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INVESTIGATIONS OF CHEMICAL PROCESSES OF $O^+ + H_2$ ($V = 0, J = 0$) REACTION USING THERMAL VARIATION IN THE IONOSPHERIC REGIONS

by

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In this paper the chemical processes of the $O^+ + H_2 \rightarrow OH^+ + H$ reactive reaction (exothermic) investigated with the thermal variation in the ionosphere by combining a gas kinetic theory model. Collision energy, reaction rate constant and total cross-sections as a function of ionospheric altitude and temperature are calculated. Also, all the other parameters related with the ionosphere are calculated for the $38.40^0N, 39.12^0E$ co-ordinates and year, day, and time taken as 2009, equinox and solstice, local time (12:00), respectively. It was found that the collision energy, reaction rate constant and cross-section values are decreasing with the increment of the ionospheric height and temperature. The total collision number takes the maximum values at lower ionosphere where the temperature is smallest and decreases with increasing height in upper ionosphere. The mean free path was found to close to each other and decay to zero nearly at 150 km for all months. It is estimated that the amount of energy which is released during the reaction can cause deterioration at the high level.

Key words: *ionosphere, chemical processes, exothermic reaction,
        gas kinetic theory*

Introduction

The Earths ionosphere is located at the height of 60-1000 km containing free electrons and ions [1]. Changes in the ionospheric system are crucial importance on communications, navigation and the exploration of the near Earth space. Thus the study of the ionospheric phenomena has become an important field of present days research [2, 3].

The presence of ionosphere is a consequence of the absorption of photo-ionizing radiation from the Sun. The ionosphere is composed of different regions [4]. Solar radiation leads to ion-electron production and heating via photo-electron energy degradation, with EUV wavelengths dominating in the lower thermosphere (*E* and *F*1 regions) and UV and X-ray wavelengths dominating in the mesosphere (*D* region). These processes occur over the entire sunlit side of the Earth. On the night side, resonantly scattered solar radiation and starlight are important sources of ionization for the *E* region [5, 6].

The ionosphere has a very complex structure due to its physical and chemical composition. The description of the photo-chemical processes and the ionosphere chemical kinetics in the theoretical model, with the account of chemical composition of the neutral particles and

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ions considered, includes the processes of photo-ionization, photo-dissociation, dissociative recombination, radiative recombination, collision mechanism, *etc.* [7, 8].

The role of O^+ and H_2 particles in the Earths ionosphere chemistry is very important according to density changes in the upper and lower ionosphere so many researchers have done studies on these particles. In these studies, theoretical models have been used to investigate the effects of artificially injected H_2 gas on plasma densities in the ionospheric F region and the overlying protonosphere. It has been found that the release of modest amount H_2 gas can produce significant perturbations in the ionosphere and protonosphere [9].

Another model provides a description of active experiments in the ionosphere involving injections of gases such as H_2, H_2O, and CO_2. However, in this work that performed generally for F region, the range validity of the use of analytic block is confined to the case of injection of a small mass of the gas at 200-250 km heights, at which strong shock waves are not produced on the separation boundary [10].

The H^+ and O^+-based studies made to answer the question of the source of observed annual variations in plasmaspheric density. It has been observed that the modeled plasmaspheric density in June is greater than that in December [11].

Also the effect on ionosphere of O^+ and H_2 was separately investigated by them and no attempt was made the effects on the earth ionosphere by combining kinetic theory based models with the cross-sections in the 0.02-0.1 eV collision energy range and state-to-state rate constants values for the $O^+ + H_2 \rightarrow OH^+ + H$ reaction that have been obtained using a quantum wave packet method.

In this study, total reaction rate constants and cross-sections obtained for the reaction [12] previously;

$$O^+ + H_2 \rightarrow OH^+ + H$$
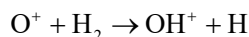
and used to investigate the effects in the ionosphere.

Methodology

The theoretical analysis of ionosphere chemistry modification must be carried out due to a large number of factors, such as the great increases in the energy regime of the earth ionosphere system, the change in density and temperature during the collision and the abrupt disconnections. Also, several statistical quantities such as the mean free path, collision frequency, potential energy barrier and total number of reactive collisions must be taken in to account and so shall find quantitative relationships between statistical quantities characterizing molecular collisions (such as mean free path, *etc.*) and basic physical properties of the gas (such as concentration, temperature, height, *etc.*). These terms are closely related to each other and to other fundamental molecular quantities.

