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Stratospheric NO_2 Content according to Data from Ground-Based Measurements of Solar IR Radiation

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Abstract—Atmospheric NO_2 content data obtained from regular ground-based measurements of solar IR radiation in the St. Petersburg region using a spectrometer with a high spectral resolution are analyzed. The absorption spectra of the NO_2 multiplet in the vicinity of ~2915 cm^{-1} allow one to obtain data on variations in the stratospheric total content of NO_2 in 2009–2011. The accuracy of these data is estimated from their comparison with data obtained from independent ground-based and satellite measurements. The parameters of the seasonal cycle of the stratospheric content of NO_2 are estimated. The body of data accumulated during these measurements in the IR region made it possible to isolate the component of a daytime photochemical increase in the stratospheric content of NO_2 and estimate its rate.

Keywords: nitrogen dioxide, spectroscopic measurements, Fourier interferometer
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1. INTRODUCTION

In the absence of lower tropospheric pollution, the basic portion of atmospheric nitrogen dioxide (NO_2) is concentrated in the stratosphere. Nitrogen dioxide enters the group of nitric oxides (NO, NO_2, and NO_3) that are closely interrelated through both photolysis and oxidation reactions [1]. Both NO and NO_2 (NO_x) turning into each other are formed in the stratosphere mainly due to the oxidation of nitrous oxide (N_2O) [2]. In this case, the NO_x group, on the one hand, participates in the catalytic destruction of ozone and, on the other hand, decelerates this destruction: it transforms active (in relation to ozone) chlorine and hydrogen compounds into inactive ones such as $ClONO_2$ and HNO_3 [2]. Thus, regular measurements of the stratospheric content of NO_2 are urgent for the problem of monitoring the ozonosphere. However, the current estimates of multiyear NO_2 trends for the stratosphere are of a contradictory character, and the reasons for these long-term changes are not entirely clear (see, for example, [3, 4]).

The atmospheric content of NO_2 has been measured using different methods and instruments for several decades. A major portion of ground-based remote observations is being carried out within the framework of the International Network for the Detection of Atmospheric Composition Change (NDACC) [5], which is a global network of stations at which long-term measurements of the gas composition of the atmosphere are performed. At these stations, the spectrometry of zenith-scattered visible solar radiation in the twilight and of direct solar IR radiation in the daytime is used to measure the stratospheric content of NO_2 [5]. The pioneering monitoring of the stratospheric content of NO_2 was carried out in the late 1980s to early 1990s in the Soviet Union at the Kislovodsk high-altitude (by measurements of direct solar radiation) and Zvenigorod (by measurements of zenith-scattered solar radiation) scientific stations of the Institute of Atmospheric Physics, Russian Academy of Sciences [6, 7]. On a global scale, the content of NO_2 has been measured for many years and is being measured now within the framework of a number of satellite experiments. In particular, a large amount of data on the vertical distribution of NO_2 has been obtained due to eclipse measurements of solar IR radiation (with HALOE and ACE-FTS satellite instruments) and visible radiation (with SAGE I–III and ACE-MAESTRO instruments), limb measurements of IR radiation (with ILAS I–II and MIPAS instruments), measurements of visible radiation (with an OSIRIS instrument), and due to measurements of visible radiation during the setting of stars (with a GOMOS instrument). In addition to both eclipse and limb satellite measurements, the global distribution of the NO_2 content throughout the atmospheric thickness has been monitored in the last decades with scanning satellite spectrometers by nadir measurements of outgoing visible radiation (GOME 1–2, SCIAMACHY, and OMI).

Since 2009, scientists from the Research Institute of Physics, St. Petersburg State University (RIP

