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Real Atmosphere Laboratory Measurements of the 118-GHz Oxygen Line: Shape, Shift, and Broadening of the Line

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For the first time the 118-GHz line of the oxygen molecule was investigated in the laboratory under a real atmosphere. The experiment was carried out by modern resonator spectroscopy methods on the laboratory air at atmospheric pressure. The shape of the line under the real atmosphere was found to fit the Van Vleck–Weisskopf profile within experimental accuracy. The air broadening parameter value was defined as 2.14 ± 0.07 MHz/Torr. The observed atmosphere oxygen line central frequency was found to be shifted down at about 150 MHz from the line center measured at low pressures, which gives a value of -0.19 ± 0.08 MHz/Torr for the air shift parameter. A comparison with previous investigations is presented and reprocessing of some experimental results of other authors was carried out. Results of reprocessing agree with the findings of the present paper.

INTRODUCTION

The single isolated 118-GHz 1- line of the O_2 molecule—one of the major permanent components of the atmosphere—is also one of the few lines of major interest for remote sensing of the atmosphere. By its origin it belongs to the magnetic fine structure spectrum of the molecule, the rest of which is confined around 60 GHz. It is widely used at the present time for airborne and satellite atmosphere remote sensing, in particular for temperature measurements and temperature profile recovery (*1–3*). Some of the new microwave sounding instruments which are currently in the planning stage for use on weather satellites in the next few decades will be among those utilizing the oxygen 118-GHz line. Since this line starts from the lowest rotational and fine structure level it was chosen for detection of molecular oxygen in astronomical objects planned for the ODIN satellite mission (*4*).

The accuracy of laboratory measurements of the spectral parameters of the lines used for remote sensing sets a limit on the absolute accuracy of recovered parameters of atmosphere. Among the parameters of the line studied were lineshape, pressure line broadening, and the line central frequency pressure shift. Let us consider briefly the state of knowledge of these parameters prior to our work.

The shape of the 118-GHz oxygen line at up to atmospheric pressure was studied earlier in the laboratory, although not in air but in pure oxygen (*5*). Pure oxygen was used because of weakness of the line; still a 500-ft-long absorption cell was used (*5*). Studies of the shape led the authors of (*5*) to conclude that the Van Vleck–Weisskopf profile was inconsistent for fitting their results.

Laboratory measurements of the self-broadening parameter of the 118-GHz line in pure oxygen go back to (*5–8*). But only in (*9*) were both self-broadening and broadening by main components of atmosphere measured, thus permitting one to calculate an air broadening parameter from experimental data. Measurements of (*9*) were performed by a microwave spectrometer at low (from 0.07 up to 2.4 Torr) pressures. In (*5*) the measurements in pure oxygen were performed by two methods at low (less than 4 Torr) and higher (up to atmospheric) pressures, which led correspondingly to two values of the self-broadening parameter differing by 11%. The authors of (*10*), for their model of millimeter-wave propagation through the atmosphere, used the value of self-broadening for the 118-GHz line obtained in (*7*) and the coefficients necessary for the calculation of air broadening from their own measurements of the 9+ line in the 60-GHz range, assuming the independence of the effectiveness of foreign perturbers on the quantum numbers of fine structure lines. But the authors of (*9*) found a more than 10% difference between the effectiveness of foreign perturbers for the 118-GHz line as measured by them and as accepted by the authors of (*10*). Line parameters of the 118-GHz line accepted in upgraded versions of program databases [(*11*) and subsequently (*12*)] of the millimeter-wave propagation through the atmosphere model (MPM) are nearing, in value and estimated accuracy, those obtained in (*9*).

In none of the previous studies was the pressure shift of this line center noticed.

In the present work the 118-GHz oxygen line was for the first time experimentally investigated by microwave methods directly in the air at atmospheric pressure using modern resonator spectroscopy techniques (*13*).

