**H$_2$O$_2$ photoproduction inside H$_2$O and H$_2$O:o$_2$ ices at 20–140 K**

Mikhail Yu. Kulikov$^{1,3}$, Alexander M. Feigin$^{1}$ & Otto Schrems$^2$

We report the results of laboratory measurements of H$_2$O$_2$ production inside thin (50 nm thickness) H$_2$O and H$_2$O:o$_2$ ice samples irradiated by 121.6 nm photons at different temperatures. In the case of H$_2$O ice, H$_2$O$_2$ is formed at the temperatures below 60 K. In the case of H$_2$O:o$_2$ ice, H$_2$O$_2$ is formed in the 20–140 K range. For H$_2$O:o$_2$ = 9:1 ice, we derived H$_2$O$_2$ photochemical quantum yield as a function of sample irradiation temperature. The obtained data can be used for evaluation of H$_2$O$_2$ photoproduction at the surface of astrophysical water ice bodies and inside the particles of Noctilucent Clouds in the Earth’s atmosphere.

It is well known that surfaces of most icy bodies in the outer Solar System and interstellar space consist mainly of water and are regularly bombarded with energetic particles and photons. This irradiation triggers a spectrum of physicochemical processes inside solid phase$^{1,4}$: the formation of primary products (H, OH, H$_2$, and O); their fast recombination or leaving from the initial position with subsequent diffusion inside ice; reactions between them, with H$_2$O or impurities; appearance of secondary products (HO$_2$, HO$_3$, H$_2$O$_2$, O$_2$, O$_3$); trapping of primary and secondary products by the ice matrix and their accumulation; and the flow of products into gas phase. The characteristics of these processes greatly depend on the characteristics of irradiation, ice type, its thickness, temperature, additives, and others. The end products such as H$_2$O$_2$, O$_2$, O$_3$, etc., both in solid and gas phase are of considerable interest for astrophysics as they are all oxidizing agents and may provide a source of chemical energy as a fuel for extraterrestrial life$^5$.

The established detection of H$_2$O$_2$ on Europa’s surface$^6$ and the discussed existence or absence of H$_2$O$_2$ on Enceladus, Ganymede, and Callisto$^7$ stimulated extensive laboratory studies of the mechanisms of formation and measurement of the parameters of producing concentrations of this component in high-purity H$_2$O ice and H$_2$O ice with different additives irradiated by energetic particles$^{8-14}$. In particular, it was shown that, as compared to H$_2$O ice, the presence of O$_2$ greatly increases the production of H$_2$O$_2$ and other products (HO$_2$, HO$_3$, and O$_3$), especially at relatively high irradiation temperatures of 80–120 K. At the same time, except for a few works, significantly less attention was paid to investigation of H$_2$O$_2$ production by VUV photons. In particular, Gerakines et al.$^{15}$ and Schriver et al.$^{16}$ reported about H$_2$O$_2$ formation in H$_2$O ice at 10 K irradiated by microwave discharge hydrogen flow lamps. Yabushita et al.$^{17}$ found out H$_2$O$_2$ presence in H$_2$O ice after its irradiation by 157 nm photons at 90 K. Shi et al.$^{18}$ measured H$_2$O$_2$ in porous H$_2$O + O$_2$ ice irradiated by 193 nm photons at 40–78 K. Thus, many details of H$_2$O$_2$ production by VUV photons, the temperature dependence in the first place, are still understood poorly.

This work reports the first results of laboratory measurements of H$_2$O$_2$ production inside thin H$_2$O and H$_2$O:o$_2$ ice samples irradiated by 121.6 nm photons in the temperature range of 20–140 K. We discuss possible implications of the obtained results at the surface of astrophysical water ice bodies and inside the particles of Noctilucent Clouds in the Earth’s atmosphere.

**Noctilucent Clouds**

There exists at least one analog of such water icy bodies regularly irradiated by VUV photons in the Earth’s atmosphere. Each summer at polar and middle latitudes, one can observe the highest atmospheric clouds called Noctilucent Clouds (NLCs). They appear in mesopause region (altitudes range of 80–90 km) at the temperatures of 120–150 K$^{19,20}$. Since the clouds discovery$^{21}$, there were many discussions about their nature (see reviews by Gadsden & Schröder$^{19}$ and by Thomas$^{20}$). Only recently, the infrared spectra of clouds showed$^{22}$ that NLCs consisted mainly of water ice. Thus, it is not doubt now that clouds form by condensation of water vapour and can influence on gas-phase chemistry of this region due to water vapour is its key parameter.

$^{1}$Institute of Applied Physics of the Russian Academy of Sciences, 46 Ulyanov Str., 603950, Nizhny, Novgorod, Russia. $^{2}$Alfred Wegener Institute Helmholtz Centre for Polar and Marine Research, Am Handelshafen 12, D-27570, Bremerhaven, Germany. Correspondence and requests for materials should be addressed to M.Y.K. (email: mikhail_kulikov@mail.ru)
In the conditions of daytime mesopause, water vapour is subjected to intensive solar VUV radiation (121.6 nm, so called the Lyman–α line) and the reaction \(H_2O + h\nu \rightarrow H + OH\) provides the main chemical source of the family of odd hydrogen (HO\(_x\): H, OH, and HO\(_2\))\(^{24}\). In turn, the reactions with participation of HO\(_x\) components (HO\(_x\) + H ↔ O \(_x\), O + OH ↔ O\(_2\) + H, O + HO\(_2\) ↔ O\(_2\) + OH, and O + OH ↔ O\(_2\) + HO\(_2\)) remove the components of the odd oxygen family (O\(_3\): O(D), O(P), and O\(_2\)). Therefore, the appearance of NLCs is expected to reduce the concentrations of water vapour and HO\(_x\) and to increase Ox. However, rocket measurements of the concentration of atomic oxygen made during several campaigns demonstrated unpredicted O depletion around \(2860 \text{ cm}^{-1}\)\(^{25}\).

