Absolute intensity measurement of a v_3 ozone line at saturated vapor pressure with a laser heterodyne spectrometer

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Abstract. A laser heterodyne spectrometer had been developed ten years ago at the Reims GSMA laboratory (France). This high-resolution spectrometer is used for the first time to carry out absolute intensity measurements. This type of spectrometer exhibits a well-known and very narrow apparatus function ($0.0002\,\mathrm{cm}^{-1}$). Spectra of ozone were recorded at saturated vapor pressures of ozone at liquid argon temperature and the low pressures were checked by ultraviolet absorption. Results concerning the v_3 (10, 5, 6) → (9, 5, 5) ozone line are presented.

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The Groupe de Spectrométrie Moléculaire et Atmosphérique (GSMA, Reims, France) Laboratory has developed for several years high-resolution heterodyne spectrometers for laboratory and atmospheric ozone studies in the 10 µm region. The instrument was primarily designed as a single-beam spectrometer [1]. Then it was transformed into a dual-beam spectrometer to avoid slow drift phenomena [2]. This apparatus was fully used to measure ozone line frequencies [3]. For heterodyne experiments, the light to be analyzed is superimposed on a quadratic optical detector together with the radiation of a coherent optical oscillator. The sensitivity of this coherent detection was improved by many orders of magnitude compared with that of the direct detection mode. Heterodyne spectroscopy allows Doppler-limited resolution and absolute frequency and intensity accuracy. For the first time, this high-resolution spectrometer was used to measure absolute intensities. It has the great advantage of a well-known and narrow apparatus function in contrast to many other spectrometers.

The ozone molecule is very reactive, so we have to avoid its decomposition. This decomposition during the experiments is the main error source in quantitative measurements. One solution is to record spectra with the saturated vapor pressure of liquid ozone in the cell. Then,

the pressure remains constant during the experiments and its value is checked by UltraViolet (UV) absorption. The three techniques (heterodyne spectrometry, saturated vapor pressure and the UV-absorption method) are combined and enable us to present the absolute frequency position and intensity of the v_3 (10, 5, 6) → (9, 5, 5) line.

1 Experimental details

1.1 Preparation of liquid argon

Commercial liquid argon was not easily available to us so we had to prepare it in the laboratory. Liquid argon is obtained from gaseous argon liquified at liquid nitrogen temperature. Gaseous argon C is supplied by Air Liquide, France, with the following characteristics: $H_2O \le 3$ ppmv, $C_nH_m \le 1.5$ ppmv, $O_2 \le 3$ ppmv, and $N_2 \le 10$ ppmv. The boiling point of argon (87.2 K) is higher than that of nitrogen (77.3 K). So, gaseous argon can be liquified when it is cooled by liquid nitrogen in a copper coil. A dewar contains liquid argon and a stirrer is used to avoid a temperature gradient. Just after the liquid argon preparation, its temperature is lower than the exact boiling point of argon. The liquid is not pure argon. During the day, however, the temperature of the mixture increases asymptotically to the argon boiling point and auto-purification takes place.

1.2 Ozone fabrication

The ozone studied in the absorption cell was prepared by total conversion of oxygen. The design of this apparatus was similar to that of Griggs [4]. It consists of a cylindrical pyrex capacitor. The electrodes are made of copper foil in close contact with the glass and the applied voltage is 12 kV/400 Hz. Oxygen N45 supplied by Air Liquide, France, has the following characteristics: $H_2O \le 5$ ppmv, $CO_2 \le 0.5$ ppmv, $N_2 \le 10$ ppmv, $CO \le 0.5$ ppmv, $CH_4 \le 0.5$ ppmv, and $Ar \le 30$ ppmv. Ten Torr of gaseous oxygen is introduced into the reaction vessel. This

capacitor is immersed into a dewar containing liquid nitrogen. At this temperature, the oxygen remains in the gas phase because the saturated vapor pressure of oxygen at 77 K is 130 Torr. On the other hand, ozone is liquid at 77 K because the saturated vapor pressure of ozone at this temperature is $1.7 \cdot 10^{-3}$ Torr. Thus, the oxygen which is converted to ozone in the discharge is condensed. The conversion is completed when a purple glow can be seen inside the discharge capacitor. At this point, we pump on the liquid ozone to remove the residual oxygen. The ozone amount is sufficient to make sure that the ozone saturated vapor pressure will always remain. Liquid nitrogen is then replaced by liquid argon. When the pump is stopped, the Baratron gauge pressure increases, indicating that the saturated vapor pressure exists in the cell.

