The Wulf bands of oxygen

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Abstract

The Wulf bands of oxygen in the 240–290 nm spectral region are caused by collision-induced absorption of the Herzberg III ($A^3\Delta_u$–$X^3\Sigma_g^-$) system. These bands had been previously attributed to the oxygen dimer, $(O_2)_2$. Under atmospheric conditions the Wulf bands are thus the long-wavelength extension of the Herzberg continuum. Absorption of solar radiation by the Wulf bands may be an additional source of NO in the stratosphere. © 1998 Elsevier Science B.V. All rights reserved.

From the near infrared to the near ultraviolet, bands associated with oxygen are prominent features in the spectra of the Earth's atmosphere. These features are all relatively weak (with the exception of the Schumann–Runge system, $B^3\Sigma_u^-$–$X^3\Sigma_g^-$, near 200 nm) but they appear because of the high pressures and long path lengths used when recording atmospheric spectra. Atmospheric bands associated with oxygen also appear in emission in, for example, aurora and airglow [1]. It is the absorption of oxygen along with ozone and water vapor that primarily determines the spectral composition of the solar radiation that reaches the surface of the Earth in the near-infrared to near-UV region.

In the near-UV spectral region some of the weak oxygen bands overlap with those of the strong Hart-ley bands of ozone that are used to retrieve tropospheric ozone concentrations [2]. Tropospheric ozone concentrations are generally increasing and are of concern because of their deleterious effect on human health. At the low resolutions (typically 16–100 cm^{-1}) routinely used for the determination of ozone in the troposphere, the diffuse Hartley bands and the interfering oxygen bands show a similar structure. The position and intensity of the weak oxygen bands thus need to be known for reliable ozone retrievals.

Oxygen produces spectral features by three distinctly different physical mechanisms: monomer absorption, dimer absorption and collision-induced absorption (CIA). Historically, atmospheric scientists have not always distinguished between the absorption of $(O_2)_2$ and collision-induced absorption (an enforced dipole transition) of O_2 caused by another atmospheric constituent, M (e.g., [3]).

In the near-UV region from 290 nm to the dissociation limit at 242 nm (41260 cm^{-1}) as shown in Fig. 1, there are three overlapped forbidden absorp-