The concentration of those ions formed as a result of the H\(_2\)O\(_2\) photoproduct that may accumulate in NLCs.

Note that the experimental evidence of H\(_2\)O\(_2\) concentration increase in the presence of clouds was obtained long ago. Arnold and Krankowsky\(^{28}\) presented results of several rocket mass-spectrometer measurements of H\(_2\)O\(_2\)\(^+\) ions above Andoya (Northern Norway, 69\(^°\) N) taken in different seasons. The model estimates of the concentration of those ions formed as a result of the H\(_2\)O\(_2\)\(^+\) + O\(_2\) ↔ H\(_2\)O\(_2\)\(^+\) + \(O_2\) reaction agreed well with the results of measurements made in different seasons, except summer. The authors conjectured that the discrepancy was caused by the increased H\(_2\)O\(_2\) concentration in the summer time. Later measurements\(^{29}\) revealed positively charged clusters containing H\(_2\)O\(_2\) in the presence of NLCs particles. The researchers arrived at the conclusion that for such clusters to be formed, the concentration of H\(_2\)O\(_2\) must be much higher than the expected level.

Experimental Results

Hydrogen peroxide was found by detecting the IR absorption band of 2850–2860 cm\(^{-1}\) in FTIR spectra of H\(_2\)O and H\(_2\)O\(_2\) ice samples as the result of their irradiation by calibrated source of 121.6 nm photons at high vacuum conditions. For more details please see Methods.

The results of 1 hour irradiation of thin ice samples by Lyman–α photons at the photon flux intensity \(I_o = 5 \times 10^{14}\) photons/(cm\(^2\)-s) are presented in Fig. 1. One can see that, in the case of H\(_2\)O ice (Fig. 1a), H\(_2\)O\(_2\) is formed at temperature of irradiation \(T_o \leq 60\) K, and the temperature rise from 20 to 60 K results in a monotonic decrease of the integrated area of the 2850–2860 cm\(^{-1}\) band \(S_{H_2O}\) at 2860 cm\(^{-1}\). The experiments with thin water ice samples doped with O\(_2\) give more interesting results (see Fig. 1b).

First, H\(_2\)O\(_2\) is formed in the entire studied temperature range of 20–140 K. Second, the temperature dependence of \(S_{H_2O}\) is nonmonotonic, so that it attains its maximum \((-0.38 \pm 0.057)\) cm\(^{-1}\) at about 100 K. Third, typical values of \(S_{H_2O}\) at 20–60 K are essentially higher that the maximum recorded in experiments with H\(_2\)O ice at 20 K \((-0.085 \pm 0.013)\) cm\(^{-1}\). Forth, H\(_2\)O\(_2\) peak position lays at 2850 cm\(^{-1}\) in the range of 20–100 K and shifts to 2852–2854 cm\(^{-1}\) at the temperatures 120–140 K. Note also, in both cases, there are no new features at 1039, 1142, and 1259 cm\(^{-1}\) (see Fig. 1c) which can be attributed to O\(_3\), HO\(_2\), and HO\(_3\) correspondingly\(^{11,12}\).

Figure 2a shows the examples of \(S_{H_2O}\) dependencies on irradiation time (VUV fluence) at \(I_o = 5 \times 10^{14}\) photons/(cm\(^2\)-s). Note firstly, the present results are in a qualitative agreement with H\(_2\)O\(_2\) temporal evolution obtained in earlier laboratory studies of the formation of this component in H\(_2\)O ice irradiated by energetic particles\(^{13,14}\) and photons\(^{15}\). The temporal evolution of \(S_{H_2O}\) can be divided into two parts: growth stage when \(S_{H_2O}\) increases monotonically, and saturation stage. In both cases, \(S_{H_2O}\) is saturated after ~1 hour irradiation. In the case of H\(_2\)O ice, the growth stage continues for ~20–30 min and can be described by a quadratic function of irradiation time (VUV fluence). This corresponds to the results of irradiation of H\(_2\)O ice by Lyman–α photons at 10 K obtained by Gerakines et al.\(^{15}\). In the case of H\(_2\)O\(_2\) ice, the growth stage continues for ~10 min and can be described by a linear function of irradiation time (VUV fluence). Such behavior of \(S_{H_2O}\) in the case of H\(_2\)O\(_2\) ice was found at other photon flux intensities. It means that, in the case of H\(_2\)O\(_2\) ice, the H\(_2\)O\(_2\) production during the growth stage can be fit successfully to a (pseudo) first-order reaction. We can conclude that the rate of H\(_2\)O\(_2\) production is proportional to \(I_o\) and can determine the H\(_2\)O\(_2\) photochemical quantum yield \((\gamma_{H_2O_2})\), the number of molecules of H\(_2\)O\(_2\) generated per a Lyman–α photon absorbed by ice) as a function of \(T_o\) following, for example, Cooper et al.\(^{12}\) and Hand and Carlson\(^{14}\). For this, we carried out special experiments with H\(_2\)O\(_2\) ice at lowdose \(= 3 \times 10^{12}\) photons/(cm\(^2\)-s) at which the growth stage continued more than 100 min. The Fig. 2b shows the examples of \(S_{H_2O}\) dependencies on irradiation time (fluence) at \(T_o\) with corresponding linear fits whose values of slope are presented on Fig. 2c.

Estimation of H\(_2\)O\(_2\) Concentration and H\(_2\)O\(_2\) Photochemical Quantum Yield.

