

Molecular absorption Cross-Sections *

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RÉSUMÉ. — *Les données récentes concernant la section efficace d'absorption lumineuse de molécules d'intérêt aéronomique sont présentées. Trois aspects en sont discutés qui ont respectivement trait à la photodissociation, à l'atténuation du rayonnement actinique solaire et aux applications analytiques de l'ultraviolet à l'infrarouge.*

ABSTRACT. — *Recent data concerning the luminous absorption cross section of molecules presenting an aeronomic interest are presented. Three aspects are discussed, respectively dealing with the photodissociation, the attenuation of actinic solar radiation and with analytical applications from the ultraviolet to the infrared.*

I. INTRODUCTION

As it has already been pointed out by many authors, the absorption properties of atmospheric molecular constituents are of fundamental importance in the understanding of the planetary atmospheres. While absorbing radiation the molecules can dissociate into fragments which can possibly be in excited or ionized states before initiating chemical chain reactions distributing the energy. They can have a screening effect by which they protect other atmospheric gases from chemically active radiations. Eventually the absorption cross sections are the key of the quantitative analysis of atmospheres when optical techniques are used in aeronomy to study atmospheric compositions. The two first aspects are usually the only ones to have been considered. They usually involve energies of at least one eV corresponding to

wavelengths smaller than 12 000 Å. The third aspect concerns also radiative processes occurring at larger wavelengths at which little quantitative laboratory work has been done recently. Consequently this third aspect will only be mentioned in this article, the purpose of which is to consider the laboratory data published from 1968 up to date in order to provide the continuity after the review presented in september 1968 by Huffman (1969) at the 8th IAGA meeting on laboratory measurements of aeronomic interest. Recently, Hudson [1971] has reviewed ultraviolet photo-absorption cross sections for molecules of astrophysical and aeronomic interest. He has quoted references to those papers containing in his opinion, the most reliable data up to October 1969. The main results published since then concern oxygen, ozone and carbon dioxide.

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II. OXYGEN

In the 1200 to 1300 Å region Ogawa and Yamawaki [1970] have performed several measurements. In the 1187 and 1307 Å optical windows, their results agree with the former values obtained by Watanabe et al. [1953] while they disagree with Watanabe et al. [1968] in the 1307 Å window. New measurements have been reported in the 1068, 1094 and 1108 Å windows by Huffman et al. [1971]. They have confirmed that the Lyman α line so important for the chemistry of neutral and ionized species in the *D* region is located on the short wavelength wing of the oxygen optical window, by measuring the respective absorption of the components of the apparent doublet having a separation of 0.09 Å caused by self-absorption. A similar conclusion had already been reached by Ogawa [1968] and by Gailly [1969].

The understanding of the absorption in the spectral range of the Schumann-Runge bands has been improved by the work performed by Ackerman et al. [1970] who have designed a model of absorption based on experimental data available. These data are mainly the rotational structure of the bands determined by Brix and Herzberg [1954] and by Ackerman and Biaumé [1970], the width of the rotational lines given by Ackerman and Biaumé [1970] and the values of oscillator strengths published by various authors [BETHKE, 1959; HUDSON and CARTER, 1968; HARRIS et al., 1969]. As far as the contribution of continuous absorption is concerned the introduction of the Herzberg continuum has appeared to be sufficient to represent the experimental cross sections within the experimental error.

Recently, Ogawa [1971] has determined extensively the pressure effect already studied at some wavelengths in the Herzberg continuum and in the Schumann-Runge bands by Heilpern [1941], Ditchburn and Joung [1962] and Scharadanand [1969]. In the bands, he has also measured the absorption cross section between rotational lines and has attributed the total amounts measured to continuous absorption. His data are shown in Figure 1 and are compared with the computed values of Ackerman et al. [1970] in Figure 2 and 3. The absorption due to the overlapping wings of the rotational lines appears to be sufficient within the probable error to explain Ogawa's values. The addition of the measurements obtained at the absorption minima to those obtained by Ackerman et al. [1969] in some cases very close to the center of rotational lines appears to be very useful. Hudson et al. [1969] have measured for rather large wavelength intervals effective absorption "factors". The photodissociation coefficient of oxygen as a function of altitude computed on the basis of these factors has been compared by Kockarts [1971] with coefficients based on the high resolution absorption spectra of Ackerman et al. [1970]. The results

