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The noctilucent cloud (NLC) spectral observations in Kazakhstan in 2006–2007

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The results of the noctilucent cloud (NLC) spectral observations from Kazakhstan are presented. The NLC spectra are supposed to be formed due not only to scattering, but also to luminescence of cloud particles.

Keywords: Noctilucent cloud (NLC); Spectrum; Scattering; Luminescence

1 Introduction

The NLC spectral observations that had taken place previously (e.g., Piazzi 1886; Störmer 1933; Astapovich 1939; Bronshten and Grishin 1970; Fogle and Haurwitz 1966; Vasilyev 1967; Savigny et al. 2004) were not numerous. There was little information from them, and their interpretation was ambiguous. Besides, the problem of possible NLC luminescence (in order to explain unusual "bluish-silver-steel" hue of the NLC) was repeatedly discussed. In particular, a relation between zenithal distances of the NLC field visual upper boundary and lighting conditions was considered by Chistyakov and Tejfel (1953), and Chistyakov and Tejfel (1956). In the case of luminescence this relation must approximately correspond to the passage of solar rays (that illuminate the NLC) above the ozone layer absorbing solar UV radiation. Unfortunately, these types of regular observations are not carried out any more.

We can understand it if we know that the account of twilight influence on the NLC spectrum is very difficult because of low NLC position over the horizon. Obtaining the real NLC spectra is a problem that is complicated enough. Mostly, NLC are observed within 3–15° over the horizon after the sunset, against the dusty twilight segment. Its brightness, color and, certainly, spectral characteristics change depending on such factors as observation time, azimuth and the Sun immersing depth behind the horizon, also on the NLC field altitude over the horizon, and weather conditions. A big city neighborhood, with intensive street illumination, adds some additional spectral lines of mercury and neon lamps to the twilight segment spectrum. Besides, all the characteristics listed above change from day to day during the observation season. One should also consider the complicated dependence of air masses on the geometry

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of incident solar radiation and the geometry of observation of the NLC field and twilight segment. We should also keep in mind a non-uniform vertical distribution of absorbing gases (ozone and water vapor).

2 Apparatus. Observation and processing methods

For NLC observation we have developed and then made up a light grasped (1:1.5) celestial spectrometer with the angular field of 20° along all the spectral slit length. Our spectrometer is of moderate resolution, with the transparent diffraction grating having 250 touch/mm and with the first order spectrum registration on the large-formatted (36×24 mm^2) CCD camera of STL11000M. In order to minimise the second order spectrum blending effect at the $\lambda>700$ nm spectral range, the glass filter of KS-14 was used. For a confident identification of the NLC spectral details registered, the additional digital camera was used. It was placed on the same platform as the spectrometer. Their optical axes' directions coincided. The linear dispersion was 8.2 Å/pixel. The spectrometer maximum spectral resolution was the same. The spectral range observed was from 380 nm to 1000 nm. We paid special attention to the scale conformity between the NLC fields registered in the pictures and their spectrograms (Fig. 1).

Using the basic stars' (Capella and Polaris (α UMi)) spectrograms we defined instrumental profiles of the oxygen (O_2) and water vapor (H_2O) telluric bands for some air masses. These were taken into account during processing the twilight segment and NLC spectrograms. In order to define the spectrometer pass-function we also use the Polaris and Capella's spectra. Using the spectrometer's pass-function and the energy absolute distribution in the solar spectrum (Makarova and Kharitonov 1972) we have calculated what the solar spectrum would be out of the Earth's atmosphere bounds if it was registered with our spectrometer.