1.3 Pressure measurement

In order to measure absolute intensities, the ozone abundance has to be known with an accuracy better than 1%. Thus, one can see the importance of the exact knowledge of the saturated vapor pressure at those low pressures. There are three possibilities to know the ozone pressure:

Baratron gauge pressure

A MKS Baratron model 122AA capacitance manometer (max. 1 Torr) is used to measure the gas pressures. The precision of the measurement depends on the decade used on the Baratron gauge and on the stability of the temperature. The room is temperature regulated and, under our conditions, the gas pressures can be measured with $\pm 2\%$ accuracy of the reading. This value is given by the documentation of MKS instruments [5].

A problem arises from some residual leak into the cell (approximately $30 \cdot 10^{-3}$ Torr/h). A spectrum is recorded in approximately 15 min. So, with the 1 Torr Baratron gauge and for the low pressures used ($40 \cdot 10^{-3}$ Torr), the Baratron reading gives the total pressure (ozone + air). The partial air pressure, however, has no influence on ozone line broadening. Therefore, the Baratron gauge is used to check the total pressure and to verify that we are still in a Doppler system.

Pressure known by argon temperature

The ozone saturated vapor pressure corresponding to the liquid argon temperature can be calculated by [6]

$$\log P \,(\text{Torr}) = A + \frac{B}{T(\text{K})}, \tag{1}$$

where $A = 8.750$ and $B = -885.4$ represent constants for temperatures from 80 to 87 K, T is the temperature of liquid argon in K and P is the ozone pressure in Torr.

The problem of this method is that it implies to know the temperature exactly. This temperature varies mainly with impurities and a little with the atmospheric pressure [7]. The argon temperature is measured by a platinum resistance system. A precision of $0.1°$ introduced in (1) on the temperature of argon implies that the precision of this method is limited to 3%.

UV pressure determination

A good solution to accurately obtain the saturated vapor pressure of ozone is to carry out an UV-absorption experiment. Before or after recording the InfraRed (IR) spectrum, we pass an UV beam through the IR cell. The UV beam from a mercury lamp is mechanically chopped (211 Hz). A lens ($f = 50$ mm) permits to focus the beam along the cell. An UV filter selects the Hg line (253.7 nm, 297 K) whose absorption cross section is known to be $\sigma = 1.137 \cdot 10^{-17}$ cm^2 [8]. For pressure determination we have to measure the I_0 measured without ozone in the cell (during pumping) and I with the ozone vapor pressure. The signal is detected by an UV-enhanced Si photodiode and sent to a lock-in amplifier. The relationship of ozone pressure to I and I_0 is given with our units by

$$P \,(\text{Torr}) = \frac{1.3623 \cdot 10^{-22} \; T(\text{K}) \; 760}{l(\text{cm}) \; \sigma(\text{cm}^2)} \ln\frac{I_0}{I}, \tag{2}$$

where T represents the room temperature (regulated at 294 ± 0.1 K), l the cell path length (19.90 ± 0.01 cm), and σ the absorption cross section ($\sigma = 1.137 \cdot 10^{-17}$ cm^2). The precision of P depends mainly on I and I_0 precisions. The high UV photometric system stability enables an accurate determination (between 0.5 and 1%) of the ozone pressure and hence of the concentration.

1.4 Heterodyne spectrometer

The scheme of the optical part is represented in Fig. 1.