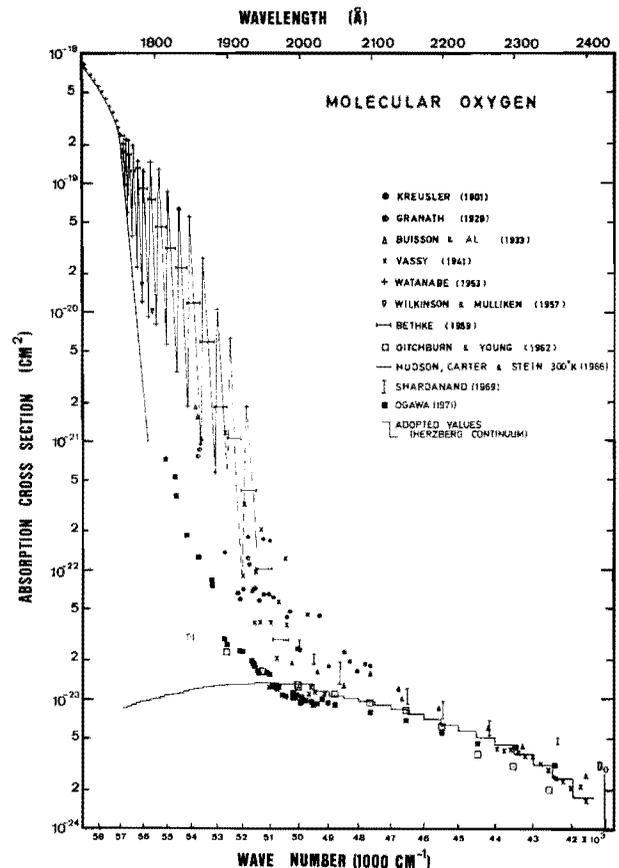


FIG. 1

Absorption cross sections of molecular oxygen obtained by Ogawa [1971] represented with values obtained by other authors and discussed by Ackerman et al. [1970].

are very similar. However the use of high resolution spectra is to be preferred when the solar zenith distance becomes important or when the effect of solar radiation on an other atmospheric constituent has to be investigated, particularly when it involves absorption bands.

Integrated absorption coefficients have been measured for the first time for the 0-0, 1-0, 2-1, 3-1 and 4-1 bands of the Schumann-Runge band system of molecular oxygen by Hasson et al. [1970]. The absorption oscillator strengths that they have also derived for other bands and which allow the comparison with previous experimental values indicate that their measurements are in agreement with the data of Bethke [1959] and of Hudson and Carter [1968]. For the Herzberg band system, Hasson et al. [1970 *b*] have measured the integrated absorption coefficient of the 7-0 band and have used it in conjunction with the relative measurements of Degen and Nicholls (25) made in emission to deduce absolute band strengths of this system which is an important feature of the ultraviolet sky emission. Acker-

