SINGLET MOLECULAR OXYGEN IN PLANETARY ATMOSPHERES[†]

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Summary

Recent observations of the oxygen airglow emissions in the different planetary atmospheres are reviewed and the vibrational development of the various emissions is discussed. A model which can describe this vibrational development is also presented. The excitation mechanisms for each of the emissions are considered and from an examination of the volume emission profiles in the Earth's atmosphere it is shown that the emissions from the low-lying states are probably excited by energy transfer from some precursor. From a comparison of the nightglows of Earth and Venus it is suggested that this precursor is the $c^1\Sigma_u^-$ state and that this is preferentially excited in the three-body recombination of atomic oxygen. It is also suggested that vibrational excitation may be extremely important in this energy transfer.

1. Introduction

In recent years there has been considerable interest in understanding the oxygen emissions of the various planetary atmospheres as these should allow the structure of the atmospheres to be studied and the temporal and spatial variations to be investigated. Unfortunately the kinetics for the excitation of these emission features are poorly understood so that the implications of the emission measurements change with each proposed excitation scheme. Recently it has become apparent that little can be learned from an isolated measurement, or study, of a solitary emission. In an effort to clarify many of the uncertainties associated with the different oxygen emissions we have studied the relationships between the various emissions in a series of coordinated rocket investigations.

In the present paper we describe measurements of the oxygen emissions in the atmospheres of Earth, Mars and Venus and use these to suggest various kinetic schemes for the excitation of the different emission features.

2. Observations

The first singlet oxygen emission feature recorded in the Earth's atmosphere was the auroral green line at 5577 Å (^1S–^1D) which was detected by Ångström [1] in the auroral spectrum, although the source of the radiation was not identified until much later [2]. Since that time other oxygen emissions have been identified in planetary atmospheres. The energy levels of molecular oxygen that are involved in the airglows of the terrestrial planets, together with the corresponding emission features, are shown in Fig. 1.
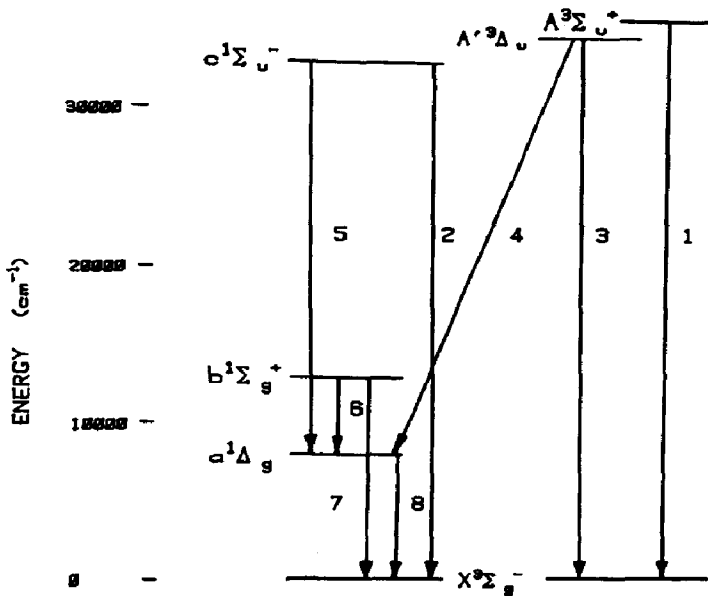

Fig. 1. Molecular oxygen energy levels: 1, Herzberg I Bands; 2, Herzberg II Bands; 3, Herzberg III Bands; 4, Chamberlain Bands; 5, Slanger Bands; 6, Noxon Bands; 7, Atmospheric Bands; 8, IR Atmospheric Bands.

The first identification of a singlet molecular oxygen emission feature was reported by Meinel [3, 4] who detected the 0–1 band of the Atmospheric Band system with an apparent intensity of 1.5 kR (1 rayleigh = 10^6 photons cm^{-2} column^{-1} s^{-1}). Recent measurements [5] would suggest that a more appropriate intensity for this feature is 300 R and that the intensity for the entire Atmospheric Band system in the terrestrial nightglow is 5 kR. Ground-based observations of the 0–0 band of the Atmospheric Band system are of course precluded because of absorption by the mass of oxygen underlying the emission region.