The radiation of two thermal sources consisting of Nernst filaments 2 mm in diameter and 25 mm in length are mixed by the ZnSe mixing plate M_2; M_2 reflects 50% of the measurement beam and transmits 50% of the reference beam. The measurement beam is chopped by a high-precision mechanical chopper C_1 (EG&G, model 197) at $\nu_1 = 211$ Hz, and passes through the absorption cell and a ZnSe lens L_2 ($f_2 = 150$ mm). The reference beam is passed through a second chopper C_2 at $\nu_2 = 2630$ Hz and a ZnSe lens ($f_3 = 200$ mm). The thermal source radiation beam is then mixed with the CO_2 laser beam by the ZnSe mixing plate M_1; M_1 transmits 95% of the thermal source and 5% of the laser beam. The laser beam comes from a continuous waveguide SAT C7 CO_2 laser with ZnSe L_1 lens ($f_1 = 50$ mm) and passes through the iris D_1. The signal is detected on D, which is a fast HgCdTe SAT C5 type photodiode operating at 77 K which acts as an optical mixer. The beam transmitted by M_0 is directed to a wattmeter or to an optical analyzer to determine the laser line. The cell is a single-path cell of 19.9 cm length with BaF_2 windows mounted at the Brewster angle. This stainless steel cell with indium rings is ozone proof. The half-concentration of ozone is obtained after approximately one week.
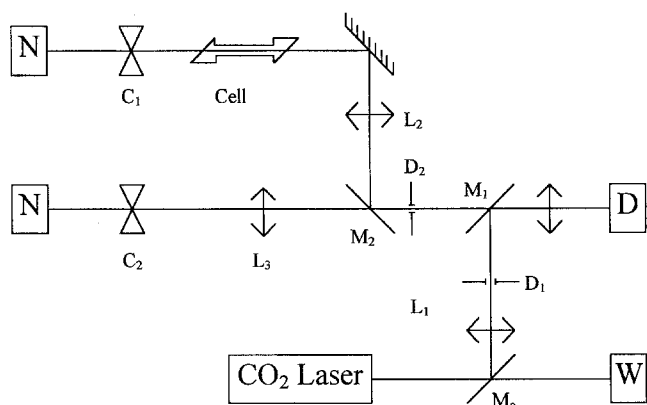
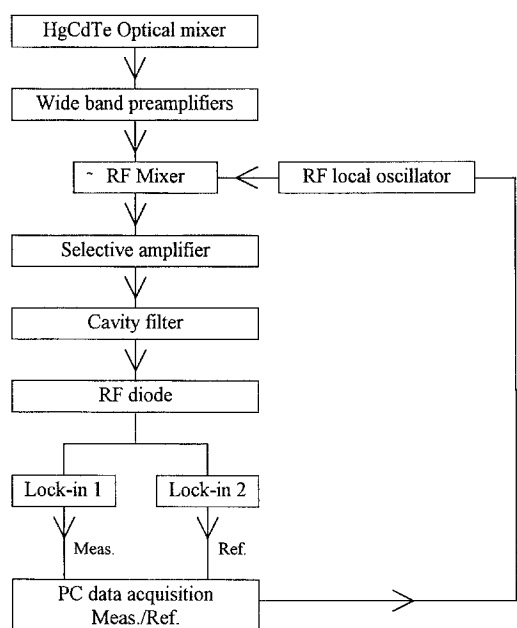Fig. 1. Scheme of the optical setup

Fig. 2. Scheme of the RF analyzer

The Radio-Frequency (RF) spectrometer has been fully described in [1] (Fig. 2).

The optical heterodyne detection translates, in the RF domain, a small part of the IR spectrum centered on the local oscillator. The heterodyne process gives the frequency differences related to the local oscillator frequency. The RF signal (v frequency) corresponds to IR signals at frequencies $v_{L_0} \pm v$: the spectrum is folded. Two low-noise amplifiers are used. A RF spectrometer analyses the corresponding signal. It consists of a fixed-frequency filter (center frequency 1500 MHz and total width half height $0.0002\,\mathrm{cm}^{-1} = 6\,\mathrm{MHz}$), a RF mixer and a local oscillator which is a microcomputer-controlled frequency synthesizer (Marconi Instruments, model 2041).

