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New measurements of the absolute absorption cross-sections of ozone at 294 and 223 K in the 310-350 nm spectral range (*)

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Résumé. — Les mesures absolues des sections efficaces de l'ozone dans le domaine 310-350 nm (système de Huggins) ont été réalisées à 294 K et 223 K à haute résolution. Les résultats proposés — en baisse par rapport à l'ensemble des données connues — sont, à un coefficient près, en très bon accord avec les valeurs (relatives) obtenues récemment par A. M. Bass et R. J. Paur avec une résolution analogue à celle de ce travail.

Abstract. — Absolute measurements of the absorption cross-sections of ozone in the 310-350 nm range (Huggin's system) were carried out at 294 and 223 K with high resolution. Our results — lower than all results known to date — are, within a coefficient, in very close agreement with the (relative) values obtained recently by A. M. Bass and R. J. Paur with a resolution similar to that used in this work.

Considering the importance of the knowledge of the exact total quantity of ozone in atmospheric physico-chemistry, it is essential to-day to be able to propose new values for O₃ absorption cross-sections at stratospheric temperature (223 K) and in the 300-350 nm spectral range of the atmospheric windows where the observations are carried out.

Right now, most of the uncertainty in estimating the quantity of ozone concentrated in the atmosphere appears to be due to the uncertainty in the absorption cross-sections partly because of the relatively unsatisfactory performances on the instruments used for former measurements and also of the indirect determination of some of the absorption coefficients at 223 K which were deduced from results obtained at room temperature.

Determination of absorption coefficients k (cm⁻¹) or cross-sections σ (cm²) ($k = 1,167 \times 10^{19} \sigma$) based upon the application of Berr-Lambert's law :

$$D = \log_{10} \frac{I_0}{I} = k\alpha \quad (1)$$

(α = reduced thickness (NTP) = $l \cdot \frac{p}{p_0} \cdot \frac{T_0}{T}$ with l = optical path : p_0 , T_0 = normal condi-

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tions; p , T = conditions of the experiment) requires in all cases in order to be precise, for the radiation intensities to be known exactly, both before and after absorption. However, concerning the knowledge of the quantity of ozone α , two methods can be used : the first one, which leads to relative measurements, consists in maintaining a constant, though unknown concentration throughout the whole experiment. The experiment is performed in a dynamical regime, with the steady flux through the absorption cell of a relatively ozone poor mixture (air + O_3). Obtention, in absolute values, of the absorption cross-sections is theoretically based on the adjustment of a single experimental value to an absolute value determined by other means. This, up to now, has been the method selected by the various teams working on the subject ; we shall mention in particular the work of A. M. Bass and R. J. Paur [1], who recently proposed values calculated after normalizing their relative results to the absolute value given by A. G. Hearn [2] in 1961 :

$$\sigma = 114.7 \times 10^{-19} \text{ cm}^2 \quad \text{at} \quad 254 \text{ nm}.$$

The second method, which is the one we have chosen, is based on the exact knowledge, at any moment, of the concentration of ozone in the absorption cell and provides absolute measurements of cross-sections at all wavelengths. The experiment is performed in a static regime in an absorption cell containing practically pure ozone [3] obtained from a known quantity of oxygen. The concentrations are determined according to the total pressure measured with a (Baratron) capacitive manometer. Knowledge of the initial pressure of oxygen p_i introduced before ozonization at an exactly measured temperature T_i makes it possible to calculate the partial ozone pressure (under the same thermodynamic conditions) present at all times in a mixture under pressure p_i :

$$p_{O_3} = 2(p_i - p). \quad (2)$$

This relation, based on the hypothesis of a degradation of ozone through the only process :

(thermic decomposition, slow at experimental temperatures), requires to minimize the interaction of ozone with the UV radiation from the continuous background source, which would produce atomic species (O^1D) particularly reactive with the walls, and therefore would distort the results expected from the reaction [3]. This requirement can be satisfied by restricting the light beam to its useful part, which reduces the evolution of the total pressure during an experiment.

At present, the results we have obtained concern the 310-350 nm range (Huggin's system) and are averaged values obtained at two temperatures (294 and 223 K) after several experiments (≥ 6) with an error bar which does not exceed :

$$\begin{array}{ll} 2 \% \text{ at high absorption levels} & (310 \leq \lambda \leq 325 \text{ nm}) \\ 4 \% \text{ at average absorption levels} & (325 \leq \lambda \leq 340 \text{ nm}) \\ 6 \% \text{ at low absorption levels} & (340 \leq \lambda \leq 350 \text{ nm}) \end{array}$$

These results deduced from recordings under high resolution ($\Delta\lambda \simeq 0.012 \text{ nm}$) carried out with a Jobin Yvon THR spectrometer were determined with a precision in wavelength position close to 0.01 nm, comparable to the above mentioned work [1] by A. M. Bass and R. J. Paur and which, in that respect, is an improvement compared to a number of previous works [4 to 6] still in use to-day in atmospheric applications. From the results of cross-sections, calculated at each 0.01 nm interval, available to us, we have extracted the values of the absorption peaks as shown in the table I.