The IR Atmospheric Band system was first detected as the 0–1 band at 1.58 μm, in the evening twilight, by Vallance Jones and Harrison [6]. From a consideration of the sensitivity of their instrumentation Chamberlain [7] suggested that the night-time intensity for the IR Atmospheric Band system would be 50 kR. This is in reasonable agreement with measured values although a global mean intensity is probably closer to 100 kR. Vallance Jones and Harrison believed that the 0–0 band at 1.27 μm would be absorbed in the lower atmosphere and so be undetectable. However, subsequent work [8] has shown that this is not the case and that the 0–0 band is in fact transmitted to the ground with a factor of 5% so that the measured emission is brighter than the 0–1 band.

Following these early measurements of the singlet emission Bates [9, 10] essentially extended the classic ideas of Chapman [11] and concluded that if the oxygen emissions are excited in the three-body recombination of atomic oxygen

$$O + O + M \longrightarrow O_2{}^* + M \tag{1}$$

then the total emission intensity could be as high as 100 kR. Since those early observations the IR Atmospheric and the Atmospheric Band systems have been extensively studied in both the day and the night-time atmosphere using rocket- and balloon-borne platforms and ground-based instrumentation.

The daytime emissions are so intense that they must result from excitation mechanisms that directly involve solar radiation. The IR Atmospheric Band system is excited through the solar photolysis of ozone in the Hartley Band:

$$O_3(^1A) + h\nu \longrightarrow O_2(a\,^1\Delta_g) + O(^1D) \tag{2}$$

and has been used to determine the upper atmospheric ozone profile [12]. There is also a small contribution from energy transfer:

$$O_2(b\,^1\Sigma_g{}^+) + M \longrightarrow O_2(a\,^1\Delta_g) + M \tag{3}$$

This IR Atmospheric Band dayglow emission has also been observed in the Martian atmosphere [13] using the Hale telescope. The Doppler shift of the emission lines, due to the relative motion of Earth and Mars, ensures that the emission is unattenuated in the terrestrial atmosphere and also provides a convenient method of calibrating the observed emission. The dayglow intensity measured by Noxon *et al.* [13] varied between 3 and 25 MR and indicated that the total ozone abundance on Mars exhibits a seasonal variation. By comparing their observations with model predictions [14] Noxon and coworkers were able to show that CO_2 quenching of the $a\,^1\Delta_g$ state occurred with a rate constant of 10^{-20} cm^3 s^{-1} so that the IR Atmospheric Band system is essentially unquenched in the Martian atmosphere. While the nightglow mechanism, which must involve the recombination of oxygen atoms in some way, must be operative during the daytime its contribution is unlikely to be greater than the normal night-time value as the atomic oxygen concentration in the nightglow region is essentially constant from day to

382

night. In the terrestrial atmosphere the lifetime of an oxygen atom at 90 km is approximately 10^6 s (1 week) so that dynamical effects will exert a significant control over the atomic oxygen concentration. Thus the small contribution of the nightglow mechanism to the observed dayglow of the IR Atmospheric Bands on Earth and Mars may be neglected.

These observations have also failed to detect emission from vibrational levels above $v = 0$ which indicates that vibrational deactivation must be rapid enough to ensure complete relaxation within the lifetime of the $a^1\Delta_g$ state; this is consistent with the laboratory studies of Klais et al. [15]. It should be noted that vibrational development would be readily apparent in the balloon-borne spectrophotometric measurements of the near-IR airglows. However, vibrational development of the Atmospheric Bands in auroral spectra has been reported by Vallance Jones and Gattinger [16, 17] and Sivjee and Deehr [18]. These investigators noted that this vibrational development was only detectable in the upper parts of auroral forms. This suggests that while significant vibrational excitation of the $b^1\Sigma_g^+$ state may occur it is rapidly relaxed.