All known studies of H\(_2\)O\(_2\) production after irradiation of different ices\(^{14,30–38}\) used the values of \(A_{H_2O_2}\) (the strength of the 2850–2860 cm\(^{-1}\) band absorption) from two sources\(^{10,40}\). Moore & Hudson\(^{4}\) measured \(A_{H_2O_2} = 2.7 \times 10^{-17}\) cm-molecule\(^{-1}\) and this value used for all temperatures. Loeffler et al.\(^{10}\) found out that \(A_{H_2O_2} = 5.7 \times 10^{-17}\) cm-molecule\(^{-1}\) at 20 K, 5.2 \times 10^{-17}\) cm-molecule\(^{-1}\) at 80 K, and 4.9 \times 10^{-17}\) cm-molecule\(^{-1}\) at 110 K. Thus, for estimation of H\(_2\)O\(_2\) column density (relative concentration) and H\(_2\)O\(_2\) photochemical quantum yield from the results presented in Figs 1 and 2c, we applied both data sets (see Fig. 3a,b). In particular, Loeffler et al.\(^{10}\) data were interpolated into the temperature regions of 20–80 K and 80–110 K, and extrapolated to the temperature region of 110–140 K.

One can see from Fig. 3a, that in the case of H\(_2\)O ice, the maximum of relative concentration H\(_2\)O\(_2\)/H\(_2\)O at 20 K is ~2% at \(A_{H_2O_2}\) from Moore & Hudson\(^{4}\) and ~1% at \(A_{H_2O_2}\) from Loeffler et al.\(^{10}\). In the case of H\(_2\)O\(_2\) ice, the
maximum of $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ at 100 K is $\sim$9% at $A_H\gamma_{\text{O}_2}$ from Moore & Hudson\textsuperscript{8} and $\sim$4.5% at $A_H\gamma_{\text{O}_2}$ from Loeffler \textit{et al.}\textsuperscript{10}. In that time, the maximum of $\gamma_{\text{H}_2\text{O}_2}$ is at 20 K (see Fig. 3b). Note also, that at the temperatures of possible NLCs existence (120–140 K), $\gamma_{\text{H}_2\text{O}_2}$ varies within $\sim$(0.009–0.031) molecules/photon at $A_H\gamma_{\text{O}_2}$ from Moore & Hudson\textsuperscript{8} and $\sim$(0.0053–0.0175) molecules/photon at $A_H\gamma_{\text{O}_2}$ from Loeffler \textit{et al.}\textsuperscript{10}.

**Discussion and Conclusion**

The possible mechanism of H$_2$O$_2$ formation during VUV irradiation of H$_2$O ice was discussed by Gerakines \textit{et al.}\textsuperscript{15} and pointed by Loeffler \textit{et al.}\textsuperscript{10} in comparison with H$_2$O$_2$ formation by ions. This component is formed due to reaction $\text{OH}^+ + \text{OH} \rightarrow \text{H}_2\text{O}_2$. The quadratic character of $S_{\text{H}_2\text{O}_2}$ dependence on VUV fluence at the growth stage (see Fig. 2a) indicates a reaction of second order. It means that two photons are needed for appearance of one H$_2$O$_2$ molecule. These photons should produce two OH close to each other due to extremely low mobility of OH in water ice below 80 K\textsuperscript{37,38}. The saturation of $S_{\text{H}_2\text{O}_2}$ after ~1 hour irradiation corresponds to the photochemical equilibrium when photoproduction is balanced by the photochemical sink due to the reactions $\text{H}_2\text{O}_2 + hv \rightarrow 2\text{OH}$ and $\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2$.

In the case of H$_2$O$_2$ ice, the linear character of $S_{\text{H}_2\text{O}_2}$ dependence on VUV fluence at growth stage (see Fig. 2a) shows us that the mechanism of H$_2$O$_2$ formation differs from the previous case. Note, Loeffler \textit{et al.}\textsuperscript{10} and Hand and Carlson\textsuperscript{14} found out the same behavior of $S_{\text{H}_2\text{O}_2}$ in H$_2$O ice irradiated by high-energy ions and electrons correspondingly. It was proposed for explanation of this, in particular, that two OH could be produced in an ion track caused by an ion\textsuperscript{10}. Evidently, this mechanism cannot be transferred on our situation. But, following Loeffler \textit{et al.}\textsuperscript{10} and Hand and Carlson\textsuperscript{14}, we can speculate that the rate of H$_2$O$_2$ formation in H$_2$O$_2$ ice irradiated by VUV photons is proportional to VUV intensity and the concentrations of H$_2$O and O$_2$. In other words, one photon, one H$_2$O molecule and one O$_2$ molecule are needed for appearance of one H$_2$O$_2$ molecule. On the other hand,
O₂ is impurity of H₂O ice and typically two O₂ molecules are separated from each other by a “paling” of H₂O molecules. So, it is hard to imagine that these O₂ molecules can participate in formation of one H₂O₂ molecule due to extremely low mobility of intermediates (such as OH and HO₂) in water ice below 80 K as above mentioned. Thus, we can conclude as a first approximation that H₂O₂ photochemical quantum yield inside VUV irradiated H₂O:O₂ ice is proportional to the relative concentration of O₂ (O₂/H₂O), when O₂/H₂O = 1.

Note, that, in the case of H₂O:O₂ ice, temperature dependences of H₂O₂ column density (N_H₂O₂) and γ_H₂O₂ shown in Fig. 3a,b allow to estimate the H₂O₂ photochemical lifetime (τ_H₂O₂) with the use of the photochemical equilibrium condition τ_H₂O₂ ⋅ N_H₂O₂ = γ_H₂O₂ ⋅ I_α. On can see from Fig. 3c that τ_H₂O₂ has a maximum at 60–80 K and the temperature rise from 20 to 60 K results in an essential increase of τ_H₂O₂. For explanation of this, we should take into account that H₂O₂ photochemical sink is due to the reactions (1) H₂O₂ + hv → 2OH and (2) H₂O₂ + OH → H₂O + HO₂. So, τ_H₂O₂ = (R₁ + R₂) / (2σ_H₂O₂), where R₁,2 are the corresponding reaction rate coefficients. Note, Loeffler et al. measured the loss of H₂O₂ in H₂O₂:H₂O at temperatures between 21 and 145 K initiated by UV photons (193 nm). They obtained that the temperature dependences of H₂O₂ photodestruction cross section (σ_H₂O₂) had a minimum at ~70 K which value was in ~5 and ~3 times more than σ_H₂O₂ at 20 K and 145 K correspondingly. Thus, following Loeffler et al., we can speculate that nonmonotonic temperature dependency of σ_H₂O₂ shown in Fig. 3c is caused by strong and nontrivial temperature dependency of cross section of H₂O₂ photodestruction by irradiation of our lamp which defines the value of R₁. More detailed analysis of obtained results is out of the scopes of this short paper.