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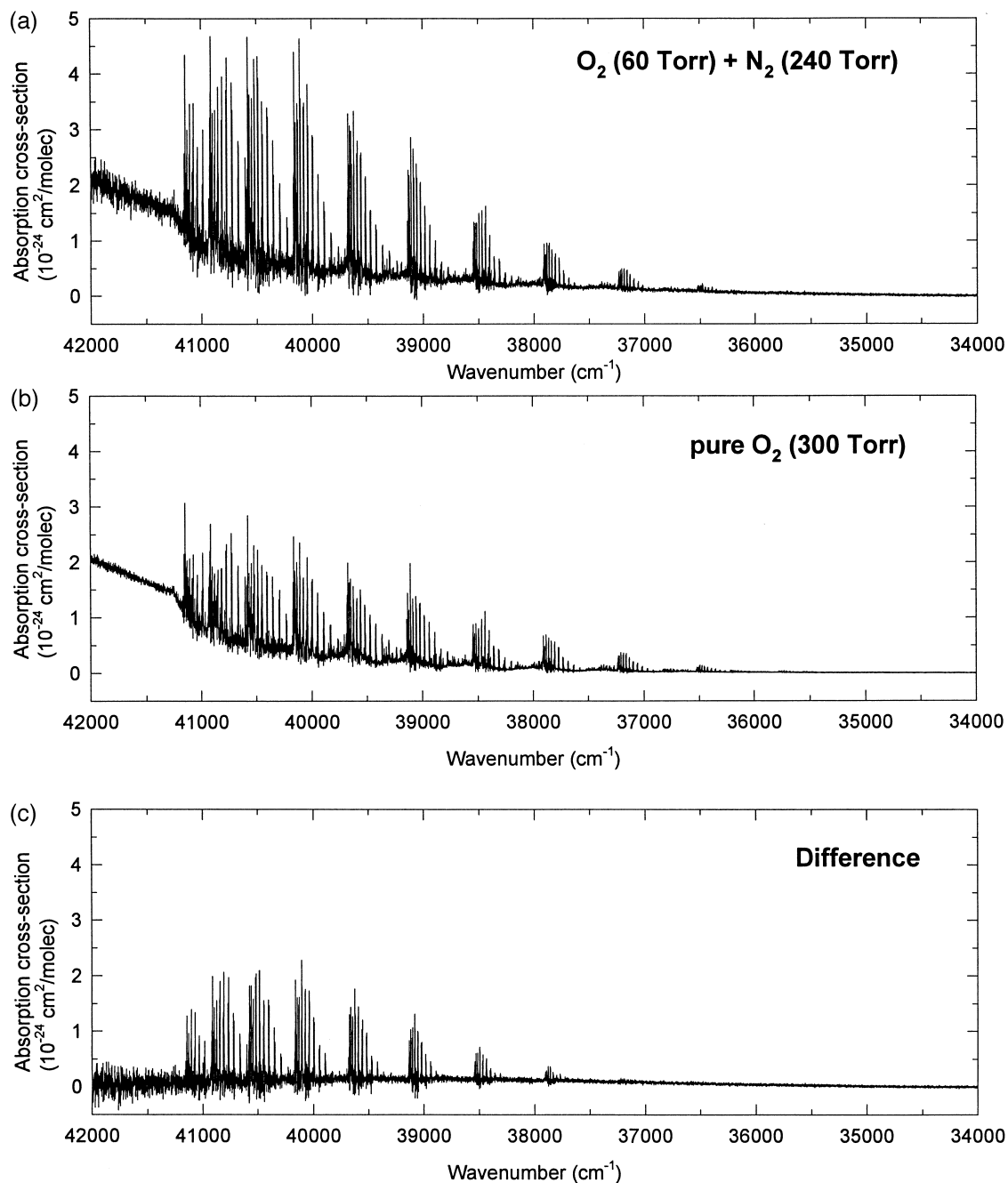
Fig. 1. Absorption spectra of oxygen in the Herzberg region with the *y*-axes in absolute cross-section units: (a) absorption at a total pressure of 300 Torr with partial pressures of 60 Torr of oxygen and 240 Torr of nitrogen; (b) absorption at the same total pressure (300 Torr) of pure oxygen; and (c) difference between (a) and (b). Note that the Wulf bands are no longer present but the discrete lines have not cancelled perfectly because the individual spectral lines of the 300 Torr pure oxygen spectrum are saturated.

tion systems of O_2, Herzberg I ($A^3\Sigma_u^+ - X^3\Sigma_g^-$), Herzberg II ($c^1\Sigma_u^- - X^3\Sigma_g^-$) and Herzberg III ($A'^3\Delta_u - X^3\Sigma_g^-$) [4,5]. The Herzberg I system is the strongest and all of the obvious sharp lines in Fig. 1 arise from it [4]. There is also an accompanying true continuum (200–242 nm) that represents bound-free transitions of O_2 from the ground state to the $O(^3P) + O(^3P)$ first dissociation limit [6]. This Herzberg continuum is the rising slope in Fig. 1 starting at 41260 cm^{-1} and proceeding to higher wavenumbers. The six lowest bound states of O_2, $A^3\Sigma_u^+$, $A'^3\Delta_u$, $c^1\Sigma_u^-$, $b^1\Sigma_g^+$, $a^1\Delta_g$, and $X^3\Sigma_g^-$, all correlate to this first dissociation limit (see fig. 4 in Ref. [6]).

The dimer (or dimol) bands of O_2 are exemplified by the

$$O_2\left(b^1\Sigma_g^+\right) + O_2\left(b^1\Sigma_g^+\right) \leftarrow O_2\left(X^3\Sigma_g^-\right)$$
$$+ O_2\left(X^3\Sigma_g^-\right) \qquad (1)$$
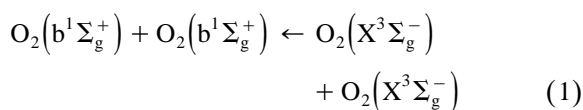
transition near 380 nm [7]. These transitions appear diffuse at high temperatures because only a small fraction of the dimers are actually bound. The bulk of the oscillator strength is thus carried by free–free transitions. Cooling the O_2 to ~ 90 K [8] or using a supersonic jet expansion increases the fraction of bound van der Waals molecules and the discrete bound–bound transitions become prominent [9]. This effect was first noted by Long and Ewing [8] and was recently confirmed at high resolution by Campargue et al. [9] for the

