Influence of molecular hydrogen on concentration of ozone in their binary mixture

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Experiments on diagnostics of $H_2{}^{18}O$ generated in the gas-phase reaction between molecular hydrogen and $^{18}O_3$ were conducted using a precision IR Fourier transform spectrometer. It was found that if the initial partial pressure of the gases is 1 Torr, $H_2{}^{18}O$ molecules are generated in the binary mixture $H_2 + {}^{18}O_3$ at a rate of 0.06 mTorr per hour.

Introduction

The influence of molecular hydrogen produced in the lithosphere on tropospheric and stratospheric ozone was considered in Refs. 1 and 2.

The hypothesis that molecular hydrogen can cause the decrease of the ozone concentration via the gas-phase reaction

$$H_2 + O_3 + M \rightarrow H_2O + O_2 + M, \qquad (1)$$

where M is a neutral molecule, e.g., N_2, was discussed in Ref. 1.

As a result, the excess concentration of water vapor is generated inside the ozone layer. This favors the formation of clouds in the stratosphere, in particular, polar stratospheric clouds.

In model calculations,[2] it was shown that transport of molecular hydrogen into the upper atmosphere leads to its spontaneous ignition at the altitude ~ 120 km and following, almost complete, burning-out in the altitude range from 165 to 200 km. At hydrogen burning, H_2O molecules and atomic oxygen are produced. Then, water molecules condense in the layer at the altitude about 85 km forming ice crystals that, in their turn, form noctilucent clouds. Atomic oxygen reacts with the atmospheric O_2 thus yielding O_3.

The productivity of this source of O_3, in Nikolaev and Fomin[2] opinion is proportional to the concentration of hydrogen near the ground. Thus, the conclusions made in Ref. 1 on the negative effect of lithospheric hydrogen on the content of ozone in the atmosphere do contradict the conclusions by Nikolaev and Fomin.[2]

The system of chain reactions considered in Ref. 2, as well as that in Ref. 1, includes the reaction of ozone destruction

$$O_3 + H_2 \rightarrow H_2O + O_2 + 92.2 \text{ kcal}. \qquad (2)$$

The rate of this reaction is unknown, and Nikolaev and Fomin[2] in their model calculations use the constant of the decay rate for the O_3 molecule at collision with the atomic oxygen:

$$O_3 + O \rightarrow O_2 + O_2 + 94.1 \text{ kcal}, \qquad (3)$$

assuming that the constants in Eqs. (2) and (3) are close because the heat efficiencies of the reactions are close.

For detailed justification of the conclusions drawn in Refs. 1 and 2, it seems to be worth studying experimentally the kinetics of formation of H_2O in the binary mixture $H_2 + O_3$ or in the mixture $H_2 + O_3 + M$.

The rate of the increase of concentration of H_2O molecules was estimated in Ref. 3 based on the assumption that the constant of reaction of H_2 with O_3 is the same as in Ref. 2. The estimates showed that in the mixture O_3:H_2:N_2 (1:1:10000) at the total pressure of 760 Torr the concentration of H_2O achieves ~ 10^{15} cm^{-3} already in 3 s after the beginning of the interaction between H_2 and O_3. To monitor H_2O formation in the mixture containing H_2 and O_3 at the partial pressure of 1 Torr, any absorption spectrometer with the sensitivity to the absorption coefficient higher than 10^{-6} cm^{-1} can be used.

The aim of this paper is to study the H_2O concentration in the mixture of H_2 and O_3 with an IR Fourier transform spectrometer.

Experimental technique and instrumentation

The experiments on detection of H_2O absorption spectra in the mixture of high-purity H_2 and O_3 were conducted with an IR Fourier transform spectrometer of the Laboratory of Molecular and Atmospheric Spectroscopy at the University of Reims (France). All characteristics of the spectrometer and the experimental technique are described in detail in Ref. 4. The optical part of the spectrometer was housed in a sealed off housing pumped out down to the pressure of 10 Torr.

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The optical path length inside the instrument was 9 m. A 31.2 cm long measuring cell was filled with the studied binary mixture $H_2 + O_3$. At the air pressure of 10 Torr inside the housing of the Fourier transform spectrometer, the absorption by $H_2{}^{16}O$ filling the instrument far exceeds the absorption by $H_2{}^{16}O$ produced in the measuring cell in the reaction (2) at the initial partial pressures of H_2 and $^{16}O_3$ equal to 1 Torr.