Thus, at the relatively high temperatures >60 K, H₂O₂ is photoproduced in H₂O:O₂ ice only. The estimated values of γ_H₂O₂ inside such ice can be used for assessing the impact of Lyman-α photons on water ice and its contribution to H₂O₂ production in different applications.

Figure 2. (a,b) Examples of integrated area of the 2850–2860 cm⁻¹ band (color circles with bars) as a function of irradiation time (fluence) at I_α = 5·10¹⁴ photons/(cm²·s) (a) and at I_α = 3·10¹³ photons/(cm²·s) (b). Dashed lines in (a) indicate linear and quadratic fits. Color lines in (b) are linear fits. (c) Slope of the fit as a function of temperature irradiation corresponding to (b).
In astrophysics, VUV irradiation competes with energetic particles bombardment and Cooper et al. measured H2O2 production inside H2O:O2 = 6:1 ice mixtures irradiated with 0.8 MeV protons. It was found that G-value (defined as the number of H2O2 molecules created per unit of absorbed energy) varied in the range of 0.2–0.4 molecules/100 eV at 50–100 K, that is close to G-value of Lyman-α photons at 50–100 K obtained in our paper. Thus, contribution of Lyman-α photons to H2O2 production is defined by the ratio between energy fluxes of photons (EFph) and energetic particles (EFep). In the case of EFph ~ EFep, photons produce approximately the same amount of H2O2 inside ice as particles. At that, as it was noted by Gerakines et al., the penetration depth for Lyman-α photons (~45 nm) in water ice is essentially less than for protons which depends on its energy (for example, 1–2 μm for 0.1 MeV protons and 22 μm for 1 MeV protons). So, one would expect the high relative H2O2 concentration in the top few tens of nm caused by Lyman-α photons. It means that H2O2 production by VUV photons can be important at EFph/EFep ≥ 10⁻².

In the mesopause region of the Earth’s atmosphere, typically EFph > EFep. But, at this moment, there is no information about containing of O2 inside water ice of Noctilucent Clouds. It is well-known that NLCs are formed as a result of gas-kinetic collision of H2O molecules with the surface of mesospheric aerosols, including adsorption and desorption properties. It is, generally, a relatively slow process, with the characteristic time (2–20 hours) depending on temperature. In the real conditions of a summer mesopause, H2O concentration in gas phase is more than 4 orders of magnitude less than the concentration of O2 in ground (triplet) state and less than daytime concentration of O2 in singlet state ((2–4)·10⁹ cm⁻³ at 80–85 km). The molecules of O2 in ground and excited states, like those of H2O, continually bombard the surface of the forming particles of clouds, adsorb on their surface and can be trapped inside the ice matrix as the NLC particles are being covered by new ice layers. This suggests that a small part of O2 molecules from gas phase may be uptaken by the forming matrix of the cloud. It is certainly hard to believe that the relative concentration of O2 inside NLC particles (O2NLC) can be equal to 10% at such high temperatures. Nevertheless, we can estimate minimum of O2NLC at which photoproduced H2O2 concentration would be comparable with the gas-phase concentration of this component.

Let us assume that is unknown H2O2 photochemical quantum yield in NLCs particles. Then the rate of H2O2 production per 1 cm³ at a certain altitude is defined by \( P_{H_2O_2} = \gamma_{H_2O_2} \cdot S_{Mie} \cdot I_{\alpha} \), where \( I_{\alpha} \) is the local flux intensity of Lyman-α photons and \( S_{Mie} \) is the Mie absorption cross-section of NLCs, \( S_{Mie} \approx S_{NLC}/4 \), where \( S_{NLC} \) is