$$O_2\left(a^1\Delta_g\right) + O_2\left(a^1\Delta_g\right) \leftarrow O_2\left(X^3\Sigma_g^-\right)$$
$$+ O_2\left(X^3\Sigma_g^-\right) \qquad (2)$$
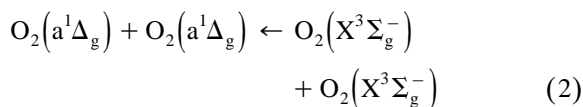
transition at 580 nm. Numerous ab initio calculations of the small interaction energy between two oxygen molecules have been published [10] to help interpret these new experiments as well as to shed light on the older oxygen dimer data.

The third type of oxygen absorption is caused by CIA as illustrated by the diffuse bands at 1.26 μm and 762 nm associated with the forbidden discrete $a^1\Delta_g - X^3\Sigma_g^-$ (0–0 band of the infrared atmospheric system) and $b^1\Sigma_g^+ - X^3\Sigma_g^-$ (atmospheric A band) transitions [11–13]. Each monomer band with discrete lines thus has an accompanying underlying diffuse band that appears at high pressure. These bands occur because the collisions lower the symme-

try in the O_2 molecule and they also induce mixing of the upper state with other states that have allowed electronic transitions to the ground state. The appearance of the CIA bands does not depend strongly on the nature of the collisional partner. Tabisz et al. [12] summarize some additional features of CIA as applicable to these near-infrared O_2 band systems.

Underlying the Herzberg systems in the near UV are some additional diffuse bands with triplet structure first seen by Wulf [14] in 1928 (Fig. 3). Huber and Herzberg [15] comment that:

At high pressure and in liquid O_2 a fairly strong progression of diffuse triplets has been studied by many investigators. This progression appears to be the analog in $(O_2)_2$ of the A′–X bands (their intensity increases with the square of the pressure).

In fact, we will show that the Wulf bands are not due to the oxygen dimer but are CIA bands.

The spectra of the Wulf bands were recorded at the University of Reims using a 50 m base-path multiple reflection cell. A total path length of 400 m was used. The measurements (2 cm^{-1} resolution) were made using a 1000 W Xe arc lamp as a source and the mobile Bruker IFS 120 M Fourier transform spectrometer of the Free University of Brussels. The 28000–42000 cm^{-1} region was covered with a UV vacuum diode detector and 1024 scans were co-added in 66 min of integration. This work is part of an extensive Brussels–Reims collaboration on the line positions, line strengths and pressure broadening coefficients of the Herzberg systems of O_2. A large number of spectra have been recorded at both low and high resolution and detailed results will be reported elsewhere [16].

The Wulf bands have the same strength and appearance as long as the total pressure is unchanged. This is illustrated by Fig. 1. In Fig. 1a, the total pressure is 300 Torr made up of 60 Torr of O_2 and 240 Torr of N_2, while in Fig. 1b the 300 Torr pure oxygen spectrum is plotted. The known density of O_2 has been used to convert the *y*-axes into absolute absorption cross-section units. The Wulf bands are the underlying structure in the baseline while the sharp structures are mainly the discrete lines of the Herzberg I ($A^3\Sigma_u^+ - X^3\Sigma_g^-$) bands. Fig. 1c is the difference between the two spectra and shows no sign of the Wulf bands. The discrete structure does

