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Atmospheric hydrogen

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FOREWORD

The paper "Atmospheric hydrogen" will be published in Planetary and Space Science.

M. Nicolet.

AVANT PROPOS

L'article "Atmospheric hydrogen" sera publié dans Planetary and Space Science.

M. Nicolet.

VOORWOORD

Het artikel "Atmospheric hydrogen" zal gepubliceerd worden in Planetary and Space Science.

M. Nicolet.

VORWORT

Die Arbeit "Atmospheric hydrogen" wird in Planetary and Space Science herausgegeben werden.

M. Nicolet.

ATMOSPHERIC HYDROGEN

by

D.R. BATES and M. NICOLET

Abstract

Attention is drawn to the possibility that $H + HO_2 \rightarrow H_2 + O_2$ may be an important source of hydrogen molecules in the lower thermosphere. It is suggested that the fractional volume abundance of hydrogen atoms (free and combined) in this region is determined by, and is not very much less than, the corresponding fractional volume abundance in the stratosphere. Any hydrogen molecules in the lower thermosphere would affect the altitude distribution of hydrogen atoms and augment their rate of escape.

Résumé

L'attention est attirée sur la réaction $H + HO_2 \rightarrow H_2 + O_2$ qui peut être une importante source d'hydrogène moléculaire dans la thermosphère inférieure. Dans cette région, l'abondance volumique relative de l'hydrogène atomique (libre et combiné) est fixée par l'abondance correspondante dans la stratosphère. La présence de molécules d'hydrogène dans la thermosphère inférieure pourrait affecter la distribution verticale de l'hydrogène atomique et augmenter le taux d'échappement.

Samenvatting

De aandacht wordt gevestigd op de reaktie $H + HO_2 \rightarrow H_2 + O_2$ welke een belangrijke bron kan vormen van moleculaire waterstof in de lagere thermosfeer. In dit gebied wordt het relatief voorkomen van de atomaire waterstof (zowel vrij als gebonden) bepaald door het overeenkomstig voorkomen in de stratosfeer. De aanwezigheid van de waterstofmoleculen in de lagere thermosfeer zou de vertikale verdeling van de atomaire waterstof beïnvloeden en ten gevolge hiervan zou er een grotere ontsnapping zijn.

Zusammenfassung

Die Reaktion $H + HO_2 \rightarrow H_2 + O_2$ wird als eine mögliche Quelle für Wasserstoff Moleküle in der niedrigen Thermosphäre vorgestellt. Es wird vorgeschlagen, dass, in dieser Schichte, die relative Konzentration in Atomwasserstoff (frei und kombiniert) durch die Konzentration in der Stratosphäre fixiert sein kann. Alle Wasserstoff Moleküle, die in der niedrigen Thermosphäre vorkommen, würden die Höheverteilung des Atomwasserstoffes ändern und die Ausströmung vergrössern.

INTRODUCTION

We shall first briefly discuss the abundance of atomic hydrogen and of its compounds near the 100 km level ; and we shall then consider atmospheric hydrogen as a whole.

1. ABUNDANCE OF VARIOUS FORMS OF HYDROGEN NEAR THE 100 KM LEVEL*

1.1 Atomic hydrogen

From measurements which Purcell and Tousey[1] made on the absorption core of the solar Lyman alpha line it has been calculated[2,3] that the number density of free hydrogen atoms at 100 km level, $n(H|100\ km)$, is some $1 \times 10^7 cm^{-3}$ (which corresponds to a fractional volume abundance $f(H|100\ km)$ of about 1×10^{-6}). The associated escape flux through the thermosphere is approximately 2×10^7 atoms $cm^{-2} sec^{-1}$.