From a great number of the NLC spectra we chose only those which corresponded to the best solar illumination of the NLC fields (a case of the solar ray passage above the 40 km level over the Earth's surface without the solar radiation appreciable extinction by the terrestrial atmosphere at all the spectral range) and with a minimum

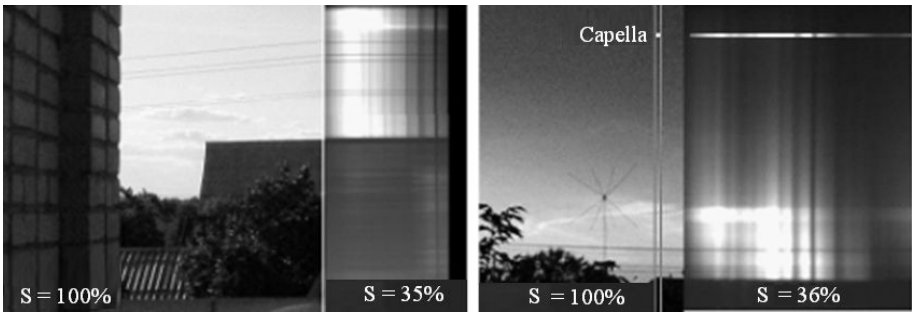


Figure 1 A scale conformity between the NLC fields registered with a camera and with a spectrometer in the afternoon and in the evening obtained using landscape details (left) and the star Capella (α Aur).

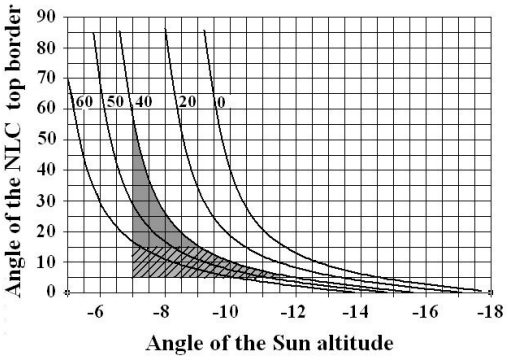


Figure 2 The NLC illumination top border dependence on the Sun immersing angles for some altitudes of the solar ray passage over the Earth's surface (km). The area shaded-striped is the best conditions for the NLC spectra measurements.

influence of adjacent parts of the twilight segment on the NLC spectra (the case is: the 8–12° angles of the Sun immersing behind the horizon and the 5–15° elevation angles of the NLC fields over the horizon) (Fig. 2).

Then the spectra of adjacent twilight segment parts being at a distance of less than 0.3 of an air mass from the NLC fields were subtracted from the NLC spectra. The NLC spectra corrected this way, and the adjacent parts of the corrected twilight segment, were then also corrected for the influence of air masses. In other words, they were taken "outside the atmosphere". Using the out-of-atmosphere NLC- and solar spectra we obtained the NLC intensities (brightnesses) as ratios of the NLC spectra to the solar ones. One of our papers (Vdovichenko, Kirienko, Sinyaeva 2009) studies the spectral properties of the twilight segment.

As an example, we give the 2007 (19–20 July) NLC spectra corrected, when there were the best observation conditions (Fig. 3).

3 Observation results and their analysis. Luminescence as one of the possible mechanisms of NLC re-radiation

For the NLC fields whose illumination conditions conformed to the requirements described above, and for the "pure" twilight segment's parts being away from them not more than by 0.2–0.3 of an air mass, we should note some features of their radiative properties.

1. As we expected, in many "pure" NLC spectra, near their top border, which is illuminated with solar rays passing through the dense layers (10–30 km) of the atmosphere, we can see a depression at a range of 500–700 nm caused by ozone absorption (Chappuis bands).

2. If the NLC fields are illuminated with solar rays passing above the 40-km atmospheric layer (where ozone absorption is negligible), then at the range of $\lambda > 450$ nm their scattering properties are well enough approximated by the dependence of $I \sim \lambda^{-n}$, where I is a scattering light brightness. As for n, then in the adjacent