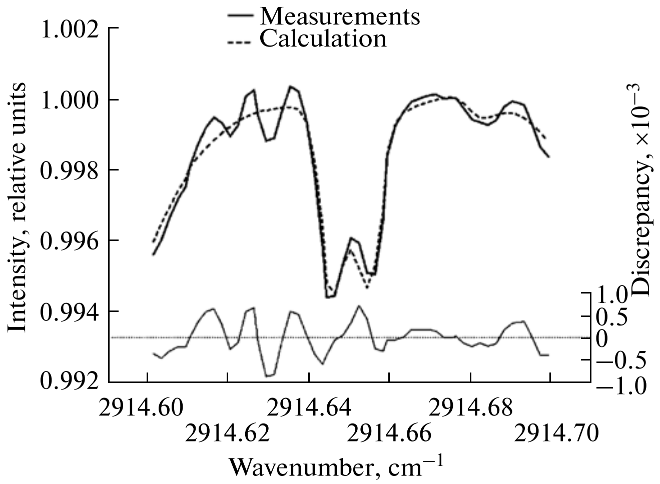

Fig. 1. An example of interpreting the spectrum of direct solar IR radiation recorded at the RIP SPbSU on April 11, 2010, at 11:59; the sun's zenith angle was 56°, and the measured vertical content of NO_2 amounted to 2.51×10^{15} mol/cm^2.

SPbSU), have regularly been measuring the atmospheric content of NO_2 in the St. Petersburg region (Petergof, 59°53′ N, 29°49′ E) using IR spectrometry according to direct solar radiation [8, 9]. In this work, the characteristics of variations in the stratospheric content of NO_2, which were obtained from an analysis of the 2009–2011 measurement results, are given; the accuracy of the IR method is analyzed on the basis of comparisons with data obtained from independent (ground-based and satellite) measurements; the parameters of the seasonal cycle of the stratospheric NO_2 content are determined; and the rate of a photochemical increase in the stratospheric daytime content of NO_2 is estimated.

2. DETERMINING THE NO_2 CONTENT FROM MEASUREMENTS OF IR RADIATION

The method of determining the NO_2 content in the atmospheric thickness is based on an analysis of the spectra of molecular absorption of direct IR solar radiation. There are several bands of strong NO_2 absorption in the infrared spectral region; however, most of these bands are overlapped by bands of strong water-vapor (H_2O) absorption. This makes these spectral regions unsuitable for ground-based measurements of the NO_2 content because of usually high H_2O concentrations at the land surface. In connection with this, a number of NO_2-absorption lines located in the vicinity of 3.4 μm prove to be more favorable in ground-based measurements [10].

The spectra of solar radiation were measured using a spectral complex developed (at the RIP SPbSU) on the basis of a Bruker-IFS125 HR spectrometer of high resolution and a solar tracking system for pointing at the sun's disk. The Bruker-IFS125 instrument is an infrared Fourier-interferometer with a spectral resolution of up to 0.002 cm^{-1} within the spectral region 1–15 μm [8]. In order to determine the atmospheric content of NO_2, measurements within the spectral microwindow 2914.6–2914.7 cm^{-1}, which includes a double vibrational–rotational NO_2-absorption line with centers of about 2914.6434 and 2914.6520 cm^{-1}, were used (Fig.1). These spectra were interpreted using the SFIT2 v3.93 software [11] developed specially for the solution of inverse problems on retrieving the vertical distributions of different gases from the results of ground-based measurements with IR Fourier interferometers. The SFIT2 algorithm is based on the method of optimum estimate (statistical regularization) and it uses a direct approach in calculating atmospheric-transmission spectra (line-by-line). The parameters of the fine structure of molecular-absorption bands, which are necessary for these calculations, were taken from the HITRAN-2004 spectroscopic database [12]. A priori information on the state of the atmosphere (on both temperature and pressure profiles) for each of the measurement days was taken from data obtained from daily aerological soundings at the Voeikovo station (59°57′ N, 30°43′ E) [13].

Figure 1 shows an absorption band within a microwindow of ~2914 cm^{-1}, which is used in determining the NO_2 content. Figure 1 contains an example of interpreting the spectrum of direct solar radiation for April 11, 2010. The disagreement between measured and calculated (on the basis of the radiation-transfer model) radiation spectra is minimized in solving the inverse problem. In addition to NO_2, the contributions of the molecular absorptions of some other components—water vapor (H_2O), methane (CH_4), and water isotope (HDO)—were taken into account in the calculations. Searching for a solution (total NO_2 content) is an iterative process whose completion criterion is the problem of convergence, i.e., the correspondence of spectral divergence to the value of instrument noise. Therefore, the estimate of noise is very important in interpreting the results of measurements and it is taken into account in the solution algorithm as a parameter of the signal-to-noise ratio. This ratio amounted to 921 for the spectrum in Fig. 1 (on average, the signal-to-noise ratio amounted to ~550). It should be emphasized that the molecular absorption in the NO_2 lines under consideration is low: its contribution to the atmospheric optical thickness amounts to only a thousandth of portions even in the line centers (see Fig. 1).