---

Figure 3. (a) H2O2 column density and its relative concentration in pure H2O ice and in H2O:O2 ice as a function of temperature irradiation corresponding to Fig. 1d. (b) H2O2 photochemical quantum yield as a function of temperature irradiation corresponding to Fig. 2c. (c) H2O2 photochemical lifetime as a function of temperature irradiation corresponding to (a,b).
the NLC surface density. According to the data of the long-term (1998–2005) measurements with the ALOMAR RMR-lidar in Northern Norway (69° N, 16° E), at the altitudes of 81–86 km $S_{\text{NLC}}$ varies within the (3−6)·10$^3$ cm$^{-2}$ cm$^{-3}$ range. Taking into consideration that at these heights in the conditions of average solar activity $L_{\text{sun}}$=3·10$^{-3}$ photons/(cm$^2$·s)24, we obtain $P_{\text{H}_2\text{O}^2}= (2.25−4.5)\times10^{-13} \text{NLC}$ molecules/(cm$^2$·s). In the real conditions of the mesopause, the NLCs particles are also irradiated by UV solar photons, which leads to H$_2$O$_2$ photodissociation in solid phase with the efficiency close to this process in gas phase. For the considered range of altitudes of 81–86 km, the photodissociation constant of H$_2$O$_2$ in gas phase $R_{\text{H}_2\text{O}_2}$ is $\sim 1.5\times10^{-4}$ s$^{-1}$. Thus, the equilibrium concentration of H$_2$O$_2$ that may be accumulated in cloud particles irradiated by Lyman-$\alpha$ photons is $P_{\text{H}_2\text{O}^2}/R_{\text{H}_2\text{O}_2}= (1.5−3)\times10^{-13} \text{NLC}$ molecules/cm$^{-3}$. Gumbel et al.23 reported the maximum of $S_{\text{NLC}}=10^{-7}$ cm$^2$/cm$^3$, which gives the estimate for the maximum values of $P_{\text{H}_2\text{O}^2}$ and equilibrium concentration of H$_2$O$_2$ to be 7.5·10$^{-14}$ molecules/cm$^3$ and 5·10$^{-10}$ molecules/cm$^3$, correspondingly. Under the conditions of NLCs existence, typical value of gas-phase concentration of H$_2$O$_2$ is $\sim 2\times10^{-10}$ cm$^{-3}$ at 81 km and decreases with increasing height down to the values less than 10$^{-11}$ cm$^{-3}$ at 86 km. Thus, the minimum of $\gamma_{\text{H}_2\text{O}_2}$, at which photoproduced H$_2$O$_2$ concentration is equal to 10$^{-10}$ cm$^{-3}$, corresponds to $2\times10^{-4}$ molecules/photon. Following our above conclusions, H$_2$O$_2$ photochemical quantum yield inside H$_2$O$_2$ ice is proportional to the relative concentration of O$_2$. Taking into consideration the measured values of $\gamma_{\text{H}_2\text{O}_2}$ inside H$_2$O$_2$ ice at the temperatures of 120–140 K, we estimate that the minimum of $\gamma_{\text{H}_2\text{O}_2}$ is $2\times10^{-4}$ molecules/photon corresponds to $O_{\text{NLC}}^2\sim (0.065−0.22)\%$ (i.e. the absolute concentration of O$_2$ in NLCs $\sim (1.4−4.9)\times10^{-5}$ cm$^3$ at $T_{\text{NLC}}$ from Moore & Hudson24 and (0.11−0.38)\% (the absolute concentration $\sim (2.5−3.3)\times10^{-5}$ cm$^3$) at $T_{\text{NLC}}$ from Loeffler et al.19. Note, that the estimated values of the O$_2$ absolute concentration in NLCs are several orders of magnitude less than typical gas-phase concentrations of this component in ground and singlet states at the altitudes of 81–86 km. To conclude, we have demonstrated for the first time that, if NLCs particles contain $\geq 0.1\%$ O$_2$, the physicochemical processes occurring in them may remarkably affect the chemical composition of the mesopause region. On the one hand, it may be a possible explanation of the results of early rocket mass–spectrometer measurements indicating increased H$_2$O$_2$ concentration in the clouds. On the other hand, H$_2$O$_2$ product of its UV photodissociation (OH), H$_2$O, O$_2$ and other impurities (for example, CO$_2$) can participate in subsequent reactions producing more complex chemical compounds inside NLCs as it takes place, for example, in the bulk of supercooled water particles. We hope that this research stimulates further experimental and theoretical investigations of the chemical composition of cloud particles. Note also that the obtained results are interesting for astrophysical applications, for example, for assessing the contribution of VUV irradiation to H$_2$O$_2$ production in the outer Solar System and interstellar space depending on temperature.

Methods

Apparatus. The experimental set-up was the same as we used under laboratory measurements of the photodesorption rate from water ice. As described by Kulikov et al.27, the apparatus consisted of a Fourier Transform Infrared Spectrometer (Bruker IFS 66v)), a closed-cycle He refrigerator (Leybold ROK 10–300), a gas preparation and inlet system (further briefly GPIS), and a high-vacuum chamber with a volume of about 1000 cm$^3$ pumped continuously by a turbomolecular pump system (Leybold-Heraeus) securing a high vacuum in the chamber down to the 10$^{-10}$ mbar range. Inside the chamber, at the cold end of the cryostat there was a vertically mounted aluminium mirror (2.5×4 cm in size) as a substrate whose temperature was precisely regulated by a temperature controller (Lake Shore, model 340). The mirror temperature could be selected in the 10–300 K range. The GPIS was equipped with baratrons and needle valves. The upper part of the high vacuum chamber had two ports, one of which was equipped with a MgF$_2$ (5 mm thick) input window for a VUV lamp. The second port had a KBr window for the IR beam of the FTIR spectrometer. The input for the VUV lamp made an angle of incidence of $\sim 45^\circ$ to the mirror surface and, according to the estimates of the manufacturer, MgF$_2$ transmitted about 60% of the quantum flux at the wavelength of 121.6 nm. As a VUV source (Lyman-$\alpha$) we used a resonance hydrogen lamp (Ophthos Instruments) containing a mixture of 10% H$_2$ and 90% Ar excited by a microwave generator (Ophthos Instruments, model MPG–4M) with a frequency of 2450 MHz. The lamp intensity was determined by the power supplied by the microwave generator (about the lamp calibration see below). The FTIR spectrometer was placed on rails allowing precise positioning of the instrument with respect to the cryostat with the sample. This was important for achieving a good overlap of the areas of the light spots from both, infrared (from spectrometer light source) and vacuum ultraviolet irradiation (from VUV lamp) of the ice film sample on the substrate. The operation of the FTIR spectrometer was PC controlled by means of software (OPUS) that permitted scanning spectra over a wide range (from 6000 to 500 cm$^{-1}$) and analyzing the obtained spectra. The spectra were recorded with a spectral resolution of 0.2−2 cm$^{-1}$ in the RAIRS mode (reflection absorption infrared spectroscopy) where the IR beam passes through the sample twice.