The third singlet emission, the Herzberg II system, was not observed in the Earth's atmosphere but was first detected in the Venus nightglow, with an intensity of 3 kR, from the Venera 9 and 10 spacecraft [19]. The emission spectrum (Fig. 2) was initially identified by Lawrence et al. [20] who showed that the principal features of the Venera spectra corresponded to the Herzberg II Bands from $v' = 0$. The other features marked in Fig. 2 have been subsequently identified in the Venus nightglow. Initially the excitation of the $c^1\Sigma_u^-$ state was ascribed to the effect of CO_2 as the third body in oxygen atom recombination (reaction (1)). However, subsequent laboratory studies by Slanger [21] have clearly indicated that the presence of CO_2 is not required and that the $c^1\Sigma_u^-$ is formed with other third bodies. These spectra are shown in Fig. 3 and clearly exhibit the same vibrational distribution as in the Venus spectrum. It should be noted that the difference in the intensity of the Atmospheric Bands ($b^1\Sigma_g^+-X^3\Sigma_g^-$) in these spectra is due to the quenching of the $b^1\Sigma_g^+$ state by CO_2. Recently Kenner and Ogryzlo [22]
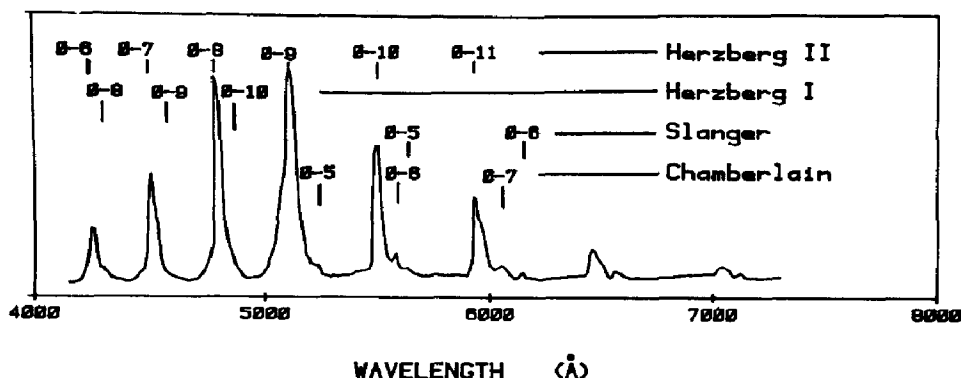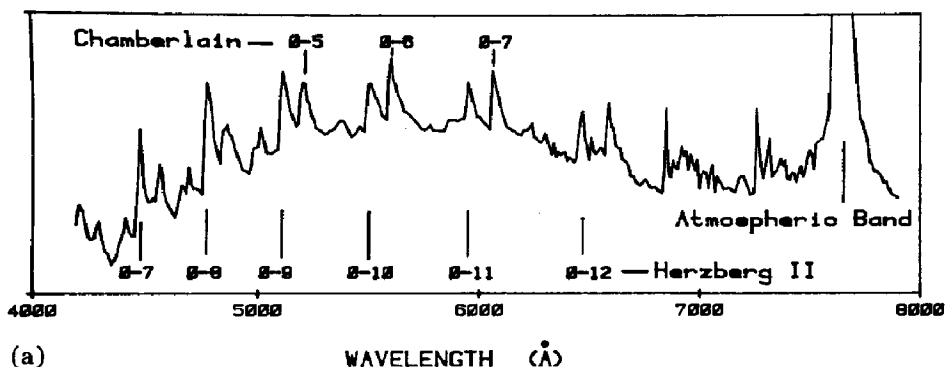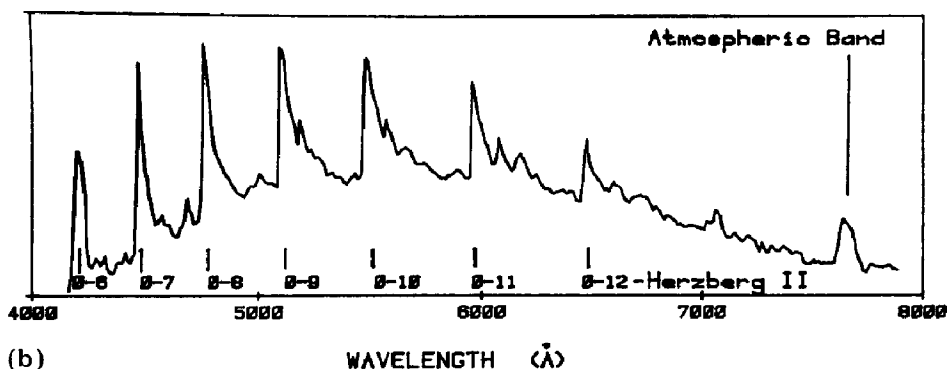

Fig. 2. Venus nightglow spectrum as measured on the Venera spacecraft [19].