Taking this circumstance into account, we used the mixture $H_2 + {}^{18}O_3$. In this case, we could detect the concentration of $H_2{}^{18}O$ in the measuring cell starting from 0.0005 Torr, since the contribution of natural $H_2{}^{18}O$ contained in the rest part of the Fourier transform spectrometer is lower.

After the cell was filled with high-purity $^{18}O_3$ and H_2 at the partial pressure of 1 Torr, the absorption spectra of $^{18}O_3$, $H_2{}^{18}O$, and $H_2{}^{16}O$ were measured simultaneously several times during five days at room temperature.

Figure 1 shows two records of a fragment of the absorption spectrum. This fragment includes two isolated spectral lines belonging to $H_2{}^{18}O$ and $H_2{}^{16}O$.

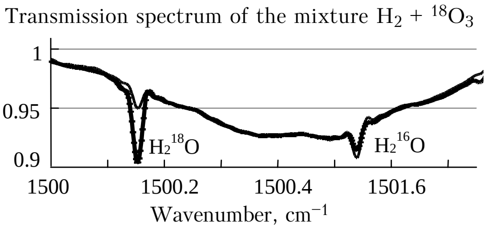

Fig. 1. Absorption spectrum recorded with the Fourier transform spectrometer once the measuring cell is filled with $H_2 + {}^{18}O_3$: within 3 h (—) and 2 days (+++).

The first spectrum was recorded once the cell was filled with the mixture $H_2 + {}^{18}O_3$ (recording duration ~ 3 h). The intensity ratio of these lines corresponds to the natural concentrations of $H_2{}^{16}O$ and $H_2{}^{18}O$ (with the allowance for the absorption cross sections) in the housing of the Fourier transform spectrometer with the 9-m long optical path.

The second spectrum was recorded 2 days after the measuring cell was filled with $H_2 + {}^{18}O_3$. One can see the marked increase in the absorption at the $H_2{}^{18}O$ line with practically unchanged absorption by $H_2{}^{16}O$.

The dynamics of the $H_2{}^{18}O$ and $^{18}O_3$ concentrations for the period of observations (up to 120 h) is plotted in Fig. 2.

In our opinion, the monotonic increase of the $H_2{}^{18}O$ concentration indicates that the reaction $H_2 + {}^{18}O_3 \rightarrow H_2{}^{18}O + O_2$ took place. The increase of the $H_2{}^{18}O$ concentration with time is almost linear with the rate ~ 0.06 mTorr/h. This rate is much less than that characterizing the reaction (2). The O_3 concentration decreases mostly due to natural degradation of ozone in the cell, and only a small part of $^{18}O_3$ molecules takes part in the gas-phase reaction with H_2. However, in the mixture $H_2 + {}^{18}O_3$ the ozone concentration decreases by approximately 5% faster than in the mixture $N_2 + {}^{18}O_3$. This was checked in a specialized experiment. We also found that as the measuring cell was filled with the mixture of high-purity N_2 and $^{18}O_3$, the ratio of the experimentally recorded absorption lines of $H_2{}^{18}O$ and $H_2{}^{16}O$ corresponded to the ratio of their natural concentrations in air filling the spectrometer's housing.

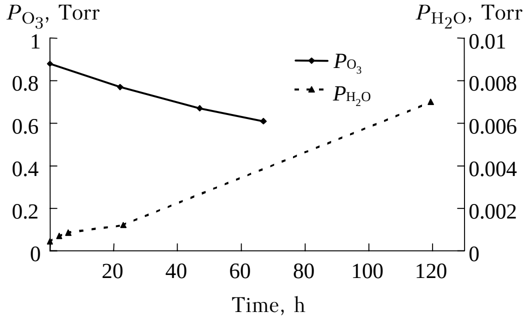

Fig. 2. Concentrations of the gases in the measuring cell as retrieved from the measured absorption spectra of the mixture $H_2 + {}^{18}O_3$.

Thus, we can state that $H_2{}^{18}O$ molecules are produced in the binary mixture $H_2 + {}^{18}O_3$ at the partial pressure of each gas about 1 Torr. Fourier transform spectroscopy allows reliable detection of the produced molecules. The yield of $H_2{}^{18}O$ is characterized by the rate ~ 0.06 mTorr/h, and the resulting concentration of $H_2{}^{18}O$ even within several days is two orders of magnitude lower than the concentration of the initial substances.

It is clear that in the atmosphere, in which O_3 and H_2 are minor constituents (in both the troposphere and stratosphere), the yield of H_2O must be even lower, at least by several orders of magnitude, although irreversibility of the reactions (1) and (2) can nevertheless cause production of the H_2O molecules.

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