not cancel perfectly in Fig. 1c because the O_2 lines are saturated in the 300 Torr pure oxygen spectrum so that the cross-sections of the strongest lines are not reliable. Similar spectra are shown in Fig. 2 using argon rather than the nitrogen used for Fig. 1. The Wulf bands thus have the same appearance and strength regardless of the nature of the three collisional partners, which were O_2, N_2 and Ar in our
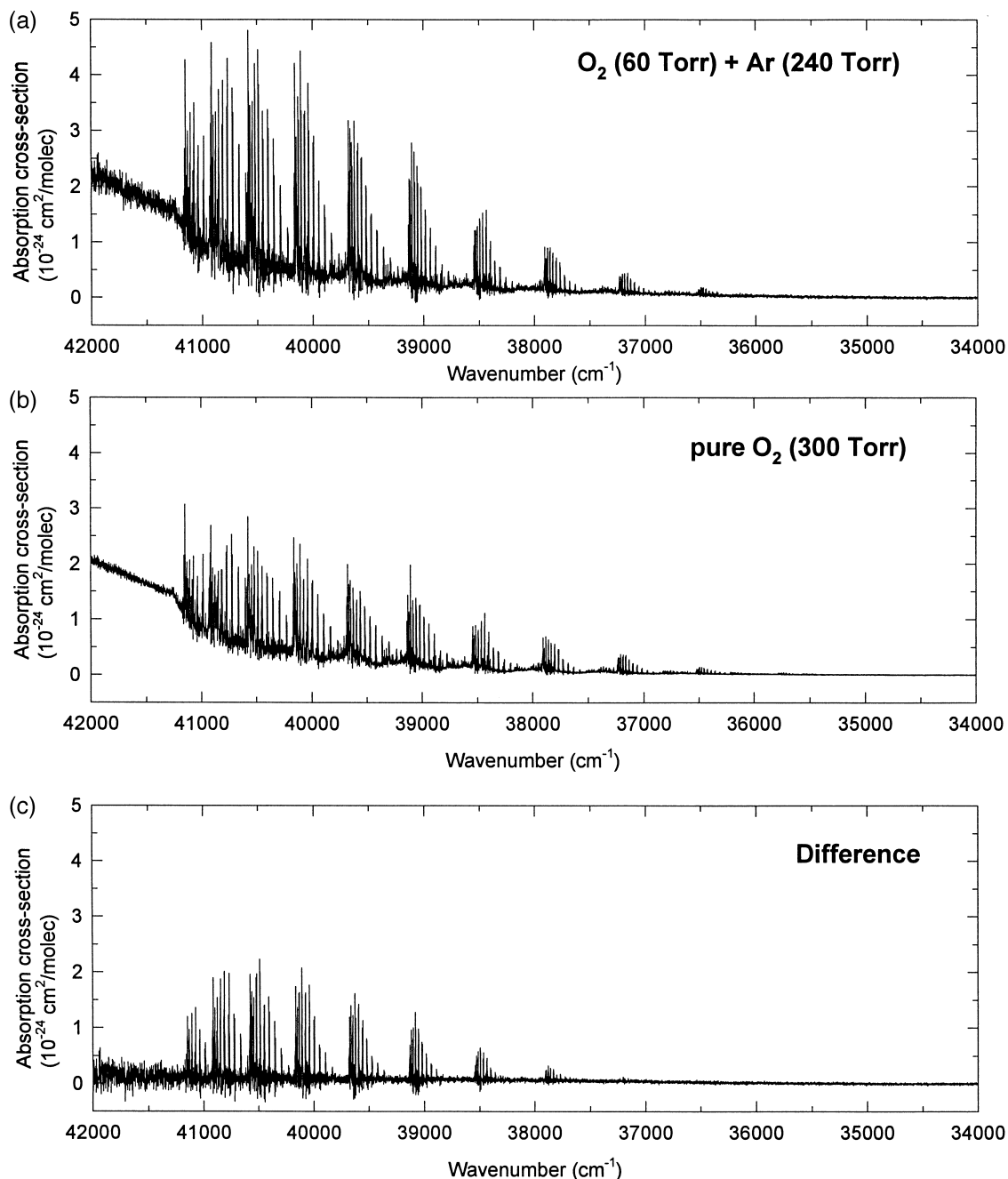

Fig. 2. This figure is identical to Fig. 1 except that in (a) argon gas has been used instead of nitrogen.

experiments. These experiments are strong evidence for CIA and against the oxygen dimer as the cause of the Wulf bands. Both CIA and dimer absorption will depend quadratically on the oxygen pressure for a pure sample but only CIA is affected by the presence of another gas, as is seen here.