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EXPERIMENT

The experimental technique used is described in detail in (*13*). Its main features include a high-quality Fabry–Perot resonator, a fast synthesized radiation source, and an IBM PC with an additional external processor and local memory for the experiment control, data acquisition, and data processing. Laboratory air inside an open Fabry–Perot resonator was used as the sample investigated. Improvements in the experimental technique in the present work included an increase in the speed of data exchange between the IBM PC and the module containing a fast radiofrequency synthesizer and data acquisition system. This improvement shortened the total time needed for the experiment and made it possible to obtain, in one experiment by the path variation regime (*13*), absorption data from the ∼15-GHz band around the 118-GHz oxygen line.

Experimental data were then processed as described in (*13*) and led to the following results.

I. The Shape of the Line Under Real Atmosphere

Knowledge of the shape of the line is necessary for calculating absorption in the atmosphere and also for defining the broadening parameter itself. Our previous studies of the shape of the 183-GHz water vapor line at atmospheric pressure (*13*) showed that the line follows the Van Vleck–Weisskopf profile up to 20 half-widths from the line center within experimental accuracy. Thus the Van Vleck–Weisskopf profile was used for fitting the experimental results of the present work on the oxygen line. Adjustable frequency-independent terms and linearly dependent frequency terms were included in the fitting model to account for nonresonance atmospheric absorption and possible apparatus function as in (*13*). This additional absorption obtained from the fit was then subtracted from the experimental points. Figure 1 presents an example of the 118-GHz oxygen line in atmosphere obtained from our experiment. The fitted Van Vleck–Weisskopf profile also presented in Fig. 1 shows agreement with our data within the experimental accuracy.

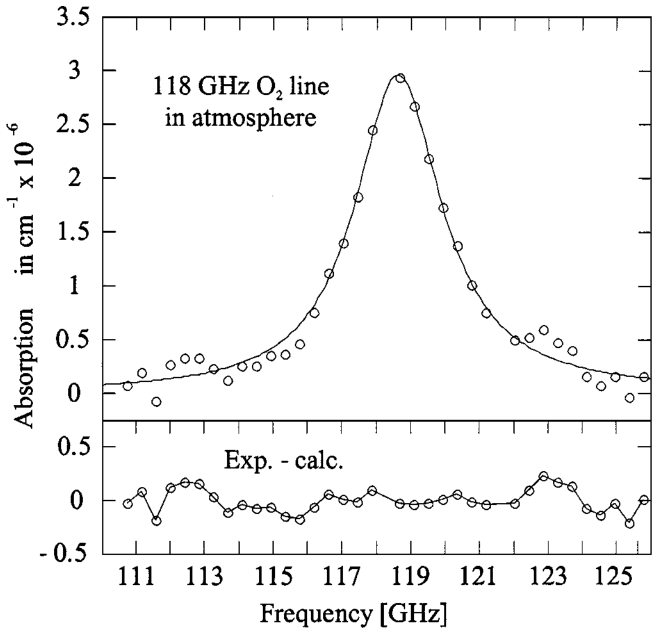

FIG. 1. Experimental points (circles) and the fitted Van Vleck–Weisskopf profile (solid line) for the 118-GHz oxygen line in real laboratory atmosphere (pressure 758 mm Hg, temperature 21.0°C, humidity 5.6 g/m3). Residuals of the fit are shown below.

We also analyzed the experimental data of (*5*) (for pure oxygen). Experimental points were taken from Figs. 2 and 4 of (*5*). First, these experimental data were reprocessed in the model used in (*5*) and results of this fitting showed good correspondence with the results obtained by the authors in (*5*), which confirmed the correctness of obtaining experimental data from (*5*). Then the experimental data of (*5*) were fitted to the Van Vleck–Weisskopf profile with the addition of an adjustable frequency-independent term. This led to a better fit to the Van Vleck–Weisskopf profile (so there would be no need to claim shape inconsistency). The possibility of the existence of such a contribution to the experimentally observed absorption in (*5*) follows from the statement of the authors of (*5*) that they measured peak absorption changes from 6.5 to 7.0 dB/km with pressure increasing from the 1-Torr range up to atmospheric pressure (see also Fig. 3 of (*5*)). The value of the frequency-independent term of the data for pressure of 700, 500, and 300 Torr (Fig. 2 of (*5*)) obtained in our fit was about 0.5 dB/km for each pressure data set, which is consistent with the aforementioned statement. This additional absorption measured at the line frequency was explained in (*5*) as being due to the wings of the oxygen lines around 60 GHz at higher pressures. But 60-GHz line wings are not sufficient to produce such a value of absorption around 118 GHz, as can be shown both by simple estimation and by calculation of the absorption by the MPM model (*10–12*) with the 60-GHz lines removed from the database. The effect of the wings appears an order of magnitude less than this additional absorption and also cannot provide the almost linear dependence of additional absorption on pressure observed in Fig. 3 of (*5*). We cannot define the origin of this additional absorption observed in (*5*) at the moment.