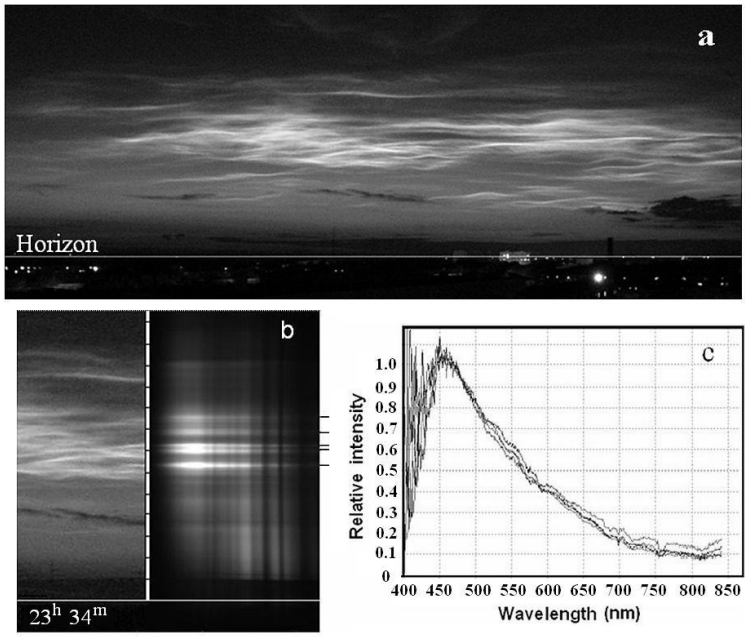


Figure 3 The NLC spectra of 19–20 July of 2007. $t_{\rm local} = 23^h34^m$, $Z = 82°$–$84°$, where Z is a zenithal distance. (a) The NLC field image. (b) The fragment of the NLC field image (left) together with its spectrogram (right). (c) Spectral distributions of the NLC relative intensity for five details (marked on the right hand side) of the fragment.

parts of the twilight segment this parameter is changed with zenithal distances but it remains less than 4 ($n < 4$), while for the "pure" NLC spectra $4 \leq n \leq 5$.

3. We should pay attention to a steep slope of intensity for all NLC fields observed at $\lambda < 450$ nm but it is absent in almost pure parts of the adjacent background. It is necessary to note that this exclusive feature of the NLC spectra (in comparison with the spectra of the twilight segment adjacent parts) occurs at the first stage of spectra processing and depends on neither the way of air mass account, nor on the kind of out-of-atmosphere solar spectrum approximation.

We shall try to analyze the NLC brightness (intensity) spectral dependences that we have obtained. They are presented in Fig. 4.

As all the NLC spectra are like each other we averaged them and drew a smooth average curve. Then we compared them with N.I. Grishin and B. Fogle's spectra (Bronshten and Grishin 1970). However, we could not do it correctly because these authors had not described in detail the standardization and calibration of their spectra. Nevertheless, we presented their results in one scale with our results in order to analyze the intensity general change with wavelengths in the NLC spectrum (Fig. 5).

First, in all three curves there is a maximum brightness at a range of 420–460 nm.

Second, in our curve (1) and in Fogle's curve (2) there is a typical intensity slope towards long waves that is usual for the function of $I \sim \lambda^{-n}$. For our NLC spectra $n \approx 5$, while for Fogle's curve it closes in 7.

It is to be noted that $n > 4$ in both considered cases, and that there is an obviously

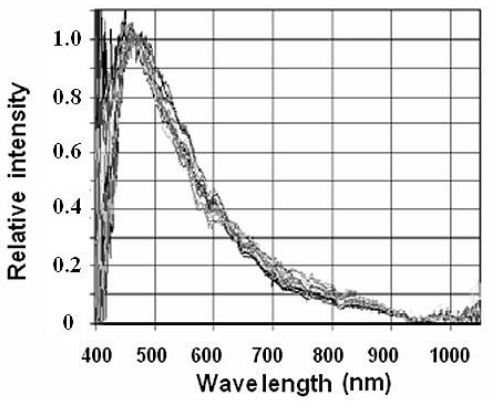


Figure 4 The summary figure of the NLC spectra obtained on 19–20 July of 2007. There are 16 spectra. Each spectrum corresponds to one measurement.

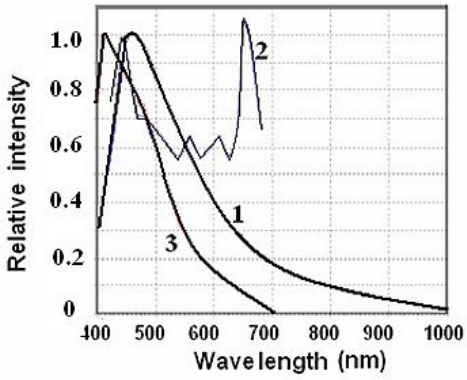


Figure 5 Comparison of the NLC relative intensity spectral distribution from our measurements (in ratios to the Sun) (curve 1) with the same from N.I. Grishin (in ratios to the maximum brightness) (curve 2) and with the same from B. Fogle (curve 3).

expressed brightness maximum at the short-wavelength range. In our opinion, most likely it signifies a luminescence phenomenon, but not Raleigh scattering on very fine particles, when $n = 4$.

