Spectroscopic diagnostics of reaction between ozone and molecular hydrogen in gaseous mixtures and in the atmosphere

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We present calculations of time behavior of the H_2O concentration in reaction between the ozone and molecular hydrogen in a three-component mixture with nitrogen as a buffer gas. It is shown that at the reaction constant equal to $3 \cdot 10^{13} \times \exp(-3000/T)$ $cm^3/(mol \cdot s)$ and proportion of partial pressures in the three-component mixture $H_2:O_3:N_2 = 1:1:10000$ at the total pressure being 1 atm, the reaction time increases to 1.5 s and the yield of H_2O molecules reaches $2 \cdot 10^{15}$ cm^{-3}. We propose to use the isotopic ozone molecule $^{18}O_3$ in the experiment. This would allow a reliable recording of $H_2^{18}O$ to be performed with any spectrometer having sensitivity no less than 10^{-6} cm^{-1}.

Introduction

The effect of molecular hydrogen, that is being released from the lithosphere, on the tropospheric and stratospheric ozone has been analyzed in Refs. 1 and 2. The conclusions the authors of these works arrived at occurred to be quite opposite.

It was hypothesized in Ref.1 that the molecular hydrogen emitted by the lithosphere may result in some decrease of the ozone concentration due to the gas-phase reaction

$$H_2 + O_3 + M \rightarrow H_2O + O_2 + M, \qquad (1)$$
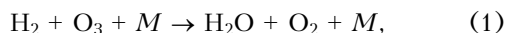
that can yield an excess concentration of water vapor at the heights of the ozone layer location. (Here M is some neutral molecule, N_2, for example). The water vapor causes formation of clouds in the stratosphere, particularly, the polar stratospheric clouds (PSC).

The model calculations[2] have shown that the generation of molecular hydrogen and its emission into top atmosphere results in its spontaneous inflammation at the heights about 120 km with its almost total burn out at the heights between 165 and 200 km. In the process of the hydrogen burning, the water vapor is formed, which drops down and condenses at the level of ~ 85 km into ice pieces forming the noctilucent clouds. Burning of the molecular hydrogen produces atomic oxygen that reacts with the molecular oxygen of the atmosphere thus yielding the ozone. The power of this source of the ozone is proportional to the hydrogen concentration in the ground layer, and this very source, is prevailing in the opinion of the authors of Ref. 2.

In the system of chain reactions considered by the authors, as in Ref. 1, the reaction of the ozone sink is taken into account

$$O_3 + H_2 \rightarrow H_2O + O_2 + 92.2 \text{ kcal}, \qquad (2)$$
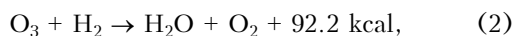
where the rate constant used is equal to that of the reaction

$$O_3 + O \rightarrow O_2 + O_2 + 94.1 \text{ kcal}. \qquad (3)$$
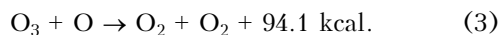
The authors of Ref. 2 reason that these constants may have close values due to similarity of the reactions and practically equal heat release.

Taking into consideration the importance of reaction (2) both for validating the hypothesis discussed in Ref. 1 and for simulating the chain of reactions from Ref. 2, the problem of finding its constant becomes very urgent.

In this paper we present some estimates regarding the possibility of measuring constants of this reaction. We also propose a measurement technique and arrangement of the experiment for achieving this task based on currently available methods of molecular spectroscopy.

Model mixture

We have validated the efficiency of the absorption spectroscopic methods using the three-component mixture of $O_3 + H_2 + N_2$ as a model one at equal proportions of O_3 and H_2, the concentrations of which were much less than those of the buffer gas N_2.

To reliably detect the H_2O molecules, appearing as a result of reactions of (1) or (2) type, it is worth using the isotopic molecule $^{18}O_3$. In this case, the measurements will not be affected by the $H_2^{16}O$ emission, adsorbed on the inner surfaces of the absorption cells, and the $H_2^{16}O$ vapor which is always present as a small admixture inside the high pressure bottles with N_2 or other buffer gases.