The scheme of interpreting spectra, which is used in the SFIT2 algorithm, implies variations in the profile of the atmospheric vertical distribution of NO_2 with respect to an a priori profile. The profile known from the US standard average annual atmosphere model was used as such a priori profile [14] (see below). The a priori uncertainty of this profile was specified in the form of a model covariance matrix with a correlation radius of 5 km and an uncertainty amount of 50% at every level. The vertical profiles of the concentrations of the other components—H_2O, CH_4, and HDO—did not vary, and only their total contents varied (profiles were scaled in height). It should be noted that the real vertical distribution of NO_2 in the atmosphere apparently differs significantly from the a priori profile chosen by us—mainly in the troposphere and especially in the surface air layer. In the vicinity of St. Petersburg, the content of NO_2 in the lower troposphere may significantly exceed its background values, which is supported by the results of independent ground-based and satellite measurements [15–17]. However, the results of tests and numerical experiments carried out with the use of different types of a priori profiles with an increased tropospheric NO_2 content did not reveal (at a reliable level) any significant sensitivity of the given measurement method to variations in the tropospheric content of NO_2. This special feature was described in [18, 19], and it was shown that such measurements yield information on the NO_2 content mainly in the stratosphere (see below).

The estimates of random error in a single measurement of the total NO_2 content in the SFIT2 algorithm amounted to ~8% on average. It should be noted that the systematic errors in determining the NO_2 content with the IR method, which are caused by an uncertainty of the vertical profile of NO_2, may amount to ~30% [20].

3. RESULTS OF MEASUREMENTS OF THE NO_2 CONTENT WITH AN IR-SPECTROMETER

From April 2009 to October 2011, all in all, 1052 IR-radiation spectra with the NO_2-absorption band in the vicinity of 2914 cm^{-1} were obtained and processed over 182 observation days (53 days in 2009, 56 days in 2010, and 73 days in 2011). Most of these measurements were taken in spring and summer (April–July) due to favorable weather conditions. The number of observation days in these months is maximal (about 30 days per month over the 2009–2011 period), and the number of observation days in November and December is minimal (3 days per month over the 2009–2011 period). The number of spectra recorded in a day varied from 1 to 16.

The daytime mean total content of NO_2 was calculated from the results of an interpretation of individual spectra. In this case, the weighted mean, in which the estimate of random error in determining the NO_2 content during the interpretation of an individual spectrum in the SFIT2 algorithm was a weight, was used as an average. Since the stratospheric content of NO_2 has a pronounced diurnal cycle that includes a daytime increase in the NO_2 content, these variations were taken into account in calculating means—measurements data referenced to the time of local noon (based on the time of recording each spectrum). The corresponding corrections were made using a photochemical model as in [17, 21] (see more details about this model below). The standard deviations in daytime means varied from 2.1% to 9.7% and, on average, amounted to 4.1 ± 1.6%. The interpretation results in the form of the daytime mean contents of NO_2 over the entire observation period are given in Fig. 2. It follows from Fig. 2 that the measured NO_2 content varies approximately from 1.5×10^{15} mol/cm^2 in January to 5×10^{15} mol/cm^2 in June–July; this corresponds to the known seasonal cycle of the stratospheric content of NO_2, which is caused, first and foremost, by the duration of daylight (which determines the duration of the N_2O_5 photolysis) and by stratospheric temperature (which determines the rate of chemical reactions and affects the ratio of nitrogen oxide concentrations in the NO_x group) [22]. As an illustration, Fig. 2 gives the corresponding (to these cycles) parameters: the duration of daylight (in hours) and stratospheric temperature at a level of 30 hPa in the St. Petersburg region according to data from the European Center for Medium-Range Weather Forecasts (ECMWF) [23]. The seasonal cycle of stratospheric temperature reruns the cycle of daylight duration; however, during some periods (in winter and spring), rapid temperature changes are observed which may affect variations in the stratospheric content of NO_2.