If we consider both the scattering on ice particles and the luminescence to contribute "themselves" to a formation process of the NLC spectra, then we can try to select both phenomena assuming the NLC-aerosol scattering is submitted the law of $I \sim \lambda^{-n}$ (at the initial approach), where n changes from 1 to 4, and an NLC spectral brightness observed is $I_\lambda = I_{\lambda\mathrm{scat}} + I_{\lambda\mathrm{lum}}$, where $I_{\lambda\mathrm{scat}}$ is a scattering spectral brightness, $I_{\lambda\mathrm{lum}}$ is a luminescence one. Then the luminescence brightness changing with wavelengths can be found with only subtraction. The results of such calculations for $n = 0, 1, 2, 3, 4$ are presented in Fig. 6.

Figure 6a presents the curves of $I \sim \lambda^{-n}$ for aerosol scattering, together with the NLC spectrum. The curves are related to the intensity at λ 900 nm. Figure 6b shows the luminescence spectrum supposed. It is obtained as $I_{\lambda\mathrm{lum}} = I_\lambda - I_{\lambda\mathrm{scat}}$, where I_λ

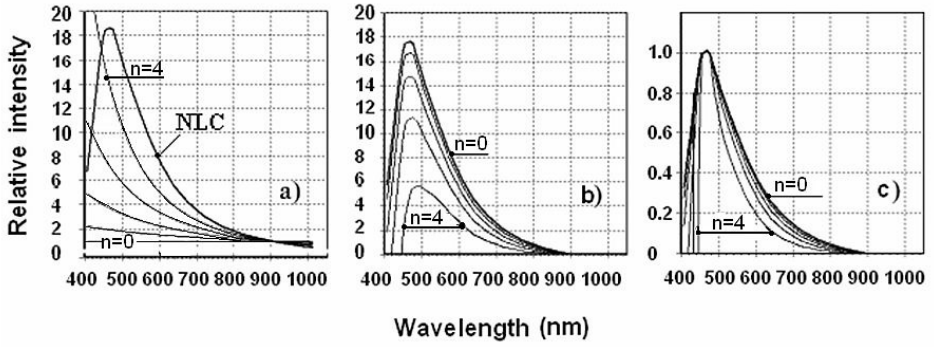


Figure 6 In here the NLC spectrum is presented as a result of the two effects (scattering and luminescence). The explanation is in the text.

is an observed intensity, $I_{\lambda\mathrm{scat}}$ is a calculated ($\sim\lambda^{-n}$) one. A minimum luminescence contribution corresponds to the Raleigh scattering, when $n = 4$, and a maximum one corresponds to the case, when $n = 0$. Figure 6c presents the same as Fig. 6b, but in ratios to the maximum intensity at λ 470 nm.

We will try to bring to light some aspects of photoluminescence as the most obvious process of luminescence in the case the NLC concerning. Of course, we mean the mesosphere conditions though some other mechanisms of luminescence should not be excluded, either.

4 Some words about photoluminescence

Tens of thousands of substances can give rise to secondary radiation (e.g., luminescence). Many living organisms, albumen combinations, microorganisms, huminous substances (some organic remain remade by nature: leaves, grass, the remains of fauna etc.) exist as aerosols (both in the atmosphere and in the waters) as is shown by Karabashev (1987), Gorshkova et al. (2009), Lavrik et al. (1999). Hydrocarbon combinations (in particular, oil products), some gases at lower pressures, and metal vapors which at the upper atmosphere exist as the products of micrometeor combustion, or substances spilling out of comets' tails, or pieces of minicomets disintegrated – all of them can be sources of luminescence. But this list is too incomplete.

