%$. Accuracy of the temperature measurements was $\pm 0.2^\circ\text{C}$. A pressure meter (600–800 mmHg range), calibrated with accuracy ± 0.05 mmHg was used for the study. Minor variations of the temperature, humidity and pressure in the course of the experiment did not exceed 1.5°C , 1 g/m^3 and 1 mmHg , respectively, and were taken into account using the MPM model [4] as described in [7]. An example of the 118-GHz oxygen line record at -21°C is given in the upper part of Fig. 1. For a comparison the line record obtained in our previous work [7] at $+22^\circ\text{C}$ and used in the present study is also shown in the figure.

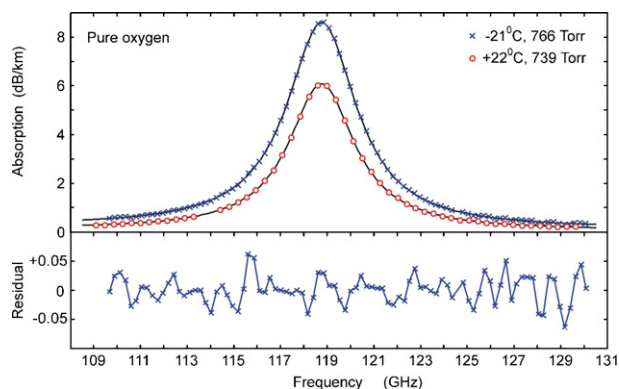


Fig. 1. Upper panel presents 118-GHz oxygen line atmospheric pressure absorption profiles. Experimental points obtained at -21 and $+22^\circ\text{C}$ are shown by crosses and circles, respectively. Solid lines correspond to the best fit of function (1) to the experiment. Lower panel is residual of the fit of the -21°C data.

3. Results and discussion

The following model function was fitted to experimental line records to determine the line parameters:

$$I(\nu) = \alpha \frac{\nu^2}{\pi \nu_0^2} \left[\frac{\Delta \nu + Y(\nu - \nu_0)}{\Delta \nu^2 + (\nu - \nu_0)^2} + \frac{\Delta \nu - Y(\nu + \nu_0)}{\Delta \nu^2 + (\nu + \nu_0)^2} \right] + (A_0 + A_1 \nu + A_2 \nu^2), \quad (1)$$

where α —the line integrated absorption coefficient, which is a product of the line intensity α_0 and the density of absorbing molecules N ; ν_0 —the line center frequency; $\Delta \nu$ —the line half width at half maximum; Y —the line mixing coefficient; A_i —variable parameters accounting for remaining sample absorption and possible unaccounted apparatus characteristics. The residual of the model function (1) fitted to the observed line is shown in the lower part of Fig. 1.

Parameters of the line (broadening, intensity and mixing coefficient) determined from fitting experimental profiles at different temperatures are shown in Fig. 2 together with their calculated dependences shown by the solid curves. Vertical bars indicate $1 - \sigma$ statistical error of the measurements. The temperature dependence of the line broadening is defined by the usual equation:

$$\gamma(T) = \gamma(T_0) \left(\frac{T_0}{T} \right)^n, \quad \gamma = \frac{\Delta \nu}{P}, \quad (2)$$

where P —pressure; γ —broadening parameter; T —temperature in Kelvin; T_0 —fixed temperature (usually 300 K). The value of the temperature exponent n and $\gamma(300)$ was found from the fit of function (2) to experimental points

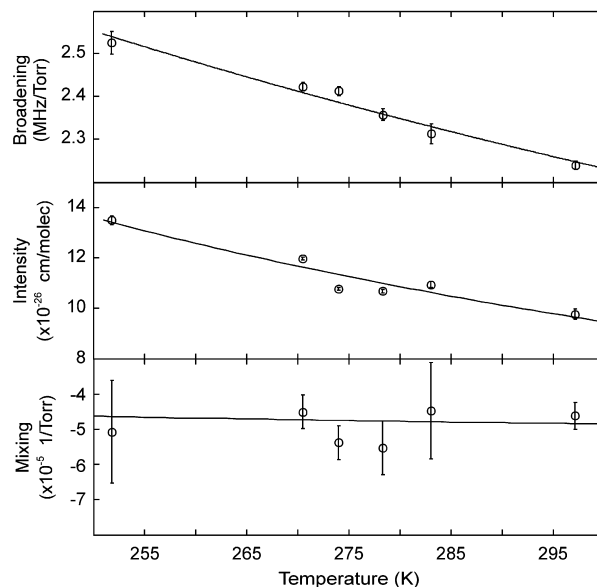


Fig. 2. Temperature dependence of the 118-GHz oxygen line parameters. Experimental points are shown together with 1σ statistical uncertainty. Solid lines correspond to calculated dependences (see text for details). The line broadening parameter is presented in the upper panel, the line intensity in the middle panel and the line normalized mixing parameter in the lower panel.

(upper panel of Fig. 2) as 0.74(5) and 2.23(2) MHz/Torr, respectively. The n value is slightly less than the value measured for this line in [5] but practically coincides within experimental uncertainty with the value measured for the 9+ oxygen line [2].

The line intensity has the temperature dependence given by:

$$\alpha_0(T) = \alpha_0(T_0) \frac{1}{T} \left(1 - \exp \left(-\frac{h\nu_0}{kT} \right) \right), \quad (3)$$

where h —Planck's constant; k —Boltzmann constant. The line intensity determined at $T_0 = 296$ K from the experiment data (middle panel of Fig. 2) fitted to function (3) constituted $9.73(29) \times 10^{-26}$ cm⁻¹/molec. This value is 2% lower than the value in the HITRAN database [9]. This discrepancy corresponds well to the 98% declared purity of our oxygen sample and confirms consistency of the experiment.

The experiment did not reveal any temperature dependence of the line center position. Averaged over all measurements, the line frequency is 118 748(4) MHz, which coincides well within uncertainty with the result 118 750.340(7) MHz known from low pressure measurements [10].

For comparison of the line-mixing temperature dependence to that of the width, and easier characterization of any difference, a normalized mixing coefficient $y(T)$ is defined as

$$y(T) = \frac{Y(T)}{P} \left(\frac{T}{300} \right)^{0.74}, \quad (4)$$

in which 0.74 is the temperature exponent obtained for the width parameter. The rather small value of the line mixing parameter and its consequently rather big uncertainty did not allow reliable determination of its temperature dependence. However data obtained after normalization as in Eq. (4) showed good agreement with the small temperature dependence of the normalized mixing coefficient calculated

using MPM for air [4], shown in lower panel of Fig. 2. Moreover the mean value of mixing parameters obtained after the normalization and recalculation to 297 K was $-4.93(42) \times 10^{-5}$ 1/Torr. This value coincides within experimental uncertainty with $-4.62(38) \times 10^{-5}$ 1/Torr measured in our previous study [7] at 297 K.

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