Reactive collision processes

Collisions are categorized into three types: elastic, inelastic, and reactive. Reactive collisions lie at the heart of the upper atmosphere chemistry. This collision type involves the production of new species, such as the reactions $O^+ + H_2 \rightarrow OH^+ + H$ and $NO^+ + e \rightarrow N + O$. Many reactive collisions occur in the ionosphere and the variety of important reactive collisions in ionospheric processes is large.

The complexity of reactive collisions is a challenge to computations as quantum mechanical of the cross-sections. An important difference in applying wave theory to reactive scattering is that the particles themselves are no longer preserved.

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The partial cross-section is obtained for total angular momentum number value and any initial quantum state (v, j):

$$\sigma_{vj}^{J}(E) = \frac{1}{2j+1}\left[P_{vj}^{JK=0}(E) + 2\sum_{K=1}^{K_{max}} P_{vj}^{JK}(E) \right] \tag{1}$$

where, P_{vj}^{JK} is the reaction probability and E – the energy.

Since the helicity coefficient, K, is zero at $j = 0$, the partial cross-section can be calculated from direct reaction probabilities for any quantum state. The total cross-section was calculated by summing partial cross-section over all j values:

$$\sigma_{vj}(E) = \frac{\pi}{k_{vj}^2} \sum_{J=0}^{J_{max}} (2J+1)\sigma_{vj}^{J}(E) \tag{2}$$

At any temperature, the formation rate of a chemical reaction is expressed as the reaction rate constant. According to the Maxwell-Boltzmann distribution, the thermal rate constant is obtained by combining the total cross-sections over all velocity vectors (or energies):

$$k(T) = \int E\sigma(E)f(E,T)\,\mathrm{d}E \tag{3}$$

where $f(E, T)$ is the Maxwell-Boltzmann distribution.

In any initial quantum state (v, j), the reaction rate constant for A + BC reactive scattering is given:

$$k_{vj}(T) = \sqrt{\frac{8k_BT}{\pi\mu^*}}(k_BT)^2 \int E \exp\left(-\frac{E}{k_BT}\right)\sigma_{vj}(E)\,\mathrm{d}E \tag{4}$$

where E is the collision energy, μ^* – the reduced mass, k_B – the Boltzmann coefficient, and σ_{vj} – total cross-section [13].

Total collision number model

A chemical reaction is explained as a simple collision with the following relative velocity dependent cross-section:

$$\sigma_{vj}(g) = \sigma_0 H(g - g_0) \tag{5}$$

where $H(g)$ is the Heaviside step function and the velocity threshold and g_0 – the velocity of relative motion which is sufficient to overcome the potential energy barrier:

$$g_0 = \sqrt{\frac{2U_0}{\mu^*}} \implies U_0 = \frac{4k_BT\mu^*}{\pi m} \tag{6}$$

where U_0 is the barrier potential energy, T – the temperature, and m – the particle mass, respectively.

The Z_{12} which is the number of reactive collisions per unit volume can be calculated. This can be done by substituting the cross-section of the chemical reaction [14]:

$$Z_{12} = 4\pi K_{12}\sigma_{vj}n_1n_2\sqrt{\left(\frac{\mu^*}{2\pi k_BT}\right)^3} \int_{g_0}^{\infty} g^3 \exp\left(-\frac{\mu^* g^2}{2k_BT}\right)\mathrm{d}g \tag{7}$$

where n_1 and n_2 are the particle densities. This equation is valid for both the forward and the reverse reaction. The main difference between this two reactions is that the forward reaction

involves the collision of different (unlike) molecules, therefore $K_{12} = 1$, while the reverse reaction involves the collision of two like molecules, therefore $K_{12} = 1/2$.

The integral in eq. (7) can be readily carried out to yield:

$$Z_{12} = K_{12} \sigma_{vj} n_1 n_2 \sqrt{\frac{8 k_B T}{\pi \mu^*}} \exp\left(-\frac{\mu^* g_0^2}{2 k_B T}\right)\left(1 + \frac{\mu^* g_0^2}{2 k_B T}\right) \tag{8}$$

The threshold velocity can be expressed in terms of the barrier potential energy, U_0:

$$Z_{12} = K_{12} \sigma_{vj} n_1 n_2 \sqrt{\overline{v_1^2} + \overline{v_1^2}} \exp\left(-\frac{U_0}{k_B T}\right)\left(1 + \frac{U_0}{k_B T}\right) \tag{9}$$

Mean free path model

The free path is the distance traveled by a molecule between two consecutive collisions. The mean free path is the average distance between two consecutive collisions of a single molecule. The ratio of the mean free path and mean free time is the average particle speed, therefore mean free path directly obtained from:

$$\lambda = \frac{1}{n \sigma_{vj}} \tag{10}$$

This result shows that the mean free path of the molecules depends only on the gas density and the cross-section of the molecules and is independent of the average molecular speed [14].