A very big study waits for NLC researchers in the future. We will have to produce an atlas of luminescence spectra of various substances. As a result of careful analysis of them, we will be able (using a method of consecutive exceptions and restrictions) to reveal the most probable applicants responsible for the NLC luminescence, and then it can be explained how these substances get to the mesosphere.

Nevertheless, some comparative analysis can be done even today. In order to identify a luminescence process, it is necessary to have at hand not only its radiation spectrum but also the exciting radiation spectrum, and we must also know an exciting light wavelength. The major characteristics of such a substance are the wavelength of the maximum radiation and the luminescence spectrum profile. The elementary fluorescence spectra look like smooth curves with the only maximum (Karabashev 1987).

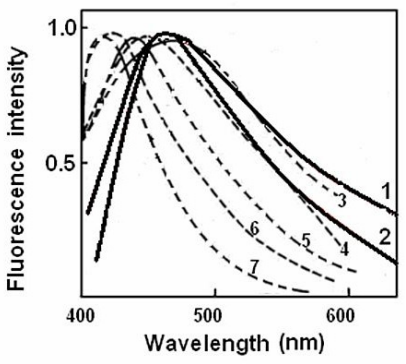


Figure 7 Our NLC spectra (curves 1 and 2) and the fluorescence spectra of chloroform solutions of some organic combinations getting into the oil composition. The spectra presented are related to the maximum radiation (Florovskaya 1957). 3, silica gel pitches at $\rho = 0.867$; 4, the same at $\rho = 0.878$; 5, the same at $\rho = 0.871$; 6, oils with $\rho = 0.835$; 7, naphthenic acids with $\rho = 0.837$.

Usually, the half-width of fluorescence spectra is 50–100 nm, and some complex substances can have the half-width of such a spectrum at almost 100 nm and even more. The fluorescence spectra are shifted towards the long-wavelength spectral region in comparison with absorption ones. And what is more, a phosphorescence spectrum is shifted farther than a fluorescence one. If the $\lambda_{\max}$ of a substance luminescence spectrum is known, one can identify this substance.

4.1 Oil and the oil product fluorescence

As a result of human activity, during the last 100–150 years, many substances penetrating into the atmosphere and into the ocean, and then from the ocean to the atmosphere again, have their own fluorescence. Oil and oil products, sewage of enterprises, waste, etc., are the most widespread pollutants. The most important chemical elements which oils consist of are carbon (83–87%), hydrogen (11–14%), sulfur (up to 5%), oxygen (up to 3%) and nitrogen (more than 1%), and also metals as trace elements. Thousands of individual organic substances consist of these elements.

It has been shown that all organic combinations getting into oil compositions are divided into: 1) not fluorescing ones, 2) fluorescing in the far UV spectrum, 3) fluorescing in the near UV- and short-wavelength visible spectrum (Fig. 7), and 4) fluorescing mainly in the visible range of the spectrum.

We cannot also completely exclude the possibility of organic matter such as decay products of comets getting into the atmosphere of the Earth from space.

In the twentieth century, in the interstellar medium, it was found (by radio astronomy methods) about a hundred different molecules – from simple molecular hydrogen (H_2) to 13-atomic cyanopolyyne ($HC_{11}N$), that is a long chain of carbon atoms closed at the ends with hydrogen and nitrogen. As for organic compounds, in interstellar space (in 1969), the first compound that had been found, was formaldehyde, and the most recent discovery, published in early 2004, has been the molecules of anthracene

($C_{14}H_{10}$) and pyrene ($C_{16}H_{10}$) containing 24 and 26 atoms, respectively. These substances belong to the group of polycyclic aromatic hydrocarbons (which are composed of some linked hexagonal rings of carbon atoms) that, for example, are components of the most part of greasy black smoke emitted by a poorly adjusted diesel engine. The group of colleagues of Adolf Witt from the University of Toledo (Ohio, USA) discovered these molecules by studying the ultraviolet spectra of the Red Rectangle planetary nebula located in the Unicorn constellation at a distance of more than two thousand light years from Earth (http:// www.vokrugsveta.ru/vs/article/1761/).