4. DATA FROM INDEPENDENT MEASUREMENTS OF THE NO_2 CONTENT

In order to analyze the quality of the interpretation of data obtained with a ground-based IR spectrometer, we used data obtained from independent spectroscopic measurements of scattered radiation in the visible region (VR) with the aid of both ground-based and satellite observation methods. In such measurements, the total content of NO_2 is determined from the spectra of radiation within a region of 400–450 nm with a resolution of ~1 nm (or higher) using the method of differential optical absorption spectroscopy (DOAS) [24].

Since 2004, scientists from the RIP SPbSU have regularly been measuring the atmospheric content of NO_2 by zenith-scattered visible solar radiation [15]. These observations are carried out under twilight conditions (during sunrise and sunset) and during daylight hours. The results of measurements in the twilight contain information mainly on the stratospheric content of NO_2 and are characterized by a hyposensitivity to the NO_2 content in the lower troposphere. To improve the accuracy of ground-based twilight sound-

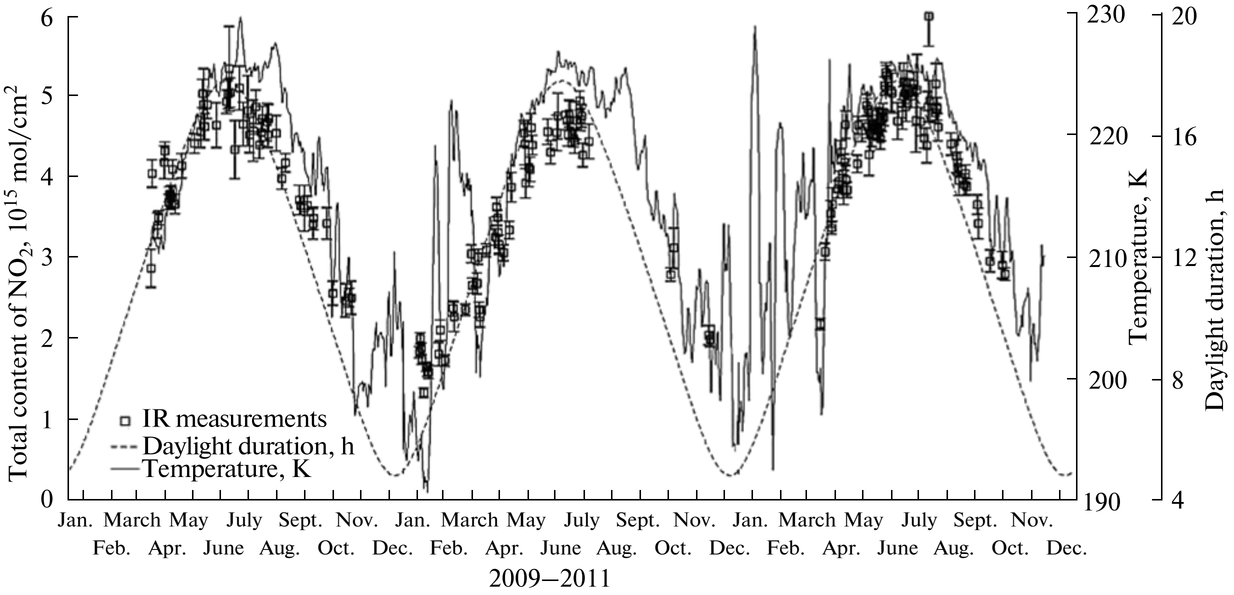

Fig. 2. Daytime means of the total content of NO_2 according to the results of IR measurements at the RIP SPbSU, the length of daylight, and stratospheric temperature (for the St. Petersburg region according to the ECMWF data [23]) on an isobaric surface of 30 hPa at 13:00 (local time) in 2009–2011.

ing, measurement results are usually averaged within the range of the sun's zenith angles 86°–91° [25]. At the RIP SPbSU, this range was reduced to 90°–91° in interpreting measurement results in order to decrease the effect of tropospheric pollution from urban sources in St. Petersburg. The results of spectral measurements were interpreted using the WinDOAS software [26]. The random error in measuring the total content of NO_2 amounts to ~10%, and the systematic error may reach 20% [25]. Within the period of measurements with an IR spectrometer (April 2009–October 2011), all in all, over 1000 twilight NO_2-content measurement runs (500 in the morning and 523 in the evening) were performed. Spectra were recorded with a ground-based instrument on the basis of an OceanOptics HR4000 spectrometer [27].