Fig. 3. Oxygen recombination spectrum (a) in a fast flow system with helium and (b) in the presence of CO_2. Both these spectra were taken from the work of Slanger [21].

have developed a source of $O_2(c\,^1\Sigma_u^-)$ state molecules in the heterogeneous recombination of oxygen atoms.

This detection of the Herzberg II emission on Venus apparently prompted a search for other oxygen emissions in the Cytherean airglow, and for the Herzberg II Bands in the terrestrial atmosphere. Initial observations were reported by Connes et al. [23] in 1979 although the measurements had in fact been made in 1973. These investigators were able to detect the IR Atmospheric Bands in both the Venus nightglow and the Venus dayglow. By comparing their observed, Doppler-shifted, spectra with the weak terrestrial emission detected in the centre of the terrestrial absorption line Connes et al. estimated that the measured Cytherean airglow intensity was 4 MR with a day-to-night variation of 1.2. However, as the clouds on Venus provide a substantial albedo this intensity must be reduced by a factor of 2.8. Thus the actual Venus airglow is approximately 1.4 MR.

In their analysis Connes et al. [23] concluded that such an intense emission could not arise from three-body recombination (reaction (1)). They suggested that catalytic cycles involving chlorine

$$Cl + O_3 \longrightarrow ClO + O_2 \tag{4a}$$

$$ClO + O \longrightarrow Cl + O_2 \tag{4b}$$

TABLE 1

Emission	Measured planetary airglows		
	Venus	Earth	Mars
IR Atmospheric	1.7 MR day	20 MR day	3 - 20 MR day
	1.4 MR night	100 kR night	
Atmospheric		350 kR day	
		5 kR night	
Herzberg I	150 R night	1 kR night	
Herzberg II	2.7 kR night	100 R night	
Chamberlain	200 R night	100 R night	
Predicted total from reaction (1)	1.8 MR night	100 kR night	600 R night

similar to the OH catalytic cycle in the terrestrial atmosphere, were responsible for the excitation. Such a cycle has been considered by Llewellyn and Solheim [24] in their interpretation of the IR Atmospheric Band emission in the terrestrial nightglow. In the latter case, the analysis requires a knowledge of the vibrational relaxation coefficients of OH* as the hydroxyl must be vibrationally excited to yield the $a^1\Delta_g$ state. However, Connes *et al.* did note that the IR Atmospheric Band oxygen emission on Venus seemed to equate with the production of oxygen atoms from CO_2 photolysis. This is of course exactly the case for the Earth as the IR Atmospheric Band emission is essentially equal to the production rate of oxygen atoms from solar photolysis [9, 10]. If this condition also prevails on Mars then we can estimate the expected Martian nightglow. For the atmospheric model of Kong and McElroy [14] we can estimate the oxygen recombination rate to be 6×10^8 cm^{-2} $column^{-1}$ s^{-1} which would result in an emission of 600 R for the entire group of oxygen emissions. This is illustrated in Table 1 which gives the measured planetary airglows and the predicted total emission from the estimated oxygen atom recombination rates.

The Herzberg II Bands were eventually identified in the terrestrial airglow by Slanger and Huestis [25, 26]. These researchers showed that the sys-
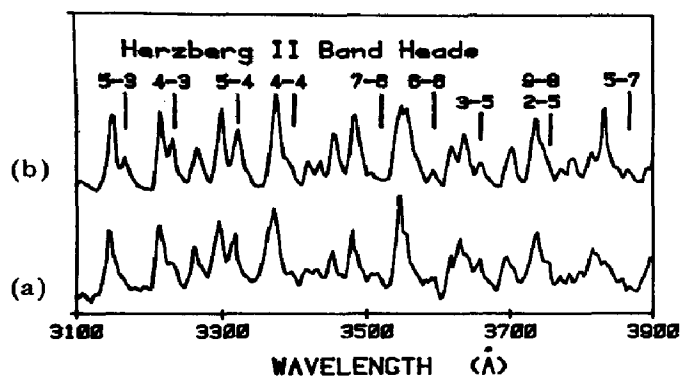

Fig. 4. (a) Terrestrial nightglow spectrum and (b) synthetic spectrum showing the presence of the Herzberg II Bands. (From Slanger and Huestis [25].)

tem is weakly emitted in the UV airglow with a vibrational development similar to that of the Herzberg I and Chamberlain Band systems. The problem of identifying the Herzberg II Bands in the terrestrial airglow is clearly apparent in Fig. 4 which shows a portion of the terrestrial nightglow spectrum analysed by Slanger and Huestis. The vibrational development is perhaps surprising in view of the vibrational relaxation observed in both the Venus airglow and the laboratory afterglows. From their analysis Slanger and Huestis [25] have estimated that the intensity of the Herzberg II system in the terrestrial airglow is 100 R. This suggests that the ratio of the IR Atmospheric to Herzberg II Bands in both the Earth and the Venus nightglow is 1000:1.