1.2 Hydroxyl and perhydroxyl

Photo-chemical equilibrium between H, OH and HO_2 is maintained in the region of the 100 km level. The main processes involved are

$$OH + O \rightarrow O_2 + H \qquad (1)$$

$$HO_2 + O \rightarrow OH + O_2 \qquad (2)$$

$$H + O_3 \rightarrow OH + O_2 \qquad (3)$$

and

$$H + O_2 + M \rightarrow HO_2 + M, \qquad M = N_2, O_2, O. \qquad (4)$$

Denoting the rate coefficient by the symbol α with the equation number as an identifying subscript we have that

$$n(OH)/n(H) = \left\{ \alpha_3 n(O_3) + \alpha_4 n(O_2) n(M) \right\} / \alpha_1 n(O) \qquad (5)$$

*In §1.1 and 1.2 we shall to a large extent be simply recapitulating, for the sake of completeness, earlier deductions of relevance.

and

$$n(HO_2)/n(H) = \alpha_4 n(O_2)n(M)/\alpha_2 n(O). \quad (6)$$

From the values of the rate coefficients recommended by Kaufman[4] we hence find

$$n(OH|100\ km) \text{ and } n(HO_2|100\ km) \ll n(H|100\ km) \quad (7)$$

1.3 Methane and water vapour

Any methane in the thermosphere is subject to rapid photodissociation by Lyman alpha, the contribution of this line to the reciprocal life, $J(CH_4)$, being about $5.5 \times 10^{-6} sec^{-1}$ at zero optical depth[5]. Moreover, even in the stratosphere and mesosphere methane is attacked by atomic oxygen[6] through

$$CH_4 + O \rightarrow CH_2 + H_2O \quad (8)$$

which has a rate coefficient

$$\alpha_8 = 6 \times 10^{-13}\ T^{1/2} \exp(-3100/T) \quad (9)$$

(deduced from experimental data obtained by Wong and Potter[7]). All significant sources of the gas are on the surface of the Earth. The diffusive upward current of CH_4 molecules is given approximately by

$$F(CH_4) = 1 \times 10^{13} f(CH_4)\left[\left\{\frac{1}{r(CH_4)} - 0.5\right\} + \Lambda\left\{\frac{1}{r(CH_4)} - 1.0\right\}\right] cm^{-2} sec^{-1} \quad (10)$$

where

$$f(CH_4) = n(CH_4)/n(M) \quad (11)$$

is the local fractional volume abundance, where

$$r(CH_4) = H(CH_4)/H(M) \quad (12)$$

the H's being the local scale heights indicated, and where Λ is the ratio of the eddy to the molecular diffusion coefficient. If this current is to replace the methane being destroyed chemically it must be of magnitude

$$F_D(CH_4) \simeq \frac{1}{2}\alpha_8 n_S(O) n(CH_4) H(CH_4) \quad (13)$$

in which $n_S(O)$ is the equilibrium number density of oxygen atoms during the sunlit hours. Combining (10) and (13) we obtain

$$\frac{1}{r(CH_4)}\left[\left\{\frac{1}{r(CH_4)} - 0{\cdot}5\right\} + \Lambda\left\{\frac{1}{r(CH_4)} - 1{\cdot}0\right\}\right] = K \qquad (14)$$

with

$$K = 5 \times 10^{-14}\alpha_8 n_S(O)n(M)H(M). \qquad (15)$$

Inspection of Table I shows that condition (14) is not readily met unless $r(CH_4)$ is considerably less than unity in the upper stratosphere (which of course implies that the fractional volume abundance $f(CH_4)$ decreases with altitude in this region). For example if $r(CH_4)$ were 0·9 at 40 km and 50 km, condition(14) would only be satisfied if the corresponding values of Λ were $2{\cdot}7 \times 10^4$ and $1{\cdot}8 \times 10^4$ respectively ; and these values seem rather high since they imply an eddy diffusion coefficient of more than 10^6 $cm^2 sec^1$ in the upper stratosphere.

Large scale motions of the atmosphere may be more effective than eddy diffusion at maintaining a mixing distribution[8]. However, the characteristic times associated with these motions are probably longer than the estimated life time

$$\tau(CH_4) = 2/\alpha_8 n_S(O) \qquad (16)$$

of a methane molecule towards chemical destruction(cf. Table I).