To estimate the characteristic rate of the reaction between H_2 and O_3 in the three-component gas mixture, we have calculated the time behavior of the H_2O concentration with the reaction constant k (2) used by the authors of Ref. 2 in their simulation, i.e., $k = 3 \cdot 10^{13} \exp(-3000/T)$ $cm^3/(mol \cdot s)$, where T is the gas temperature. At $C_{O_3} = C_{H_2}$, the change of concentration of each gas (O_3, for example) can be described[3] by the equation

$$\frac{dC_{O_3}}{dt} = - k \, C_{O_3}^2 , \qquad (4)$$

and the increase in the H_2O concentration (the product of the reaction) — by

$$C_{H_2O}(t) = C_{O_3}^0 \, (ktC_{O_3}^0)/(ktC_{O_3}^0 + 1), \qquad (5)$$

where $C_{O_3}^0 = C_{O_3}(t = 0)$.

In the binary mixture of O_3:H_2 at $T = 293$ K and partial pressure of each gas of 10 Torr, already in $t = 10$ ms the initial products have reacted almost completely. The concentration of H_2O molecules that appear as the reaction product reaches $\sim 3 \cdot 10^{17}$ cm^{-3} (Fig. 1a).
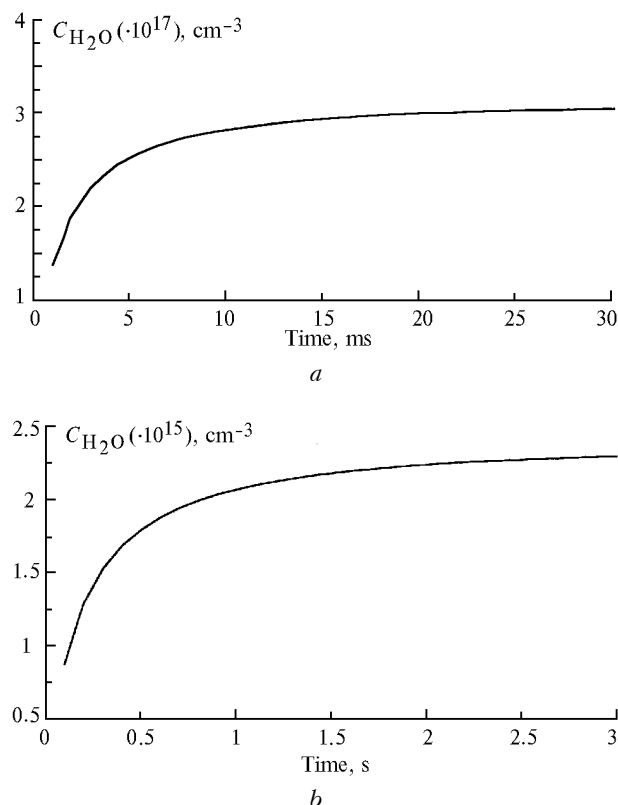

a

b

Fig. 1. Kinetics of the increase of the H_2O molecules concentration: (*a*) in a binary mixture of O_2:H_2 (1:1) at the total pressure of 20 Torr; (*b*) in a three-component mixture of O_3:H_2:N_2 (1:1:10000) at the total pressure of 760 Torr.

In the case of small abundance of H_2 and O_3 in the neutral buffer gas, for example in nitrogen, the time of the reaction increases. Figure 1*b* demonstrates the H_2O concentration growth in the above mixture at the given proportion between its components and 1 atm pressure. The time, required for complete termination of the reaction, increases to 1.5 s, and the concentration of molecules by this moment reaches $2 \cdot 10^{15}$ cm^{-3}. This time is insufficient for the processes of interaction between ozone and surface to change noticeably its concentration (Ref. 4). Therefore their influence on the reaction process may be neglected.

As seen from Fig. 1*b*, when recording the time of the H_2O kinetics in the three-component mixture with small concentrations of H_2 and O_3 relative to the buffer gas concentration, it is possible to refine the value of the constant of the reaction between the H_2 and O_3 molecules. It is profitable to conduct measurements within the time interval from 0 to some seconds. The typical concentration value of the generated H_2O vapor is $\sim 10^{15}$ cm^{-3}.