In addition to the results of independent ground-based measurements using the DOAS method, data on the total content of NO_2 obtained with the ERS-2 GOME [28], Envisat SCIAMACHY [29], Aura OMI [30], and MetOp GOME-2 satellite instruments [31] were analyzed. These instruments are spectrometers that scan space and measure outgoing (reflected and scattered) solar radiation. These measurements are performed from the near-polar solar-synchronous orbits close to the noontime. The nominal spatial resolution amounts to ~40 × 320 km^2 for GOME, ~30 × 60 km^2 for SCIAMACHY, ~13 × 24 km^2 for OMI, and ~40 × 40 km^2 for GOME-2. The stratospheric content of NO_2 determined from these measurements is close to the above estimates obtained from the ground-based measurements using the DOAS method [32]. Data obtained with the GOME (ESA version) [33], OMI (NASA version) [34], and SCIAMACHY and GOME-2 (IUPB version) [35] instruments over the points closest to St. Petersburg were used in this work. The NO_2 content in the latitude of St. Petersburg was measured with all four instruments almost every day.

5. RESULTS OF A COMPARISON WITH DATA OBTAINED FROM INDEPENDENT MEASUREMENTS

The daytime means of the total NO_2 content obtained with the IR spectrometer were compared with data (closest in time and distance) obtained from independent measurements, namely, ground-based twilight measurements (VR) and satellite measurements with the GOME, SIAMACHY, OMI, and GOME-2 instruments. As was noted above, the time variations in the stratospheric NO_2 content are characterized by a pronounced diurnal cycle; therefore, for comparison with the results of measurements in the IR spectral region, data obtained from all independent satellite and ground-based measurements were referenced to the time of local noon. A photochemical box model of the NO_2 diurnal cycle was used in calculations [36]. The diurnal evolution of NO_2 at 17 vertical levels was calculated for the St. Petersburg conditions with an interval of 1 min, and the profiles were integrated to describe the diurnal cycle of the vertical content of NO_2 and its seasonal variations.

Table 1 gives comparison results in the form of average discrepancies and correlation coefficients.

The number of intercompared daytime mean NO_2 contents varied from 140 to 180, depending on the source of independent data. According to Table 1, all data (except for GOME data) yield close estimates of disagreement with data obtained from measurements in the IR region: the average disagreement amounts to ~8% at an rms disagreement of ~10–13% and a correlation coefficient of 0.84–0.95. When compared to other data, the GOME data are in worse agreement with the results of measurements in the IR region: the rms disagreement amounts to 28%, and the correlation coefficient amounts to only 0.42. The reasons for these disagreements can be explained if the actual spatial resolution of satellite data is taken into consideration. Thus, although the OMI data refer to the points closest to St. Petersburg (the average distance from St. Petersburg to these points is ~30 km), the standard procedure of separating stratospheric and tropospheric contributions to the total content of NO_2 suggests a preliminary spatial smoothing of the global field of measured NO_2 contents [32]. Both SCIAMACHY and GOME-2 data were interpreted without preliminary spatial smoothing; however, for comparison with the results of ground-based measurements, the means of all SCIAMACHY and GOME-2 data obtained in the 200-km suburbs of St. Petersburg were used. Among satellite data, only the GOME data were obtained from individual measurements taken at a minimum distance from St. Petersburg. However, with consideration for the rough spatial resolution of these data (the nominal horizontal scale corresponding to one GOME pixel amounts to 40×320 km^2; in this case, the scale reflected by each fourth pixel reaches 40×960 km^2), the real distance from St. Petersburg may amount to hundreds of kilometers and the measured total content of NO_2 may correspond to a region that includes a low-polluted area and an area in the vicinity of St. Petersburg with a significantly polluted troposphere. Thus, when compared to data obtained from other satellite measurements and local ground-based measurements with both Ocean-Optics and Bruker instruments, the GOME data are, to a greater extent, affected by anthropogenic pollution, which results in a more significant disagreement between these data and data obtained from measurements in the IR region.