Experimental procedures. The experimental procedures were almost the same as we used under laboratory measurements of the photodesorption rate from water ice. As described by Kulikov et al.27, each experiment with a particular sample of ice was conducted in two stages. At the first stage, two background spectra with different resolution were recorded at a mirror temperature of 20 K and at a temperature of subsequent irradiation ($T_\text{irr}$). At that time, H$_2$O or H$_2$O + O$_2$ gas was got ready in GPIS. We used the oxygen (Air Liquide 5.5) with purity better than 99.9995 Vol% and triply distilled water with resistivity better than 10$^7$ ohm cm, additionally degassed by freeze/thaw cycles in vacuum conditions. As described in our previous study27, then, an ice film was prepared by depositing H$_2$O or H$_2$O + O$_2$ vapour onto the mirror at 20 K. The deposition speed and sample thickness were controlled by a needle valve and internal baratron of GPIS and by tracking the evolution of absorption bands in the FTIR spectra. More specifically, a sample was prepared by successive slow depositions of small vapour portion which were accompanied by the integrated area measurements of the water ice 3275 cm$^{-1}$ band ($S_{\text{H}_2\text{O}}$). At the end
of each sample deposition, we tried to rich the value of \( S_{H_2O} = 31 \pm 1 \text{ cm}^{-1} \) which was equivalent to \( \text{H}_2\text{O} \) column density \( N_{H_2O} = (1.55 \pm 0.05) \times 10^{17} \text{ molecules/cm}^2 \) at the strength of band absorption \( A_{H_2O} = 2 \times 10^{-16} \text{ cm/molecule} \) taken from Allamandola et al.\(^4\). Here we applied the widely used\(^4,5,6,7\) approach to estimate a column density of absorbing molecules: \( N_{H_2O} = S_{H_2O}/A_{H_2O} \). In the case of \( \text{H}_2\text{O} \) ice, the indicated values of \( N_{H_2O} \) responded to thickness sample of 50 \pm 1.6 \text{ nm} at ice density of 0.93 \text{ g/cm}^3. \) In the case of \( \text{H}_2\text{O}_2 \) ice, we might expect increasing thickness of samples not more than 10%. Thus, the thicknesses of \( \text{H}_2\text{O} \) and \( \text{H}_2\text{O}_2 \) ice samples were comparable with the attenuation depth (\( \sim 45 \text{ nm} \)) of 10.2 \text{ eV} photons in water ice and close to typical radii of NLC particles\(^8,9\). After the sample preparation, the mirror temperature was set at \( T_m \) (in the 20–140 K range) and several IR spectra of unirradiated ice were recorded. At \( T_m = 120 \text{ K} \) and above, the IR spectra showed crystalline features of all ice samples that was in accordance with composition of NLCs.\(^10\) Note also, Bartels-Rausch et al.\(^11\) discussed recently the simulations of disorder on pure ice at different temperatures below melting point \( (T_m) \) and showed that, at the temperatures 10 K below \( T_m \) disorder affected the first molecular layer of ice only. In current study, the samples consisted of more than 100 layers of water and the highest temperature in our experiments (140 K) was about 20 K below than characteristic \( T_m \) of water ice in our vacuum chamber. Thus, we can conclude that interface processes could not influence essentially on the studied processes inside ice samples.

As described in our previous study\(^12\), at the second stage, the vacuum ultraviolet lamp was switched on and the ice films were exposed to VUV radiation with intensity set by microwave generator. After each photolysis period, IR spectra of the irradiated ice films were recorded. For improving the signal-to-noise ratio we used the spectral resolution of 2 \text{ cm}^{-1} \) and a large amount of scans (2000). Hydrogen peroxide was found by detecting the IR absorption band of 2850–2860 \text{ cm}^{-1} \) in difference spectra (before and after irradiation). The band was exuded by subtracting the baseline from the spectrum in manner described, for example, in Hand & Carlson\(^13\). Values of \( \text{H}_2\text{O}_2 \) column densities were determined as \( N_{H_2O_2} = S_{H_2O_2}/A_{H_2O_2} \), where \( S_{H_2O_2} \) was the integrated area of the 2850–2860 \text{ cm}^{-1} \) band. \( A_{H_2O_2} \) was the strength of the band absorption.

**Calibration of the hydrogen discharge lamp.** The calibration was carried out in the same manner as it was described by Kulikov et al.\(^14\). Before an experiment with specific \( \text{H}_2\text{O} \) or \( \text{H}_2\text{O}_2 \) ice sample, we performed series of measurements of the absolute magnitude of the flux of Lyman-\( \alpha \) photons that reach the ice sample at different adjustments of the microwave generator power. The widely used “ozone method”\(^15,16\) was applied for the procedure. The intensity of the lamp was determined by measuring the \( \text{O}_2 \rightarrow \text{O}_1 \) conversion rate in a VUV photolyzed sample of solid \( \text{O}_2 \) at 16 K. The ozone formation as a function of photolysis time was monitored with the FTIR spectrometer via the \( \text{O}_3 \) absorption band at about 1040 \text{ cm}^{-1} \). More specifically, for finding the VUV intensity at the mirror for a specific generator output power (GOP) we made successive measurements of the integrated area of the 1040 \text{ cm}^{-1} \) absorption band \( (S_{O_3}) \) as a function of irradiation time (see Fig. 2 in Kulikov et al.\(^12\)). After that, the lamp intensity at this GOP was determined as \( I_0 = dS_{O_3}/dt \cdot (Y \cdot A_{O_2}) \), where the derivative \( dS_{O_3}/dt \) was found by the linear part of the function \( S_{O_3}(t) \). \( Y \) was the quantum yield for the formation of \( \text{O}_3 \) from \( \text{O}_2 \), and \( A_{O_2} \) was the strength of the band absorption. The value of \( Y \cdot A_{O_2} \) was adopted from Cottin et al.\(^17\) and was equal to 8.4 \times 10^{-13} \text{ cm-photon}^{-1}. \) We obtained that, depending on GOP varied within the range of 4–120 W, the photon flux intensity varied within the range 5 \times 10^{12}–10^{13} \text{ photons/(cm}^2\text{·s)}. The stability of lamp intensity at the fixed GOP was checked by means of photodiode SXUV300 (International Radiation Detectors).