The flight of the "Stardust" spacecraft to the Wild-2 comet has given a striking result (http://stardust.jpl.nasa.gov/news/news108.html). A significant amount of linked nitrogen (in the form of methylamine or ethylamine) and a number of organic compounds, including the molecules of the set of polycyclic aromatic hydrocarbons such as anthracene and pyrene, was found in the airgel trap that was set on board "Stardust". It is not yet clear what processes lead to their formation. The primitive organic material collected is of great interest for astrobiologists, as it plays an important role in the biochemical processes on the Earth. It could be formed both in the protoplanetary gaseous-dusted cloud (from which our solar system was formed) and in the course of chemical processes in the nebulae of interstellar space.

As at present there is almost no doubt that NLC particles consist of condensation nuclei clothed in ice covers, we will give some attention to questions connected with water luminescence.

4.2 Water and the water solution luminescence

In laboratory research (Gorshkova et al. 2009; Lavrik et al. 1999), natural water has been found (under exciting UV radiation influence) to reradiate a spectral response that depends on both the exciting radiation parameters and properties of organic substances which are not eradicated from water. Usually, a simple distillation or filtration of water does not clear it of organic impurities.

These impurities originate from a humic background of the Earth atmosphere. We breathe in not pure air, but air in which there is always a humic substance. Humic substances are a product of humification, that is organic remains (leaves, grass, the remains of fauna etc.) processed by nature. The real structure of humic substances is not found yet, but the molecules making them are well known. In the vegetative remains that comprise cellulose and other carbohydrates, and also albumens, lignins, tannins etc., and in the fauna remains (microorganisms) there are phenol combinations of metabolism and disintegration products, and amino acids and peptides. Individual molecules of all the listed categories have their own luminescence either in the UV-, or dark blue spectrum.

A quantum yield of fluorescence of humic combinations (that exist in fresh or salty water) can reach several percent. However, we can detect and control extremely small densities of substances (up to 10^{-12}–10^{-6} g/ml) (Karabashev 1987).

Considerable contributions to the fluorescence integrated intensity are given by albumen or phenol combinations at λ 270 nm exciting radiation.

Gorshkova et al. (2009) and Lavrik et al. (1999) affirm a dissolved organic substance (DOS) to be present in all kinds of natural water, without exception, and though its typical concentration in water can be insignificant (about 20–50 mg/l), the

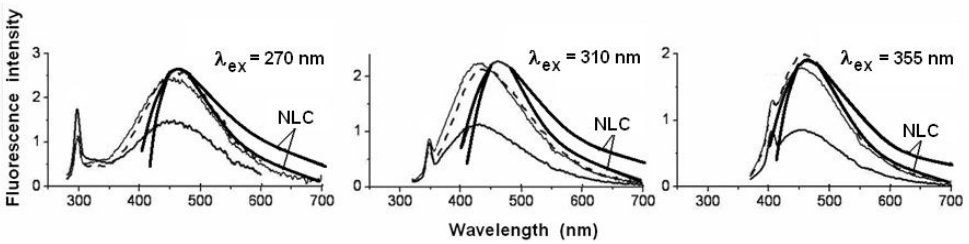


Figure 8 The NLC spectra and the usual fluorescence spectra of various-origin natural water samples (Gorshkova et al. 2009). For the spectrum excitation three wavelengths of exciting radiation in the UV region were consistently used: 270, 310 and 355 nm.

DOS(es) make a considerable "tank" of organic carbon on the Earth that exceeds the total stock of organic substance of all living organisms (!). The DOS of natural origin is one of the most important components of the fresh-water and marine ecosystems, playing a key role in the circulation of carbon and in our planet's climate changes.

Of all the DOS fluorescence physical characteristics, its spectral distribution was studied better than other ones. On average, its maximum lies at λ463 nm, and the half-width is of 130 nm. In Fig. 8 the usual fluorescence spectra of natural water samples of various origins are given.