It should be noted that the IR-measurement results systematically exceed other data, on average, by 8% (except for the GOME data: the average disagreement with these data amounts to 4%). The reasons for this systematic disagreement are, apparently, significant differences in the sensitivity of the measurement methods under comparison to the vertical distribution of NO_2 and discrepancies in the a priori data on the vertical distribution of NO_2. As an illustration, Fig. 3 gives calculated (on the basis of radiative-transport models) averaging kernels of different methods used for measuring the total content of NO_2. The SCIATRAN radiation model was used to calculate averaging kernels in the visible spectral region [37], and the SFIT2 algorithm was used to calculate averaging kernels in the IR spectral region [11]. It follows from Fig. 3 that all three measurement methods demonstrate high sensitivity to variations in the stratospheric content of NO_2 (the kernel value is close to 1 at heights of 20–30 km). However, in the troposphere, with a decrease in height, this sensitivity decreases especially rapidly in the case of ground-based IR measurements, which is due to the strong broadening of the NO_2 absorption lines in the troposphere from ~0.001 cm^{-1} in the stratosphere to ~0.1 cm^{-1} at the land surface: the molecular absorption recorded in the line center is determined by the Lorentz profile, which is characterized by a decrease in the coefficient of absorption with an increase in pressure, i.e., with a decrease in height. The results of calculations show that even a hundredfold increase in the content of NO_2 in the lower 1-km layer (which corresponds to the layer of its constant concentration equal to a maximum surface value of 50 μg/m^3 observed at the measurement point) cannot be detected in the IR measurements. The twilight measurements are slightly more sensitive to the similar variations in the surface content of NO_2: the calculated contribution to the total NO_2 content determined from measurements may amount to 10–30%, depending on the season. However, such high concentrations with a powerful vertical mixing in the measurement region are seldom recorded. Thus, one can assume that the results of both ground-based twilight (VR) and IR measurements furnish information mainly on the stratospheric component of the total content of NO_2 and that these measurements are low-sensitive to its tropospheric content. Unlike ground-based measurements, the nadir satellite measurements have some sensitivity to the tropospheric content of NO_2, which may result in a satellite estimate of the stratospheric content of NO_2 that is too high under the

Table 1. Both mean (Δ) and rms (σ disagreements between the results of IR measurements and the data obtained from independent measurements of the total NO_2 content in the St. Petersburg region in 2009–2011 in relative units (%) and the coefficient of their correlation (R)

Instrument	Δ	σ	R
VR	+8	11	0.89 ± 0.02
ERS-2 GOME	+4	28	0.42 ± 0.07
Envisat SCIAMACHY	+8	13	0.84 ± 0.02
Aura OMI	+9	10	0.95 ± 0.01
MetOp GOME-2	+8	11	0.89 ± 0.02