**References**

1. Westley, M. S., Baragiola, R. A., Johnson, R. E. & Baratta, G. A. Photodesorption from low-temperature water ice in interstellar and circumsolar grains. *Nature* 373, 405–407 (1995).
2. Tabushita, A., Hama, T. & Kawasaki, M. Photochemical reaction processes during vacuum-ultraviolet irradiation of water ice. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews* 16, 46–61 (2010).
3. Johnson, R. E. & Quickenden, T. I. Photolysis and radiolysis of water ice on outer solar system bodies. *J. Geophys. Res. Res.* 102, 10985–10996 (1997).
4. Baih, D. A., Fami, M., Vidal, R. A. & Baragiola, R. A. Radiolysis of water ice in the outer solar system: Sputtering and trapping of radiation products. *J. Geophys. Res.* 106, 33285–33290 (2001).
5. Chyba, C. F. Energy for microbial life on Europa. *Nature* 403, 381–382 (2000).
6. Carlson, R. W. et al. Hydrogen peroxide on the surface of Europa. *Science* 283, 2062–2064 (1999).
7. Newman, S. F., Buratti, B. J., Jauern, R., Bauer, J. M. & Momary, T. W. Hydrogen peroxide on Enceladus. *Astrophys. J.* 670, L143–L146 (2007).
8. Moore, M. H. & Hudson, R. L. IR detection of H2O2 at 80 K in ion-irradiated laboratory ices relevant to Europa. *Icarus* 145, 282–288 (2000).
9. Loefller, M. J. & Baragiola, R. A. The state of hydrogen peroxide on Europa. *Geophys. Res. Lett.* 32, 17202 (2005).
10. Loefller, M. J., Raut, U., Vidal, R. A., Baragiola, R. A. & Carlson, R. W. Synthesis of hydrogen peroxide in water ice by ion irradiation. *Icarus* 180, 265–273 (2006).
11. Cooper, P. D., Moore, M. H. & Hudson, R. L. Infrared detection of HO2 and HO2 radicals in water ice. *J. Phys. Chem. A* 110, 7985–7988 (2006).
12. Cooper, P. D., Moore, M. H. & Hudson, R. L. Radiation chemistry of H2O + O2 ices. *Icarus* 194, 379–388 (2008).
13. Loefller, M. J. & Baragiola, R. A. Is the 3.5 \text{ μm} infrared feature on Enceladus due to hydrogen peroxide? *Astrophys. J.* 694, L92–L94 (2009).
14. Hand, K. P. & Carlson, R. W. H2O2 production by high-energy electrons on icy satellites as a function of surface temperature and electron flux. *Icarus* 215, 226–233 (2011).
15. Gerakines, P. A., Schutte, W. A. & Ehrenfreund, P. Ultraviolet processing in interstellar ice analogs. 1. Pure ices. *Astronomy and Astrophysics* 312, 289–305 (1996).
16. Schriver, A., Coanga, J. M., Schriver-Mazzuoli, L. & Ehrenfreund, P. FTIR studies of ultraviolet photo-dissociation at 10 K of dimethyl ether in argon and nitrogen matrices, in the solid phase and in amorphous water ice. *Chem. Phys. Lett.* 386, 377–383 (2004).
17. Tabushita, A., Hama, T., Iida, D. & Kawasaki, M. Hydrogen peroxide formation following the vacuum ultraviolet photodissociation of water ice films at 90 K. *J. Chem. Phys.* 129, 014709 (2008).
18. Shi, J., Raut, U., Kim, J.-H., Loeffler, M. & Baragiola, R. A. Ultraviolet photon-induced synthesis and trapping of H₂O₂ and O₃ in porous water ice films in the presence of ambient O₂: Implications for extraterrestrial ice. *Astroph. J. Lett.* **378**, L3 (2011).
19. Gadsden, M. & Schröder, W. Noctilucent clouds (Springer Verlag, 1989).
20. Thomas, G. E. Mesospheric clouds and the physics of the mesopause region. *Rev. Geophys.* **29**, 553–575 (1991).
21. Lübken, F. J. Thermal structure of the Arctic summer mesosphere. *J. Geophys. Res.* **Atmos.** **104**, 9135–9149 (1999).
22. Jesse, O. Auffallende Abenderscheinungen am Himmel. *Meteorol. Z.* **2**, 311–312 (1885).
23. Hervig, M. *et al.* First confirmation that water ice is the primary component of polar mesospheric clouds. *Geophys. Res. Lett.* **28**, 971–974 (2001).
24. Brasseur, G. P. & Solomon, S. *Aeronomy of the middle atmosphere: Chemistry and physics of the stratosphere and mesosphere* (3rd ed) (Springer Science & Business Media, 2005).
25. Gumbel, J., Murtagh, D. P., Espy, P. J. & Witt, G. Odd oxygen measurements during the Noctilucent Cloud 93 rocket campaign. *J. Geophys. Res.* – *Space Phys.* **103**, 23399–23414 (1998).
26. Murray, B. J. & Plane, J. M. C. Modelling the impact of noctilucent cloud formation on atomic oxygen and other minor constituents of the summer mesosphere. *Atmos. Chem. Phys.* **5**, 1027–1038 (2005).
27. Kulikov, M. Y. *et al.* Technical Note: VUV photodesorption rates from water ice in the 120–150 K temperature range – significance for Noctilucent Clouds. *Atmos. Chem. Phys.* **11**, 1729–1734 (2011).
28. Arnold, F. & Krankowski, D. Measurements of H₂O₂⁻ ion in the D-region and implications for mesospheric hydrogen peroxide. *Geophys. Res. Lett.* **1**, 243–245 (1974).
29. Kopp, E., Eberhardt, P., Herrmann, U. & Bijon, L. G. Positive ion composition in the high-latitude summer D region with Noctilucent Clouds. *J. Geophys. Res.* **Atmos.** **90**, 13041–13053 (1985).