The Wulf bands appear more clearly in Fig. 3 where a preliminary, partly successful attempt has been made to remove the discrete lines of the Herzberg systems. The triplet structure, as noted by Herzberg [5] and others [17,18], is very similar to the triplet splitting in the $A'^3\Delta_u$ state caused by spin–orbit coupling. We have made this comparison more quantitative by using the prescription recommended by Tabisz et al. [12] for simulating CIA spectra (Fig. 3). Although the simulation in Fig. 3 is still preliminary, the agreement between observed and calculated spec-

tra is already good with the Raman-like rotational selection rules ($\Delta J = 0, \pm 2$) giving rise to the necessary triplet Q-branch features.

The only previous recognition of the CIA origin of the Wulf bands seems to be the comments made by Goodman and Brus [19] in their paper on the matrix isolation spectroscopy of O_2. Because the solid-state analog of the Wulf bands appeared even when the O_2 was diluted in several cryogenic solids, they could not be due to the oxygen dimer. Indeed Goodman and Brus's statement that

the effect of a nearest neighbor is simply to break the $\Delta \Lambda$ selection rules and to increase the $^3\Delta_u{-}^3\Sigma_g^-$ dipole strength

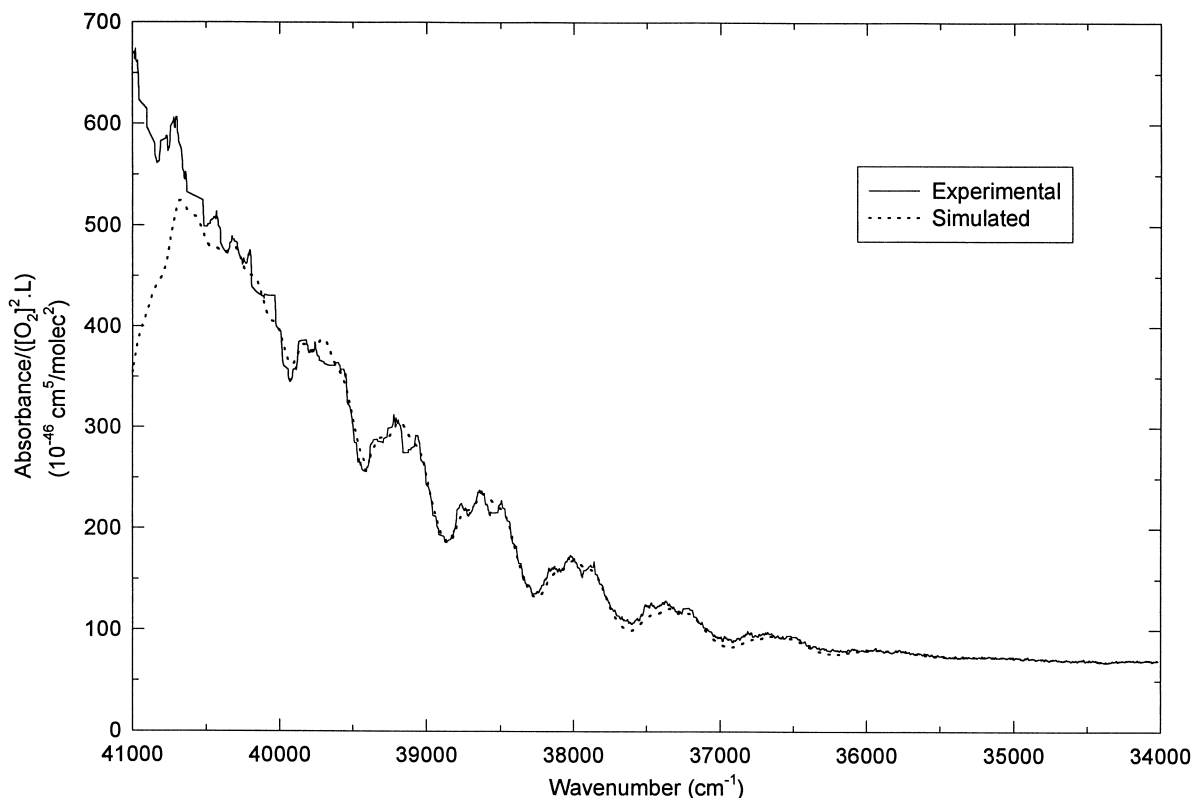is equally valid in the gas phase. It has been established that collisions in the gas phase [20] or in a