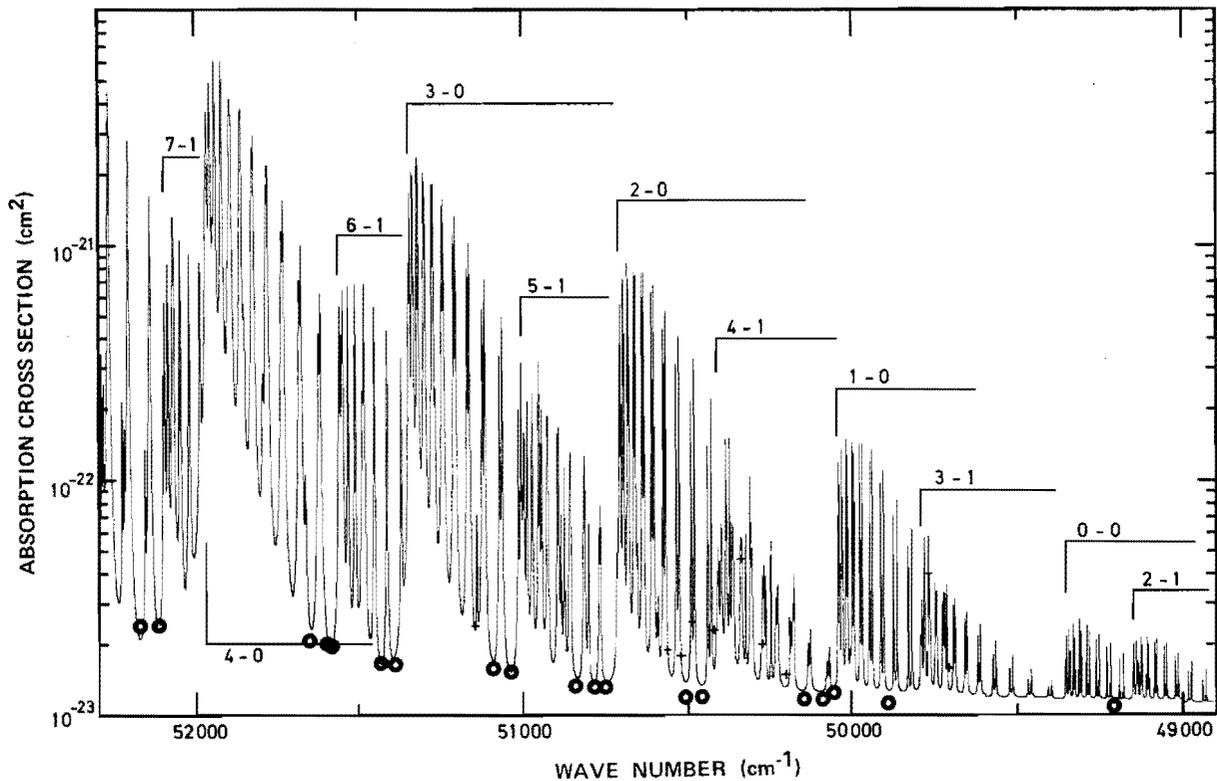


FIG. 2

Absorption cross section of molecular oxygen versus wave number. The computed (—) and measured (+) values of Ackerman et al. [1970] are shown with the measured (O) values of Ogawa [1971] from 48 900 to 52 300 cm^{-1} .

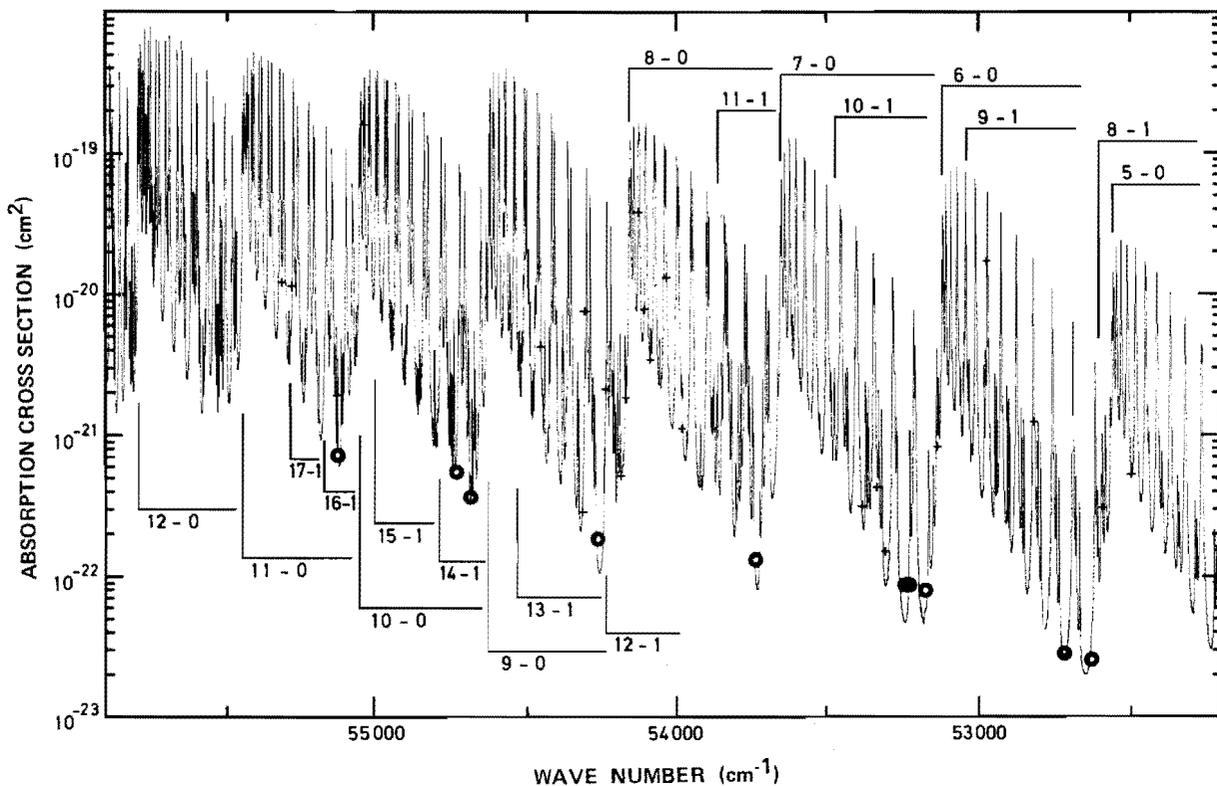


FIG. 3

Absorption cross section of molecular oxygen versus wave number. The computed (—) and measured (+) values of Ackerman et al. [1970] are shown with the measured (O) values of Ogawa [1971] from 52 200 to 55 900 cm^{-1} .

man [1971] has published selected absorption cross section for O_2 and O_3 averaged over wavelength intervals suitable for mesospheric photochemical calculations.