3. Analysis

In an attempt to understand these oxygen emissions in the airglows of the terrestrial planets we have investigated the relationships between the various emissions and the importance of vibrational development. In an analysis of the Barth excitation mechanism for the auroral green line in the airglow McDade et $al.$ [27] have developed a model that can explain the vibrational development of the $c^1\Sigma_u^-$ state. These researchers assume that the $c^1\Sigma_u^-$ state is formed in reaction (1), in some vibrational level above $v = 10$, and have shown that the observed vibrational distribution in the terrestrial nightglow can be matched if the excited molecules suffer single-quantum vibrational deactivation and electronic quenching by atomic and molecular oxygen. The rate coefficients used in the analysis were those measured by Kenner and Ogryzlo [22] and the derived height profiles of the fractional vibrational populations are shown in Fig. 5.

There is some support for the validity of this vibrational relaxation model. McDade et $al.$ [28] have applied a similar model to the Herzberg I system in the terrestrial airglow and in a recent measurement of the UV nightglow Sharp [29] has obtained results in complete agreement with their calculations. However, a separate study by Witt et $al.$ [30] has suggested that the adoption of Schwartz–Slawsky–Herzfeld-type coefficients within such a model may be invalid. Unfortunately it must be noted that the problem of a "shuttle-type glow" does exist for many rocket probes and could seriously affect the measurements [31].

If the $c^1\Sigma_u^-$ state is the precursor for the other oxygen emissions and we assume that the model developed by McDade et $al.$ [27] is correct then we may attempt to understand the chemistry of these emissions. The important reactions are

$$O_2(c^1\Sigma_u^-) + O \xrightarrow{k_5} O_2{}^{**} + O \tag{5}$$

$$O_2(c^1\Sigma_u^-) + O_2 \xrightarrow{k_6} O_2{}^* + O_2 \tag{6}$$

where $O_2{}^{**}$ and $O_2{}^*$ are the other electronic states. If in the terrestrial atmosphere $k_5[O] \gg k_6[O_2]$, as suggested by the laboratory measurements [22],
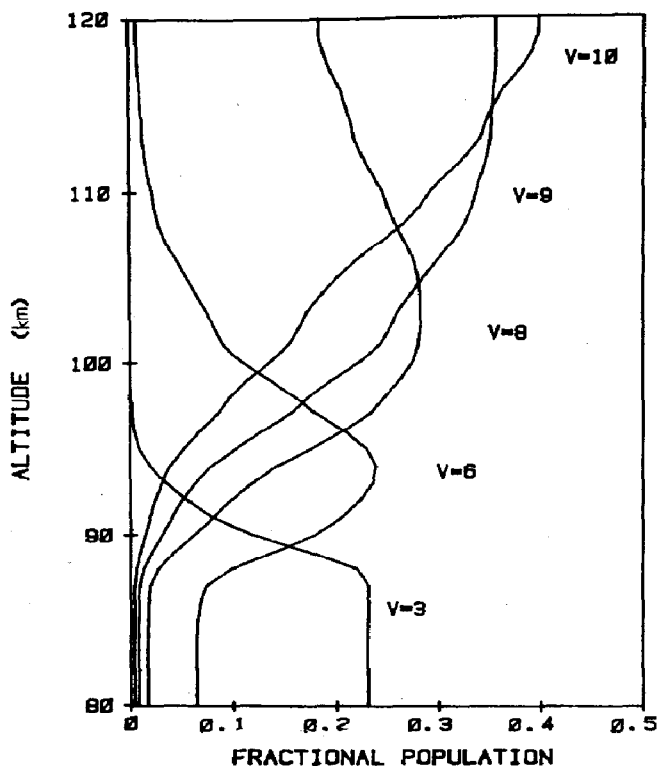
Fig. 5. Fractional populations of the various vibrational levels of $O_2(c^1\Sigma_u^-)$ in the terrestrial atmosphere.