The water-soluble products of decomposition of substances of vegetative origin are easily formed under natural conditions and can be transferred as aerosol. That explains a universal prevalence of the "blue" fluorescence (Kalle 1963). Some corresponding observations have been carried out in the Baltic and North Seas, in some parts of the Atlantic and Pacific oceans (at the temperate and tropic latitudes), which are: Bay of Biscay, Canary current, the Sargasso and Caribbean Seas, the Panama Canal, the equatorial current in the Pacific ocean and the southern part of its tropical zone, the Kurosivo current's region, etc. The layers at different conditions of the DOS formation, including the ones at depths of about 10 km, were surveyed. In total, more than 200 samples of water were taken. It was reliably established that by a constant spectral structure of exciting radiation the form and reciprocal correlation of the spectral band intensities of the DOS luminescence do not practically change across the World Ocean, and poorly depend or do not depend at all on the structure and origin of waters. On the contrary, if the spectral structure of exciting radiation changes, then a DOS luminescence band forms and also the position of the maximum in it strongly changes.

Let us consider whether there are some necessary conditions for luminescence to occur around the mesopause.

From Fig. 9 we can see that most of sunlight with $\lambda = 0.01$–0.18 μm is absorbed in the atmosphere layers at altitudes above 100 km. The radiation of $\lambda = 0.2$–0.3 μm is, mainly, absorbed at the altitudes that are more or equal to 30–40 km. The main gaseous components, which are responsible for sunlight absorption in the UV spectrum, are specified in Fig. 9 (O_2, O, N_2, N, NO, O_3).

Atmospheric nitrogen and oxygen are responsible for absorption in the extreme ultraviolet spectral region. The O_2 and N_2 molecules strongly absorb sunlight at the spectral range from 100 to 200 nm. All these components play an important role in

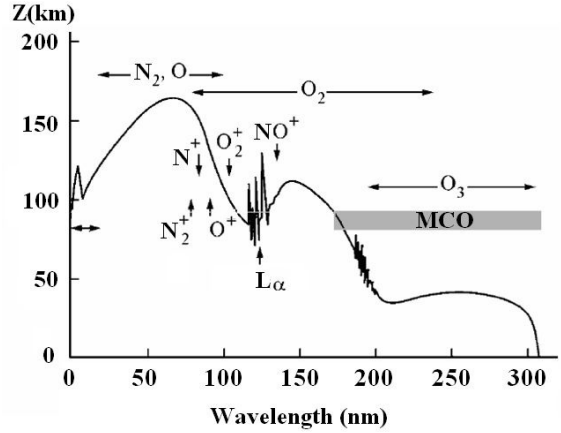


Figure 9 The atmosphere altitudes, where atmospheric optical thickness (beginning from the upper boundary) is 1 (Goody and Yung 1989).

the sunlight absorption in the upper atmosphere and are responsible for its thermal regime, and also for the ionosphere formation. The ozone molecules play a considerable role in absorption of solar UV radiation. Thus, just the Hartley and Huggins ozone bands are very important in the mesosphere and stratosphere thermal regime formation: the temperature maximum at about the 50 km altitude (stratopause) is just caused by radiation heating. Besides, the ozone absorption protects the Earth's surface from the solar extreme UV radiation that is dangerous for the Earth's biosphere.

It follows from the above that the NLC cannot be irradiated with radiation that is shorter than 170 nm as it is absorbed by the upper atmosphere layers. However, the spectral range of more than 170 nm is quite accessible to fluorescence excitation, all the more so that the spectral region of water (H_2O) absorption maximum section is at a spectral range between 170 and 180 nm.

Light scattering, at all altitudes of the terrestrial atmosphere, is mainly of aerosol character, i.e., it is defined by the abundance of scattering particles, to a marked degree, than by air density fluctuations (Rosenberg 1963). Even without considering the possible mechanisms of moisture and aerosol transport to high altitudes (it is a separate independent problem), we can already use this experimentally established fact in considering the key questions connected with the probable presence of not only water vapor, but also humic or techno-genesis aerosol particles (capable of fluorescence) in the NLC formation region. We can reveal (using a fluorescence technique) very small concentrations of some substances, such as 10^{-9} and even 10^{-12} g/ml (Karabashev 1987). Besides, an effective fluorescence section is ten orders of magnitude higher than a Raleigh scattering one (Timofeev and Vasilyev 2007).

Conclusion

In conclusion we can note the following.