In this table, we have also indicated the ratios between our values and those of Bass and Paur. The comparison we can thus establish is particularly interesting as, for the first time, it, shows a

Table I. — *Cross-section values of absorption maxima in the spectral range 310-350 nm.*

$T = 294 \text{ K}$			$T = 223 \text{ K}$		
λ	σ	Ratio BDM/BP (*)	λ	σ	Ratio BDM/BP (*)
3 494.7	0.034 0	—	3 495.10	0.012 0	—
3 486.3	0.024 9	—	—	—	—
3 471.6	0.048 1	—	3 472.0	0.042 1	—
3 456.7	0.064 8	—	—	—	—
3 439.5	0.127 3	0.732	3 439.7	0.126 8	—
3 431.4	0.086 6	0.787	3 432.1	0.049 9	—
3 420.5	0.071 3	0.735	3 418.7	0.031 4	—
3 401.3	0.196 7	0.826	3 401.2	0.167 1	0.960
3 394.9	0.145 0	0.806	3 394.3	0.068 7	0.968
3 372.0	0.348 2	0.866	3 372.0	0.333 4	0.969
3 364.4	0.242 2	0.824	3 364.7	0.180 8	0.932
3 337.5	0.539 0	0.879	3 336.7	0.497 2	0.960
3 332.0	0.340 0	0.804	3 331.0	0.221 8	0.969
3 310.5	0.775 6	0.887	3 310.5	0.717 4	0.958
3 303.8	0.674 2	0.898	3 303.3	0.599 6	0.961
3 295.6	0.449 7	0.842	3 295.9	0.278 3	0.925
3 279.2	1.186 1	0.881	3 279.1	1.170 4	0.962
3 272.2	0.858 9	0.845	3 271.9	0.724 5	0.943
3 254.7	1.365 1	0.888	3 254.7	1.196 6	0.959
3 248.2	1.644 4	0.879	3 248.2	1.595 8	0.956
3 242.1	1.200 3	0.885	3 241.8	0.881 8	0.879
3 226.3	2.179 1	0.890	3 226.1	1.993 4	0.943
3 220.3	2.236 2	0.889	3 220.1	2.069 7	0.906
3 213.0	1.702 2	0.849	3 213.6	1.233 5	0.874
—	—	—	3 204.9	1.767 3	0.857
3 199.5	2.920 7	0.870	3 199.7	2.667 4	0.918
3 194.7	2.848 6	0.868	3 194.4	2.507 2	0.883
3 180.0	3.310 1	0.885	3 180.1	2.814 4	0.913
3 175.8	3.791 0	0.883	3 175.7	3.415 8	0.918
3 170.1	3.704 6	0.872	3 170.5	3.158 0	0.926
3 155.2	4.875 9	0.858	3 155.1	4.448 7	0.913
—	—	—	3 148.2	3.862 9	0.868
3 134.5	6.144 7	0.863	3 134.2	5.613 9	0.916
—	—	—	3 113.0	7.307 2	0.874

(*) BDM = Brion, Daumont, Malicet.

(*) BP = Bass, Paur.

very close agreement — in relative values — at two different temperatures and within the whole spectral range under study, between two series of measurements obtained independently as well as with slightly different methods (see Fig. 1).

Fig. 1. — Comparison of BDM data with those of Bass and Paur.

Furthermore, we can note that, at the only wavelength allowing the comparison so far ($\lambda = 334.15$ nm) we obtained — in absolute value — a result quite similar to Hearn's (2) ($\sigma = 0.427 \times 10^{-20}$ cm² (Hearn); $\sigma = 0.416 \times 10^{-20}$ cm² (this work)). However, generally speaking, our values are lower than all the absorption cross-sections measured to this day (see table in particular). This fact, which seems to imply a reevaluation (by approximately 4 %) of the total concentrations of atmospheric ozone, confirms a conclusion recently proposed by other researchers in our laboratory [7] who have improved a method of carrying out similar measurements using IR spectroscopy.

We think that those three observations should allow us to conclude that the results we propose are valid, not only relatively (comparison with A. M. Bass and R. J. Paur) but also intrinsically (comparison with Hearn and with the atmospheric results obtained from IR measurements).

This needs to be confirmed by further comparison for final conclusions. Extension of our work in the 300-310 nm range — which requires to adapt our experimental equipment to determine larger cross-sections — should rapidly give us a second opportunity for comparison with A. G. Hearn ($\lambda = 302.1$ nm).

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