II. Shift Parameter

The existence of a pressure shift of the 118-GHz oxygen line has never been mentioned before, and all investigators have used the center line frequency value measured at low pressures as a fixed parameter. We took the frequency of the line center as an adjustable parameter in our experimental data fitting. In all our experiments we found that the center frequency obtained from the fit of the atmospheric line is lower than the center frequency of the oxygen line measured at low pressures (e.g., 118.750343 GHz (*14*)). For example, the frequency of the center of the line record shown in Fig. 1 was found to be 118.581 GHz. If one interprets this effect as due to the pressure shift, then the

TABLE 1
Air Broadening Parameters of the 118-GHz Oxygen Line (MHz/Torr)

From measured in (*9*)	2.19 ± 0.09
From measured in (*15*)	2.15 ± 0.09
Measured in this work	2.14 ± 0.07

air lineshift parameter for this 1- oxygen line can be estimated by averaging all of our data as -0.19 ± 0.08 MHz/Torr. Measurements were done on laboratory air. At the moment we cannot determine separately the contributions of oxygen, nitrogen, and water vapor to the shift observed.

It seemed of interest to reanalyze also the only large enough previous set of laboratory measurements of this line up to the atmospheric pressure in pure oxygen given in (*5*). Reprocessing of the data of (*5*) with the center frequency as an adjustable parameter revealed a similar trend of the pressure-broadened line center position to the lower frequencies (visible in Fig. 4 of (*5*) directly). Our fitting of the experimental points taken from Figs. 2 and 4 of (*5*) gave a value of -0.1 ± 0.06 MHz/Torr for the average pressure self-shift parameter. This self-shift value is found to be close (in terms of combined accuracy of the two experiments) to the air shift value. The pressure broadening produced by oxygen, nitrogen, and water vapor as perturbers of oxygen fine structure lines was previously found to be similar (*9, 11*); such similarity though could not be expected *a priori* for the shifts.

III. Broadening Parameter

The result of averaging our measurements of the air broadening parameter along with the results of other authors is presented in Table 1. The value of the air broadening parameter found in this work coincides within experimental errors with the values obtained earlier and has a bit better accuracy and probably better reliability as obtained from direct experiment but not from calculations.

CONCLUSION

In conclusion, let us sum up the main results of the present work. Improvements in experimental technique achieved in (*13*) and in the present work permitted for the first time the direct observation of the 118-GHz oxygen line in the laboratory at atmospheric pressure, in open atmosphere *in situ*, to obtain its lineshape, air shift, and air broadening parameters. The shape of the line under real atmosphere was found to fit the Van Vleck–Weisskopf profile. The pressure shift was observed for the first time for this type of transitions, and the air shift parameter can be estimated as -0.19 ± 0.08 MHz/Torr. The air broadening parameter is defined as 2.141 ± 0.07 MHz/Torr. The suitability of the Van Vleck–Weisskopf profile and the existence of the pressure shift of the line were confirmed by reprocessing the experimental data of (*5*). Results obtained in the present work are of pure and applied significance. In particular, once more after (*13*) it is shown that the laboratory atmospheric measurements by modern millimeter-wave resonator spectroscopy can provide the microwave atmosphere remote sensing programs by the spectral parameters of the lines of interest at the new experimental level of accuracy and reliability. The range of modern techniques developed might be extended correspondingly to studies of atmospheric lines at higher frequencies used now and planned in the future for microwave sounding.

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