The RF diode provides a signal proportional to the incident power on the photodetector. We use two lock-in amplifiers (EG&G, model 5301) to discriminate the reference and measurement signals. Each one is adjusted to the modulation frequency of one of the thermal beams. The dc output signals between 0 and 10 V are then digitized. The laboratory-developed software controls the local oscillator and the data-acquisition process. Parameters are the starting frequency of the synthesizer (1700 MHz), the frequency step (5 MHz), the power (10 dB), the number of steps (80) and the integration time (8 s/step). We choose to obtain spectra with one slow single recording. The results of the measurement are directly visualized on the screen of the computer. Reference and measurement signals are shown in Fig. 3. The abscissa represents the frequency difference between the signal frequency and the frequency of the CO_2-laser line. Transmission is proportional to the ratio of the two signals.

2 Results

Three spectra have been recorded in the same spectral region and at different stages after preparation of liquid argon. Spectra of ozone are recorded near the CO_2-laser
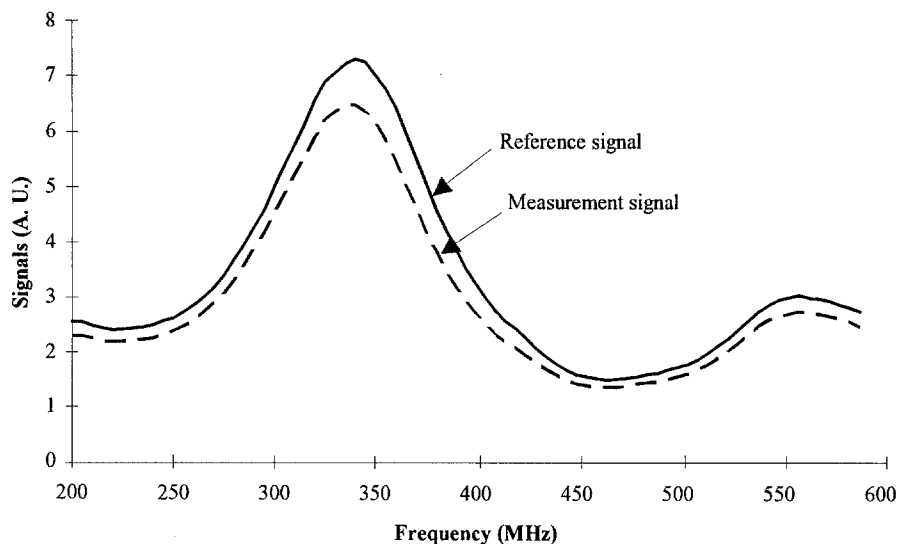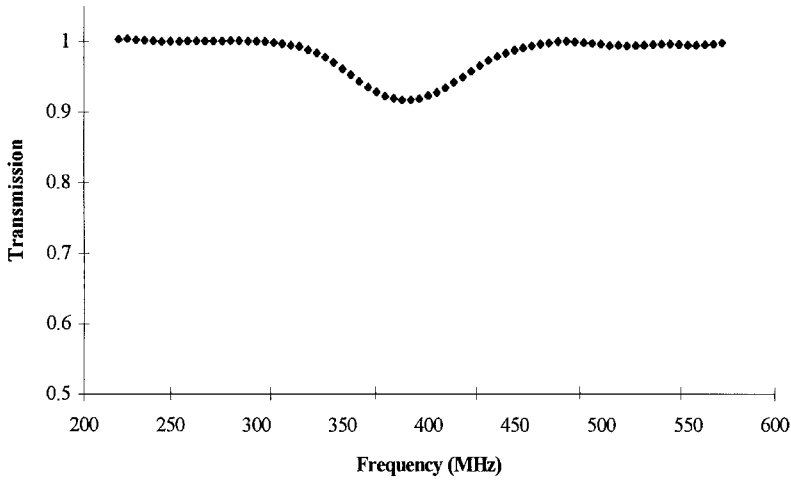