30. Comis, O., Leto, G. & Strazzulla, G. Hydrogen peroxide production by ion irradiation of thin water ice films. *Astronomy and Astrophysics* **420**, 405–410 (2004).
31. Zheng, W., Jewitt, D. & Kaiser, R. I. Formation of hydrogen, oxygen, and hydrogen peroxide in electron-irradiated crystalline water ice. *Astrophys. J.* **639**, 534–548 (2006).
32. Hudson, R. L. & Moore, M. H. Infrared spectra and radiation stability of H₂O₃ ices relevant to Europa. *Astrobiology* **6**, 483–489 (2006).
33. Loeffler, M. J. & Baragiola, R. A. Is the 3.5 μm infrared feature on Enceladus due to hydrogen peroxide? *Astrophys. J.* **694**, L92–L94 (2009).
34. Boduch, P. *et al.* Production of oxidants by ion bombardment of icymoons in the outer solar system. *Advances in Astronomy* **2011**, 1–10 (2011).
35. Do, N. H. & Cooper, P. D. Formation and reaction of oxidants in water ice produced from the deposition of RF-discharged rare gas and water mixtures. *J. Phys. Chem. A* **117**, 153–159 (2013).
36. Hand, K. P. & Brown, M. E. Keck II observations of hemispherical differences in H₂O₃ on Europa. *Astrophys. J. Lett.* **766**, L21 (2013).
37. Siegel, S., Flourny, J. M. & Baum, L. H. Irradiation yields of radicals in gamma-irradiated ice at 4.2 and 77 K. *J. Chem. Phys.* **34**, 1782–1788 (1961).
38. Bednarek, J. & Plonka, A. Single-crystal electron-spin resonance studies on radiation-produced species in the ice Ih. II. The HO₂ radicals. *J. Chem. Soc. Faraday Trans.* **83**, 3725–3735 (1987).
39. Loeffler, M. J., Fama, M., Baragiola, R. A. & Carlson, R. W. Photolysis of H₂O₂–H₂O₂ mixtures: The destruction of H₂O₂. *Icarus* **226**, 945–950 (2013).
40. Gerakines, P. A., Moore, M. H. & Hudson, R. L. Energetic processing of laboratory ice analogs: UV photolysis versus ion bombardment. *J. Geophys. Res.* **106**, 33381–33385 (2001).
41. Moore, M. H., Ferrante, R. F. & Nuth, J. A. III Infrared spectra of proton irradiated ice. *Adv. Space Res.* **32**, 1206–1225 (2008).
42. Moore, M. H., Ferrante, R. F. & Nuth, J. A. III Infrared spectra of proton irradiated ice containing methanol. *Planet. Space Sci.* **44**, 927–9351 (1996).
43. Zasetsky, A. Y. *et al.* Ice particle growth in the polar summer mesosphere: Formation time and equilibrium size. *Geophys. Res. Lett.* **36**, L15803 (2009).
44. Evans, W. P. J., Huntten, D. M., Llewellyn, E. J. & Vallance-Jones, A. Altitude profile of the infrared atmospheric system of oxygen in the dayglow. *J. Geophys. Res.* **73**, 2885–2896 (1968).
45. Baumgarten, G. & Fiedler, J. Vertical structure of particle properties and water content in noctilucent clouds. *Geophys. Res. Lett.* **35**, L10811 (2008).
46. Guzman, M. I., Häidebrandt, L., Colussi, A. J. & Hoffmann, M. R. Cooperative Hydration of Pyruvic Acid in Ice. *J. Am. Chem. Soc.* **128**, 10621–10624 (2006).
47. Allamandola, L. J., Sandford, S. A. & Valero, G. J. Photochemical and thermal evolution of interstellar/precometary ice analogs. *Icarus* **76**, 225–252 (1988).
48. von Cossart, G., Fiedler, J. & von Zahn, U. Size distributions of NLC particles as determined from 3-color observations of NLC by ground-based lidar. *Geophys. Res. Lett.* **26**, 1513–1516 (1999).
49. Eremenko, M. N. *et al.* Shape and composition of PMC particles derived from satellite remote sensing measurements. *Geophys. Res. Lett.* **32**, L16S06 (2005).
50. Bartels-Rausch, T. *et al.* A review of air–ice chemical and physical interactions (AICI): liquids, quasi-liquids, and solids in snow. *Atmos. Chem. Phys.* **14**, 1587–1633 (2014).
51. Leto, G. & Baratta, G. A. Ly- α photon induced amorphization of I, water ice at 16 Kelvin. Effects and quantitative comparison with ion irradiation. *Astronomy and Astrophysics* **397**, 7–13 (2003).
52. Cottin, H., Moore, M. H. & Bénilan, Y. Photodestruction of relevant interstellar molecules in ice mixtures. *Astroph. J.* **590**, 874–881 (2003).

**Acknowledgements**

Experimental part of the work was performed within the framework of the state assignment No. 0035-2019-0008. Processing of experimental data was supported by the Program of the RAS Presidium No. 5 (project No. 0035-2018-0002). Theoretical part of the work was funded by RFBR (project No. 17-05-01142). The data used in this study can be downloaded from [http://www.iapras.ru/english/structure/dep_240/dep_240.html](http://www.iapras.ru/english/structure/dep_240/dep_240.html).

**Author Contributions**

All authors contributed to the conceiving ideas, data interpretation and writing. O.S. and M.Y.K. carried out the experiments.

**Additional Information**

**Competing Interests:** The authors declare no competing interests.