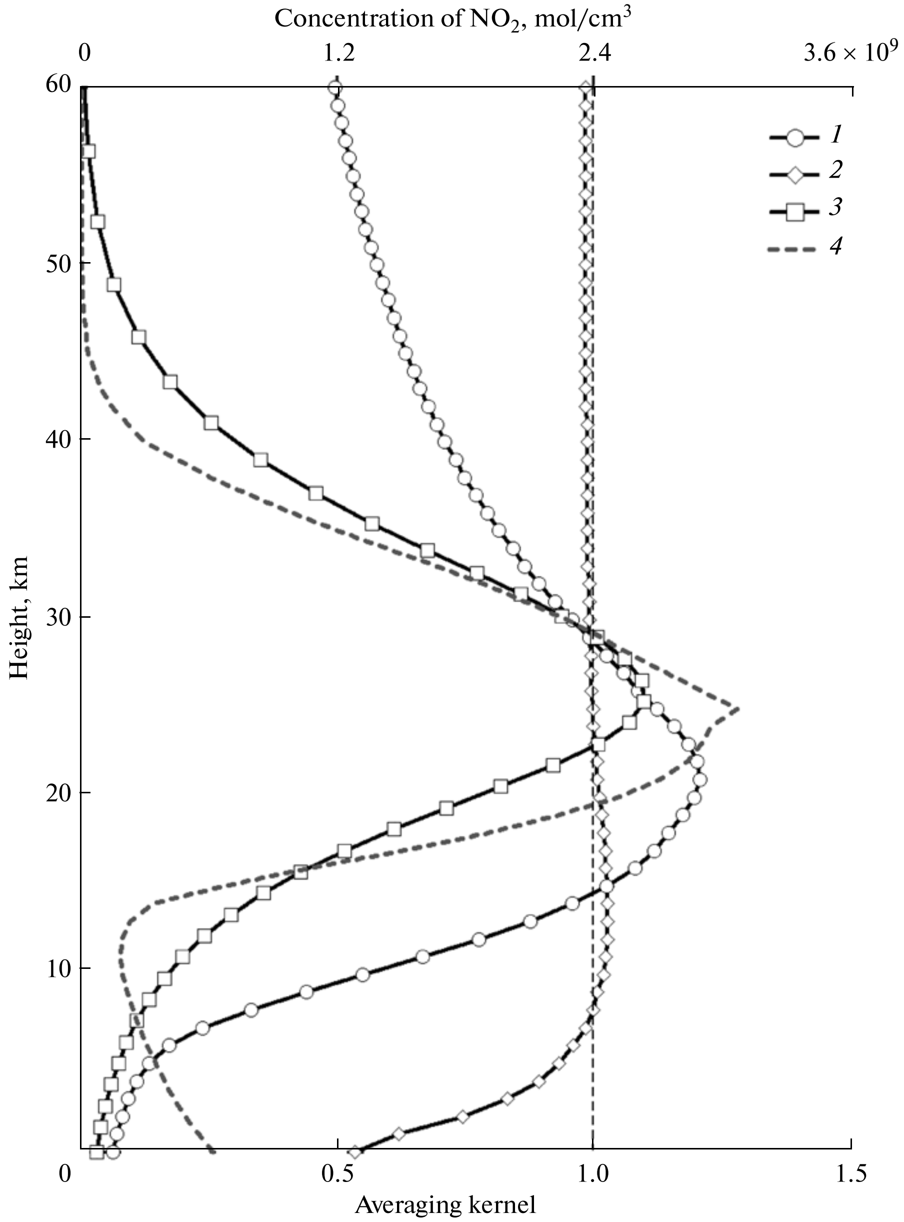

Fig. 3. Averaging kernels for different methods of measuring the total content of NO$_2$: (*1*) ground-based twilight measurements (VR) at a solar zenith angle of 90°, (*2*) nadir satellite measurements at a solar zenith angle of 50°, and (*3*) ground-based IR measurements. Curve *4* shows the a priori profile of NO$_2$ (US standard).

measurement conditions of intensive tropospheric pollution. At the same time, such a low sensitivity of the ground-based IR measurements to the tropospheric content of NO$_2$ implies a high dependence of the measured total content of NO$_2$ on its a priori tropospheric concentration. Unlike the independent measurement results used here, in which the a priori tropospheric NO$_2$ content is assumed to be zero (see, for example, [38]), the US standard initial profile (see Fig. 3), in which the tropospheric content of NO$_2$ amounts to ~8% of its total content, was used as an a priori one in interpreting the IR-measurement results. This value corresponds to the estimates of systematic disagreements given in Table 1. In fact, the systematic disagreement may be somewhat smaller, because the nadir satellite measurements have a certain sensitivity to the tropospheric NO$_2$ layer (see Fig. 3), but this sensitivity depends significantly on the sun's daytime height, i.e., on the season (the sensitivity is lower at the sun's low position in winter). A relatively small average disagreement (~4%) between ground-based (IR) and satellite (GOME) data can partially be explained by the higher sensitivity of satellite measurements to the tropospheric NO$_2$ content in combination with a