Fig. 3. Reference and measurement signals

Fig. 4. Experimental ozone spectrum

Table 1. Experimental results

	1	2	3
P(Baratron) [Torr]	0.0212 ± 0.0004	0.0338 ± 0.0006	0.0393 ± 0.0008
Argon temperature [K]	84.9 ± 0.1	86.7 ± 0.1	87.3 ± 0.1
P(temperature) [Torr]	0.0210 ± 0.0006	0.0340 ± 0.0010	0.0400 ± 0.0012
P(UV method) [Torr]	0.0215 ± 0.0002	0.0341 ± 0.0002	0.0399 ± 0.0003
Wave number [cm^{-1}]	1048.6737 ± 0.0004	1048.6737 ± 0.0002	1048.6738 ± 0.0003
Fit intensity [$cm^{-1}/(molecule \cdot cm^{-2}$]	$0.184 \cdot 10^{-19} \pm 0.006 \cdot 10^{-19}$	$0.184 \cdot 10^{-19} \pm 0.005 \cdot 10^{-19}$	$0.189 \cdot 10^{-19} \pm 0.007 \cdot 10^{19}$
LW intensity [$cm^{-1}/(molecule \cdot cm^{-2}$]	$0.187 \cdot 10^{-19}$	$0.185 \cdot 10^{-19}$	$0.187 \cdot 10^{-19}$

line $9P18$ ($1048.6608\ cm^{-1}$). The recorded ozone line is $v_3(10,\ 5,\ 6) \rightarrow (9,\ 5,\ 5)$ with saturated vapor pressures varying from 0.02 to 0.04 Torr.

One recorded spectrum is shown in Fig. 4. It consists of 80 points every 5 MHz in order to avoid the effect of the apparatus function. This apparatus function has been recorded [2]. Its width (6 MHz) is smaller than the full Doppler linewidths under study (60 MHz). So, we record spectral lines with almost their true line shapes. Experimental spectra are compared and fitted with theoretical ones using a nonlinear least-squares method with a Voigt profile [3]. No apparatus function is introduced in the fit.

For each spectrum, we have three pressures: the pressure given by the Baratron gauge after leak correction denoted P (Baratron), the pressure calculated by argon temperature denoted P (temperature) and the pressure given by the UV-absorption method. The three values of pressure are consistent with each other but the value of P (O_3) by the UV-absorption method is more precise. This value is used for the frequency and intensity determination.

Two methods were employed for the determination of S: the fit program and the method of equivalent widths [9] to verify that the apparatus function has no effect. The results are listed in Table 1. We can see that the intensity values given by the method of equivalent widths are close to the values given by the fit. Thus, we can verify that the

apparatus function does not interfere.

The average value of the results for the $v_3(10,\ 5,\ 6) \rightarrow (9,\ 5,\ 5)$ ozone line gives

$$v = 1048.6737 \pm 0.0003\ cm^{-1},$$

$$S = (0.186 \pm 0.006) \cdot 10^{-19}\ cm^{-1}/(molecule \cdot cm^{-2})$$

The intensity error (3%) is related to the low absorption depending on the cell path length.

3 Conclusion

The laser heterodyne spectrometer developed at the laboratory has permitted absolute wave number and intensity measurements of the $v_3(10,5,6) \rightarrow (9,5,5)$ ozone line. The spectra were recorded with the pressure given by the ozone saturated vapor pressure in a liquid argon. This method avoids the effects of decomposition and has the advantage to keep a constant O_3 pressure which can be checked by the UV-absorption method during the experiment. The obtained values of frequency and intensity are very consistent with the calculated value of the AFGL HITRAN database [$v = 1048.6736\ cm^{-1}$ and $S = 0.186 \cdot 10^{-19}\ cm^{-1}/molecule \cdot cm^{-2})$] [10] for which the intensity was given from 5 to 6%.

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