Unless the values adopted for α_8 and $n_S(O)$ are much too high it seems possible from the two preceding paragraphs that $f(CH_4)$ falls off through the upper stratosphere ; and in any event it is certain that it falls off at greater altitudes. Since $f(CH_4)$ is only 1.5×10^{-6} in the troposphere we may safely assume that

$$n(CH_4) \mid 100 \text{ km}) \ll n(H \mid 100 \text{ km}) \qquad (17)$$

Table I. Parameters relating to the disappearance of methane in the stratosphere

Altitude z(km)	30	40	50	Ref.
T(°K)	235	268	274	(5)
H(M)(cm)	7.0×10^{5}	8.0×10^{5}	8.2×10^{5}	(5)
n(M)(cm^{-3})	3.7×10^{17}	8.5×10^{16}	2.4×10^{16}	(5)
n(O)(cm^{-3})	1×10^{9}	1×10^{10}	2×10^{10}	(11)
α_8($cm^3 sec^{-1}$)	1.7×10^{-17}	1.0×10^{-16}	1.2×10^{-16}	formula (9)
K	2.2×10^{2}	3.4×10^{3}	2.3×10^{3}	formula (15)
Λ if r(CH_4)0.5	1.1×10^{2}	1.7×10^{3}	1.2×10^{3}	formula (14)
Λ if r(CH_4)0.9	1.8×10^{3}	2.7×10^{4}	1.8×10^{4}	formula (14)
τ(CH_4)(sec)	1×10^{8}	2×10^{6}	8×10^{5}	formula (10)

Each CH_4 molecule broken down by process (8) ultimately yields two H_2O molecules. There is no sufficient photo-chemical sink of water vapour in the region concerned. Consequently water vapour must flow downwards through the stratosphere.

Photo-dissociation of water vapour occur in the thermosphere. The reciprocal life of an H_2O molecule bathed in solar radiation, $J(H_2O)$, is not known accurately but the contribution to it from the continuum has been estimated[9] to be $1 \times 10^{-5} sec^{-1}$ at zero optical depth and that from Lyman alpha has been estimated[5] to be at least $1 \times 10^{-6} sec^{-1}$. In view of (7) it is clear that reformation of water vapour by

$$OH + OH \rightarrow H_2O + O \tag{18}$$

and

$$OH + HO_2 \rightarrow H_2O + O_2 \tag{19}$$

may be disregarded near the 100 km level even though both processes are very rapid (cf. review by Kaufman[4]). The diffusive upward current

$$F(H_2O) \simeq 1 \times 10^{13} f(H_2O)\left[\left\{\frac{1}{r(H_2O)} - 0{\cdot}6\right\} + \Lambda \left\{\frac{1}{r(H_2O)} - 1{\cdot}0\right\}\right] cm^{-2} sec^{-1} \tag{20}$$

is much more important. By an argument similar to that used in connection with the distribution of methane it may be seen that $r(H_2O)$ must be less than unity above the mesopause. Accepting that $f(H_2O)$ falls off sharply through the thermosphere and that it does not exceed about 3×10^{-6} in the upper stratosphere[10] we see that

$$n(H_2O|100\ km) \ll n(H|100\ km). \tag{21}$$

1.4 Molecular hydrogen

Though the photo-dissociation of water vapour proceeds mainly through

$$H_2O + h\nu \rightarrow H + OH \tag{22}$$

it may proceed partly through[12]

$$H_2O + h\nu \rightarrow H_2 + O \tag{23}$$

Another, probably much more important, source of molecular hydrogen is

$$H + HO_2 \rightarrow H_2 + O_2. \tag{24}$$

The yield from this must be very great indeed. Kaufman[4] estimates that the rate coefficient α_{24} exceeds 3×10^{-12} cm^3 sec^{-1} at 300°K and that the activation is not more than 2 kcal.