Results

The reaction dynamics of the $O^+ + H_2 \rightarrow OH^+ + H$ reactive reaction have been investigated in this study. Ionospheric temperature and density data are obtained from International Reference Ionosphere website [15, 16]. All parameters are calculated for the 38.40^0N, 39.12^0E co-ordinates and year, day and time are taken as 2009, equinox and solstice, local time (12:00), respectively.

The O^+ is active particle and H_2 molecule is stationary in this reaction. Also, we need to match the reaction formation temperature with ionospheric temperature. The variation of O^+ and H_2 density and ion temperature are given in figs. 1-3. The O^+ density take maximum value at about 250-300 km for graphically same all the equinox and solstice days. The H_2 density
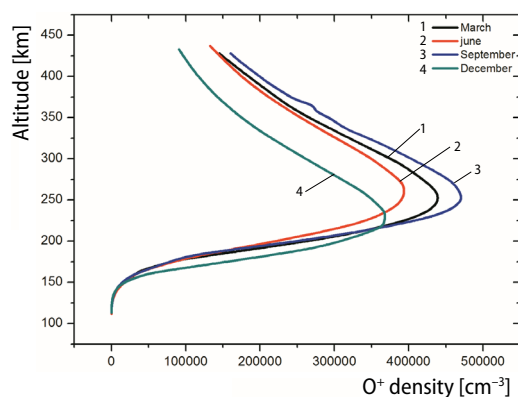

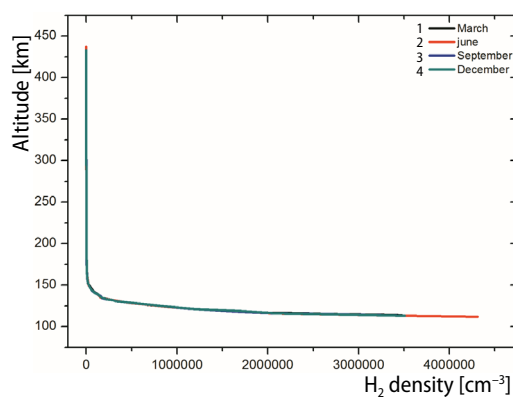**Figure 1. Variation of O^+ density with the ionospheric height**

Figure 2. Variation of H_2 density with the ionospheric height [5] (*for color image see journal web site*)

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is found much concentrated at the subionosphere. But ion temperature values are nearly close to each other and also increase with height for all days.

The variation of rate constant and cross-section of this reaction in the ionosphere due to the previous assumptions are shown in figs. 4 and 5, respectively. The rate constant and cross-section values display the same behavior in the ionosphere. They take the biggest values in lower ionosphere and begin decrease fastly to near 150 km and continue very slowly to high altitudes.

We have calculated total collision number of two particles, $Z_{O^+H_2}$, and mean free path by using the eqs. (9) and (10), respectively. The variations of these calculations in the ionosphere are given in figs. 6 and 7.
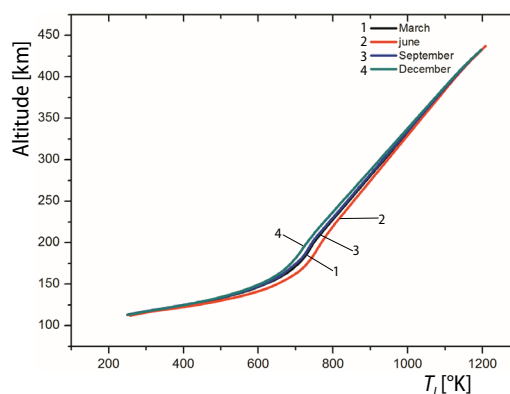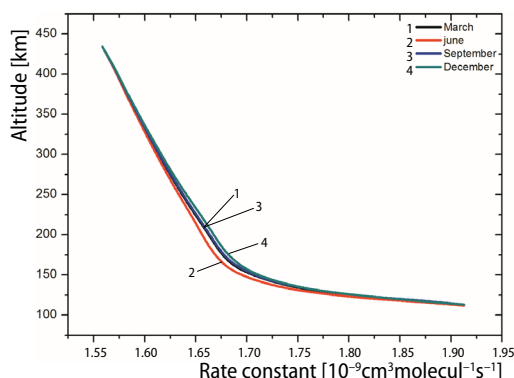