Fig. 3. The Wulf bands of oxygen obtained by manually removing the discrete oxygen lines of the Herzberg systems and then smoothing the result (solid line). Each triplet in the Wulf bands is a collision-induced vibrational band of the Herzberg III system ($A'^3\Delta_u{-}X^3\Sigma_g^-$, not an oxygen dimer band. The dashed line is the calculated collision-induced absorption spectrum based on the experimental parameters of the Herzberg III system [16], the prescription of Tabisz et al. [12] and a single vertical scaling factor. The poor agreement between observed and calculated spectra at the high-wavenumber end is caused by the omission of the Herzberg continuum from the simulation.

condensed phase [19,21] more readily enhance the intensity of forbidden $\Delta \Lambda = \pm 2$ transitions such as the Wulf bands. Watson [22] has suggested to us that collisional mixing of the $A'^3\Delta_u$ state with the nearby $B^3\Sigma_u^-$ state through the quadrupolar operator might be responsible for the Wulf bands. This type of mixing is not possible for the $A^3\Sigma_u^+$ and the $c^1\Sigma_u^-$ states, accounting for the relative strength of the Wulf bands.

The oxygen transitions seen at high pressure and for the solid have been conveniently summarized by Krupenie [23]. He notes that in 1932 Fickelnburg and Steiner [24] suggested that the Wulf bands are due to CIA but in 1934 Fickelnburg [25] changed his mind and attributed them to the oxygen dimer.

Our results are also related to the work of Blake and McCoy [26] who concluded that the pressure dependence and the lack of significant temperature dependence, as noted by Shardanand [27,28], of the bound-free Herzberg continuum (200–242 nm) adjoining the Wulf bands is mainly due to CIA. Absorption of solar radiation in the Herzberg continuum is the main source of atomic oxygen in the stratosphere [26]. Under atmospheric conditions the CIA part of the Herzberg continuum cross-section is dominant over the pressure-independent contribution from oxygen monomer absorption [26–28]. This means that in the Earth's atmosphere the Wulf bands represent the long wavelength extension of the Herzberg continuum into the bound region of the oxygen atom interaction potential. In both cases collisions have induced the forbidden $A'^3\Delta_u$–$X^3\Sigma_g^-$ transition, and our new cross-sections (Fig. 1, [16]) support this interpretation (i.e., they are continuous across the dissociation limit at 41260 cm^{-1}, Fig. 1).

The physical origin of the Wulf bands has important atmospheric implications. Recently Zipf and Prasad [29] found that a small amount of NO was produced by irradiation of air in the Herzberg band region (210–400 nm). The production of NO_x ($NO + NO_2$) in their experiments had a quadratic pressure dependence and they suggested that the mechanism involved the photochemistry of the 'N$_2 \cdot$O$_2$ dimer'. Because the Wulf bands are caused by CIA (i.e., free–free absorption of $O_2 \cdot M$) rather than the oxygen dimer ($O_2 \cdot O_2$), then under atmospheric conditions M is likely to be N_2. Thus absorption of solar radiation by the Wulf bands may represent a previously unknown source of NO in the stratosphere which will effect the ozone concentration through the well-known NO_x catalytic cycle [1].

In conclusion, we have found that collision-induced absorption rather than the oxygen dimer is the cause of the Wulf bands of oxygen that appear in the near-ultraviolet spectra of the Earth's atmosphere. Under atmospheric conditions the Wulf bands and the Herzberg continuum thus have the same origin. This result may have important atmospheric implications since absorption of solar radiation in the Wulf bands may be an additional source of stratospheric NO molecules. This source of NO has not been considered in the current generation of chemical models of the atmosphere.

Note added in proof

Three papers (G.Ya. Zelikina, V.V. Bertsev, M.B. Kiseleva, Optics and Spectroscopy 77 (1994) 513, G.Ya. Zelikina et al., ibid. 81 (1996) 685 and Y. Oshima, Y. Okamoto, S. Koda, J. Phys. Chem. 99 (1995) 11830) dealing with the 200–280 nm absorption spectra of mixtures of oxygen and foreign gases at high pressures (10–100 atm) have been brought to our attention. These papers are generally in agreement with our work.

Acknowledgements

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