It is found out that in nature there is practically no pure water; it exists mainly as solutions of organic matter. Moreover, water consists not of separate molecules of H_2O, but of their clusters ($(H_2O)_m$, where m can reach some hundred thousands and more molecules), or of clathrates when other substances' molecules come in the composition of a water molecular complex. These complexes, while they are getting to the atmosphere (independently on kind of way to there or on the phase state (fluid or gaseous)), also carry away a set of organic molecules with them. Besides, organic aerosols can get there by themselves (in some independent way). Moreover, space gives some cosmic dust to the mesosphere. This material arises from sporadic meteors, annual meteorite showers or from comet tails which can be resources of different chemical combinations' ions and metal vapors. All the substances named above can come into the NLC and be some re-radiation (scattering or fluorescence) resources. At present, most NLC investigators prefer to ice nature of the NLC. In connection with it there rises the question on luminescence character of the specific ice form that can be formed under the mesopause conditions (as is known nowadays, there are 12 or 14 kinds of ice in nature). We still do not have this data in spite of the search undertaken, so we are very interested in such laboratory finds to be completely sure of our proposals of the possible luminescent nature of the NLC spectra. The authors will be very grateful for any additional material concerning this theme.

The detailed results of this investigation can be found in the authors' monograph entitled "The Mesospheric Noctilucent Clouds: Problems and Solutions" (Vdovichenko and Kirienko (2012)).

References

Astapovich I.S. (1939) Izv. AN USSR (in Russian), series geograph. and geophys., 2, 183.

Bronshten V.A., Grishin N.I. (1970) Noctilucent clouds (in Russian), "Nauka", Moscow, 360 pp.

Chistyakov V.F., Tejfel V.G. (1953) (in Russian) J. ATsirk AN SSSR 139, 9.

Chistyakov V.F., Tejfel V.G. (1956) (in Russian) Bull. VAGO 19, 53.

Florovskaya V.N. (1957) Luminescent-bituminological method in oil geology (in Russian), Moscow University Press, Moscow, 291 pp.

Fogle B., Haurwitz B. (1966) (SSRV 6 279F Kluwer Academic Publishers Provided by the NASA) Astrophysics Data System, 280.

Goody R.M., Yung Y.L. (1989) Atmospheric radiation. Theoretical Basis N.Y. Oxford Univ. Press, 519 pp.

Gorshkova O.M., Patsaeva S.V., Fedoseeva E.V. et al. (2009) (in Russian), J. Water: chemistry and ecology 11, November, 31.

Kalle K.(1963) Über das Verhalten und die Herkunft in der Gewässern und in der Atmosphäre vorhandenen himmelblauen Fluoreszen Dt. Hydrogr. Zs. 16 4.

Karabashev G.S. (1987) Fluorescence in the ocean (in Russian) "Hydrometeoizdat", Leningrad.

Lavrik N.L., Andreevsky V.M., Markushin Yu.Ya. et al. (1999) J. Chemistry in interests of a sustainable development **7**, 2.

Makarova E.A., Kharitonov A.V. (1972) Energy distribution in the solar spectrum and the solar constant (in Russian) "Nauka", Moscow.
Piazzi S.C. (1886) Nature **34**, 311.
Rosenberg G.V. (1963) The twilight (in Russian) Gos. izd. phys.-math. literature, Moscow, p. 380.
Savigny C., Kokhanovsky A., Bovensmann H. et al. (2004) J. Advances in Space Research 34, 851.
Störmer C. (1933) Oslo Univ. Obs. Publ. 6.
Timofeev Yu.M., Vasilyev A.V. (2007) Basics of theoretical atmospheric optics (in Russian), St.-Petersburg, 152 pp.
Vasilyev O.B. (1967) Astrophysical research of noctilucent clouds (Russian) (Astrosovet AN SSSR, Moscow).
Vdovichenko V.D., Kirienko G.A., Sinyaeva N.V. (2009) (Russian) Izvestiya NAN RK Ser. phys.-math. 4, 120.
Vdovichenko V.D., Kirienko G.A. (2013) The mesospheric noctilucent clouds. Problems and solutions (in Russian), 290 pp., www.lap-publishing.com, design 81372 ISBN 978-3-659-36492-1.