Figure 3. Ion temperature change in the ionosphere
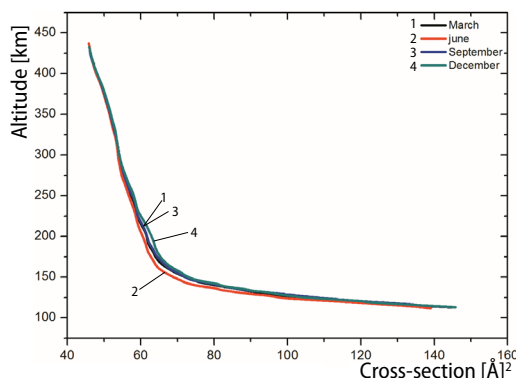

Figure 4. Rate constant variation with altitude

Figure 5. Cross-section change in the ionosphere
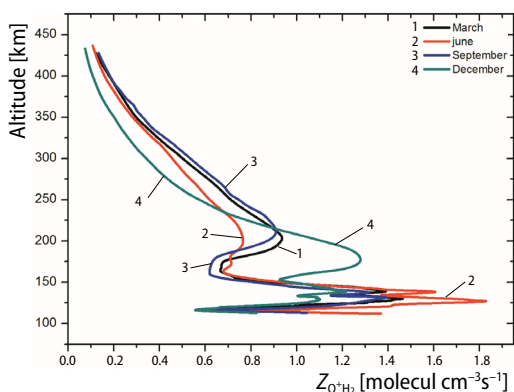

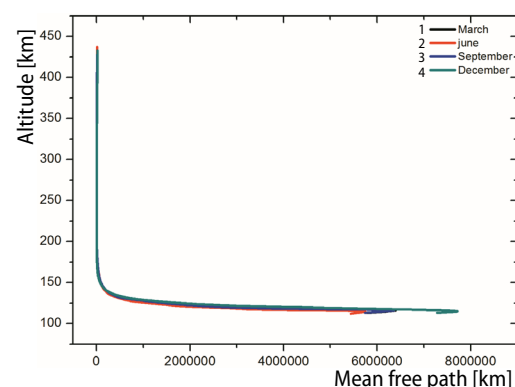**Figure 6. Variation of the total collision number of the reaction in the ionosphere**

Figure 7. Mean free path change in the ionosphere (*for color image see journal web site*)

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Conclusions

In this paper we have analyzed $O^+ + H_2 \rightarrow OH^+ + H$ reactive reaction with combining quantum mechanical processes with ionospheric conditions.

The reaction rate constant and cross-section values which have obtained from quantum wave packet method are associated to the ionosphere. Both of them are decreasing with height and there is not a big change between the equinox and solstice days.

The $Z_{O^+H_2}$ take the maximum values at the lower ionosphere and decrease with increasing height in upper ionosphere. The reason of the maxima of the total collision number at the subionosphere is the density of the H₂ molecule is too much at the lower ionosphere and decreasing dramatically with the ionospheric height. Also, O⁺ ion density is very small at these altitudes. Collision processes in June are greater than December expect between 150-220 km, as defined Guiter *et al.* [11]. Because, there is no any regular increase or decrease according to reaction cross-section, rate constant and ionospheric conditions. The maximum ionospheric perturbation scale height in four months is June with altitude between 113 and 260 km, while the minimum perturbation distance is December with altitude between 113 and 174 km. The ionosphere is exposed to sunlight longer in June than in December so that the dynamic processes for present reaction formed as intense in June.

The distance for the realization of reaction (mean free path) is much closed to each other and goes to zero nearly at 150 km for all months. The most appropriate collision interval is occurred at 3681 km in September.

Consequently, H₂ is most abundant particle in the universe and is formally found in molecular structure in significant quantities in the near-earth environment. So, it is an important constituent in the lower Earth ionosphere. The effect of H₂ concentration on the calculations of total collision number for the lower ionosphere is greater than O⁺ concentration, while the effect of O⁺ ion density for the upper ionosphere is greater than H₂ density.

Acknowledgment

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