The principal sink of molecular hydrogen is

$$H_2 + O \rightarrow OH + H. \tag{25}$$

Measurements by Clyne and Thrush[13] over a range of temperature T from 409 to 733°K indicate that

$$\alpha_{25} = 6 \times 10^{-13}\ T^{1/2}\ \exp(-4450/T). \qquad (26)$$

According to this formula α_{25} is 1×10^{-21} cm^3 sec^{-1} at 200°K, is 3×10^{-18} cm^3 sec^{-1} at 300°K, is 8×10^{-15} cm^3 sec^{-1} at 600°K and is 5×10^{-13} cm^3 sec^{-1} at 1200 °K.

Accepting for the moment that the rate coefficients are as cited we conclude that more molecular hydrogen is produced near the mesopause than is destroyed there ; that a layer of the gas is formed conceivably with $n(H_2 | 100\ km)$ well above $n(H | 100\ km)$; and that molecular hydrogen from this layer flows upwards into the higher thermosphere where process (25) followed by process (1) converts it into atomic hydrogen. The presence of molecular hydrogen would tend to increase the effective scale height of the atomic hydrogen in the lower thermosphere and would tend to make its rate of escape faster.

It is not yet possible to make a reliable estimate of the density of the molecular hydrogen layer by direct photo-chemical calculations. Great uncertainty arises from the rate coefficients. The values cited may not be the appropriate values. Thus process (23) and probably process (24) yield mainly vibrationally excited H_2 molecules. Such molecules are not readily deactivated and would be expected to react more rapidly with O atoms than do normal H_2 molecules. Laboratory studies are needed.

2. DISTRIBUTION OF HYDROGEN THROUGH THE ATMOSPHERE

The amounts of hydrogen present in the stratosphere as H_2O and CH_4 and perhaps also the amount present as H_2 are controlled mainly by phenomena on the Earth's surface and (in the case of H_2O)

by conditions near the tropopause. They determine the hydrogen content of the mesosphere and thermosphere. The distribution of the element must be such that the mean upward flow of free and combined atoms is independent of the altitude z and is equal to the mean escape flux. Though the relative amounts of the various hydrides change very much with altitude, the fractional volume abundance of all atoms of the element $f(H_\Sigma|z)$ would therefore be expected to remain approximately constant until near the top of the homosphere where it may fall because the diffusion coefficients of H and H_2 are greater than those of the other species concerned.
If we accept the current view that the stratosphere is rather dry and ignore the possibility of molecular hydrogen near the 100 km level, we find (cf. Table 2) that the fall just mentioned is by a factor of 13 which seems rather large.* We find also that the upward flux due to molecular diffusion alone is about 8×10^7 atoms $cm^{-2}sec^{-1}$ and should $f(H_\Sigma|z)$ be a decreasing function of z eddy diffusion and large scale motions of the atmosphere would tend to enhance the upward flux. In contrast, the calculated escape flux (again ignoring molecular hydrogen) is only about 2×10^7 atoms $cm^{-2}sec^{-1}$.

Table II. Fractional volume abundance $f(H_\Sigma)$ of hydrogen atoms free or combined

Region	Atom or molecule	Contribution to $f(H_\Sigma)$	Ref.
Stratosphere	CH_4	6×10^{-6}	(5)
	H_2O	6×10^{-6}	(10)
	H_2	1×10^{-6}	(5)
	total	13×10^{-6}	-
100 km level	H	1×10^{-6}	(2),(3)
	H_2	unknown	§1.4
	others	negligible	§1.2 and §1.3

* A much larger factor arises with the moist stratosphere favoured until recently.

The apparent discrepancies are not very serious in view of the uncertainties that exist. They would disappear, if $n(H_2 | 100\ km)$ were about $3 \times 10^7 cm^{-3}$. A very much larger number density would seem to be excluded unless the stratosphere is very much more humid than we have assumed. As mentioned in §1.4 reliable estimate of $n(H_2 | 100\ km)$ cannot at present be made photo-chemically. A direct measurement would be very interesting.

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