The detection in the atmosphere of molecular oxygen in the metastable $^1\Delta_g$ state by Noxon in 1961 has prompted a laboratory activity which is beginning to appear in the literature concerning absorption cross section. Some results have already been mentioned by Huffman [1969]. Since then absorption cross sections have been measured by Ogawa [1970] at some wavelengths between 1408 and 1486 Å. Some of the bands measured by Ogawa [1970] have also been observed by Donovan et al. [1970] confirming some of the observations made by Alberti et al. [1968]. Ogawa has reported values as high as $5 \times 10^{-17} \text{ cm}^2$ under some assumptions however. Cairns [1971] has obtained a value at 1045 Å equal to 10^{-17} and an upper limit ($1.4 \times 10^{-18} \text{ cm}^2$) in the 2960 to 3050 Å region. Below the ionization threshold of O_2 $^1\Delta_g$, the detailed photoionization cross section, scaled a 1067 Å to the value of $3.2 \times 10^{-18} \text{ cm}^2$ of Clarke and Wayne [1970], has been published by Huffman et al. [1971].

It should eventually be noted that photoelectron spectroscopy of O_2 $^1\Delta_g$ [JONATHAN et al., 1970] has justified the revision of the vibrational numbering of the $O_2(^2\Pi_g)$ ion.

III. OZONE

The latest results on the absorption by ozone have already been compared [ACKERMAN, 1971], with previous ones. Vigroux's early results in the Hartley continuum have been completely brought in agreement with those of Inn and Tanaka by Vigroux [1969] himself.

IV. CARBON DIOXIDE

Inn et al. [1953] have measured, as they did also for many other gases, absorption cross sections of CO_2 . On the long wavelength side their measurements ended at 1750 Å. The growing interest in CO_2 atmospheres has resulted in new recent measurements. Heimerl [1970] has extended the data towards longer wavelengths providing continuity, except for a 20 Å gap, with the results of Thompson et al. [1963]. These two last sets of cross sections exhibit values which are higher than those listed by Ogawa [1971] except for the data of Thompson et al. [1963] which fall abruptly above 1950 Å as it is shown in Figure 4.

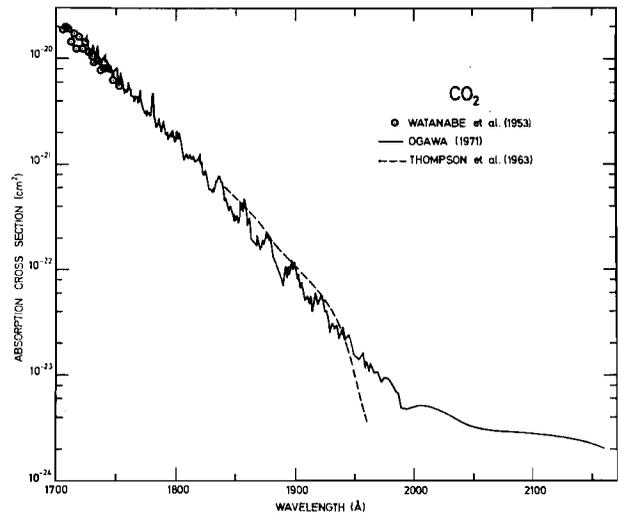


FIG. 4

Absorption cross section of carbon dioxide versus wavelength from 1700 Å to 2160 Å.

V. INFRARED ABSORPTION

More and more measurements are made of absorption of solar radiation in the atmosphere by means of balloon or rocket borne instruments in order to determine the atmospheric concentration of polyatomic minor constituents. The resolving power of the instruments is usually such that the band integrated absorption has to be related to concentrations through values obtained theoretically or experimentally in the laboratory. These two types of values have appeared to sometimes disagree especially when applications at low pressure, low concentration and low temperature have to be performed.

VI. CONCLUSION

A complete review including a critical analysis of all the quantitative data on the infrared spectra of molecules present in the atmosphere is highly recommendable since more accuracy is now required in the determination of the abundance of stratospheric and mesospheric constituents by means of optical methods yielding results which have to be compared with those obtained by means of other techniques.

As far as ultraviolet absorption and photodissociation cross sections are concerned many data are still missing concerning stable and transient species, such as HO_2 , H_2O_2 , NO_2 and HNO_3 for instance.

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