and if we identify O_2^{**} with $O_2(a^1\Delta_g)$ then essentially all quenching of the $c^1\Sigma_u^-$ state must result in the production of $^1\Delta_g$ molecules. Thus if the $c^1\Sigma_u^-$ state is the major product of three-body recombination, reaction (1), then effectively all recombinations result in the 1.27 μm emission exactly as observed in the Venus and Earth nightglow. As the peak atomic oxygen concentrations in the upper atmospheres of both planets are approximately equal then the ratio of the Herzberg II and IR Atmospheric Band emissions on the two planets should be equal. This reaction scheme also overcomes the difficulty of the negligible rate constant for the direct formation of the $a^1\Delta_g$ state in reaction (1).

Reactions (5) and (6) may also result in the production of states other than $a^1\Delta_g$. Observations of the height profiles of the Atmospheric Bands in the terrestrial nightglow [32] have shown that this emission peaks near 93 km, even under auroral conditions, and several kilometres lower than the green line and the IR Atmospheric Bands. This would suggest that reaction (6) is the source of the $b^1\Sigma_g^+$ state. In a separate investigation of the Atmospheric Bands and the oxygen green line McDade et al. [33] have shown that the apparent efficiency for $O_2(b^1\Sigma_g^+)$ formation in the three-body recombination, reaction (1), is altitude dependent in agreement with the observations of Witt et al. [34]. This matter has also been previously considered by Greer et al. [35] who showed that this altitude dependence could be

resolved if the Atmospheric Bands were in fact excited by transfer from some precursor. Following the work of Lawton and Phelps [36] Greer *et al.* identified the precursor with the $c\,^1\Sigma_u^-$ state. This identification of reaction (6) with the Atmospheric Bands is of course in complete agreement with the Venus airglow observations. The relative absence of molecular oxygen on Venus would preclude reaction (6) from being a significant quenching loss for $c\,^1\Sigma_u^-$ molecules.

To provide a check of the proposed reaction scheme it is of value to estimate the expected Herzberg I emission in the Venus nightglow. If the $A\,^3\Sigma_u^+$ state is excited in the direct recombination of oxygen atoms, reaction (1), with the same efficiency as in the Earth's atmosphere, where the third body is molecular oxygen or nitrogen, then the calculated emission, 20 kR, must be quenched on Venus to match the observed intensity, 150 R. We estimate the required quenching coefficient for

$$O_2(A\,^3\Sigma_u^+) + CO_2 \xrightarrow{k_7} O_2 + CO_2 \qquad (7)$$

to be 5×10^{-13} cm^3 s^{-1} which is in good agreement with the laboratory value of Kenner and Ogryzlo [22] for the $v = 2$ level, 7×10^{-13} cm^3 s^{-1}; this latter value presumably includes a relaxation component.

From an analysis of the altitude profile of the Atmospheric Band emission McDade *et al.* [33] have shown that for the production of the $b\,^1\Sigma_g^+$ state the total rate coefficients for reactions (5) and (6) must be in the ratio 3:1 in the terrestrial nightglow. This ratio does not agree with the laboratory values for the quenching of any excited state of molecular oxygen, including $O_2(c\,^1\Sigma_u^-, v = 0)$, by atomic and molecular oxygen. However, this ratio is in excellent agreement with the value inferred for an unidentified precursor of $b\,^1\Sigma_g^+$ in the latest laboratory studies of Ogryzlo *et al.* [37] which suggests that vibrational excitation of the precursor must be of great importance [27].

While the analysis presented in this paper has suggested that the planetary airglow emissions can be explained in terms of energy transfer it is not without difficulty. The reaction scheme indicates that essentially all recombinations lead to the $c\,^1\Sigma_u^-$ state and that only a few per cent of recombinations result in other states. If there is an important contribution to ground state formation in reaction (1), then the atomic oxygen concentrations in planetary atmospheres would have to be significantly modified from the values accepted at present. It is this uncertainty in the ambient atmospheric concentrations that is perhaps one of the major difficulties for attempts to use planetary atmospheres as a reaction vessel for the determination of rate constants.

Acknowledgments

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