Characteristics of the spectrum

To choose the absorption spectroscopy method, appropriate for measuring the time behavior of the $H_2^{18}O$ concentration, we estimate the typical values of the $H_2^{18}O$ absorption coefficients in various spectral ranges at the concentration of water vapor molecules in the air of 10^{15} cm^{-3} and the air pressure of 1 atm.
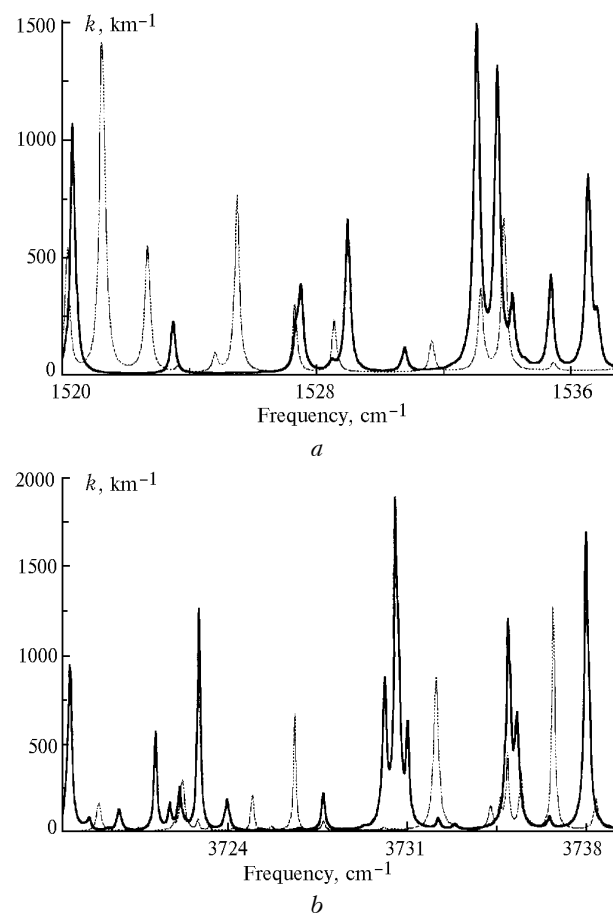

a

b

Fig. 2. Absorption spectra of $H_2^{18}O$ (solid line) and $H_2^{16}O$ (dashed line) synthesized by the data from HITRAN—96 atlas at air pressure of 1 atm and partial pressure of H_2O molecules of 10^{-3} atm.

For the most intense $H_2^{18}O$ band 010, typical value of intensity of individual vibrational-rotational lines near the band center is ~ 3 cm^{-2}·atm^{-1} (Ref. 5). At the same time, for the pressure $p_{H_2O} \sim 4 \cdot 10^{-5}$ atm

and line halfwidth ~ 0.1 cm^{-1}, the absorption coefficient χ at the line center is 10^{-3} cm^{-1}. For the bands of 001 and 100 type, the absorption coefficient is 1−2 orders of magnitude lower, i.e. at the same concentration of $H_2^{18}O$ it is ~ 10^{-5} cm^{-1}. Figures 2a and b present the fragments of the absorption spectrum for the molecules $H_2^{16}O$ and $H_2^{18}O$ in the 010 and 001 bands. These figures show a possibility of isolating the $H_2^{18}O$ line, which practically does not overlap with the absorption lines of fundamental isotope in both of the spectral ranges.

Conclusion

The above estimates show that any absorption spectrometer having sensitivity no less than 10^{-6} cm^{-1} capable of making measurements in the time interval 1 to 3 s (for the mixture $H_2:^{18}O_3:N_2 = 1:1:10000$) at a rate of 5 to 10 Hz can be used for recording the kinetics of the process of the molecules $H_2^{18}O$ formation in the above mentioned mixture. In particular, one may use a diode laser, tuned to the frequency of the $H_2^{18}O$ absorption line, with the absorbing cell (Ref. 6) or photoacoustic detector (Ref. 7).

To record the final result of the reaction (1), i.e., to determine the $H_2^{18}O$ equilibrium concentration, a Fourier−spectrometer can be used (described, for example, in Ref. 4), which allows one to record simultaneously the absorption spectrum of the initial component $^{18}O_3$ and the spectrum of the generated

$H_2^{18}O$. But the laser spectrometer with a cw or pulse-periodic laser and an absorbing cell of small volume, in which the control over the gas composition and temperature is more simple, is preferable.

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