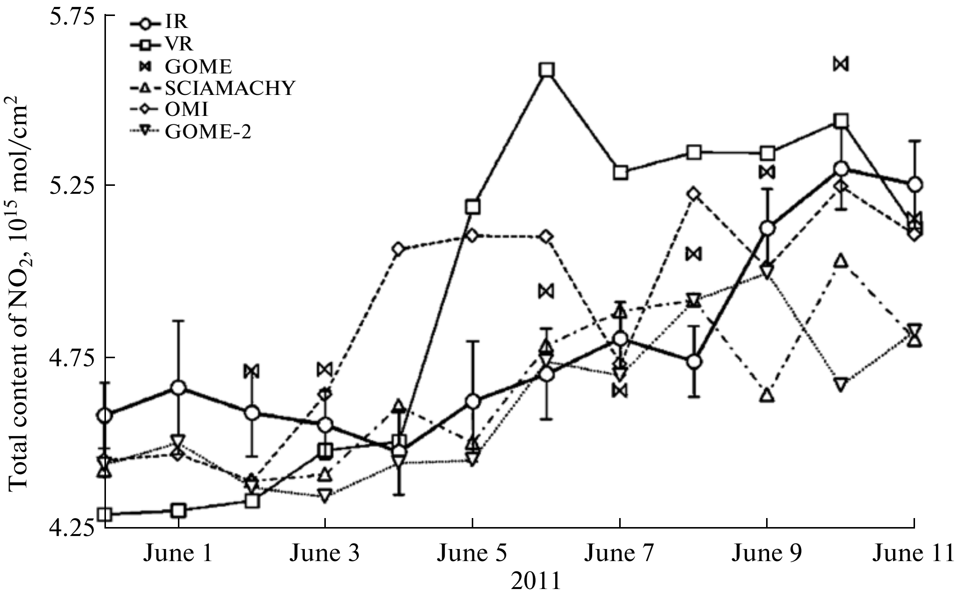

Fig. 4. Daytime mean total NO_2 contents obtained from IR measurements at the RIP SPbSU (IR); ground-based twilight measurements in the visible spectral region (VR); and daytime satellite measurements with the GOME, SCIAMACHY, OMI, and GOME-2 instruments over the period May 30–June 11, 2011. The errors in determining daytime means according to IR measurements are given.

low spatial resolution of GOME (the high probability of covering an area belonging to St. Petersburg without averaging over neighboring pixels). It follows from the comparison results that the IR-measurement data will be a certain estimation of the stratospheric content of NO_2 if they are decreased by the constant a priori contribution of its tropospheric content (~0.4×10^{15} mol/cm^2).

Figure 4 shows a comparison of all measurement data obtained within a short period of May 30–June 11, 2011, when favorable weather conditions allowed a set of daily IR measurements to be performed. This comparison shows the significant disagreements with the results of both ground-based twilight (VR) and satellite OMI measurements, which can be explained by an episodic significant contribution of the tropospheric content of NO_2 to the estimate of its total content (much less significant disagreements with both SCIAMACHY and GOME-2 data due to their averaging over a large number of individual measurements; the GOME data for this period contain a lot of omissions). However, all data given in Fig. 4 show a gradual increase in the stratospheric content of NO_2, and the average disagreements with the IR-measurement data amount to no more than 3% for different instruments.

Let us consider in more detail how the seasonal component of NO_2-content variations is pronounced in both ground-based and satellite measurement data. In spite of the fact that the main factor determining the seasonal cycle of these variations is the annual cycle of solar illumination of the atmosphere (see Fig. 2), it was noted in a number of similar investigations that the annual cyclicity observed in measurement results differed from a strictly sinusoidal form. In particular, the authors of [18] proposed that the analytical function of form (1) should be used in approximating the annual cycle for measurement data on the total NO_2 content. Such an approximation makes it possible to take into account differences in the radiuses of curvature between the maximum and minimum of the curve as well as both maxima and minima shifts resulting in curve skewness.

$$f = b - a + 2a\left\{\left[\sin\left(\pi\frac{x - x_0}{365\left(1 + ce^{-\left(\frac{x - x_p}{\sigma}\right)^2}\right)}\right)\right]^2\right\}^{\gamma}. \quad (1)$$

Here f is the measured daytime content of NO_2 on day x. Among the approximation parameters, there are seven coefficients, among which the coefficients a, b, and x_0 apply to an ordinary sinusoidal function (amplitude and initial value on the day x_0, respectively). The coefficient γ is responsible for the decrease/increase in the radius of the curvature of the minimum (maximum) of the curve at $\gamma < 1/\gamma > 1$ ($\gamma > 1/\gamma < 1$), respectively. The rest of the coefficients are responsible for the shift in the minimum and maxi-

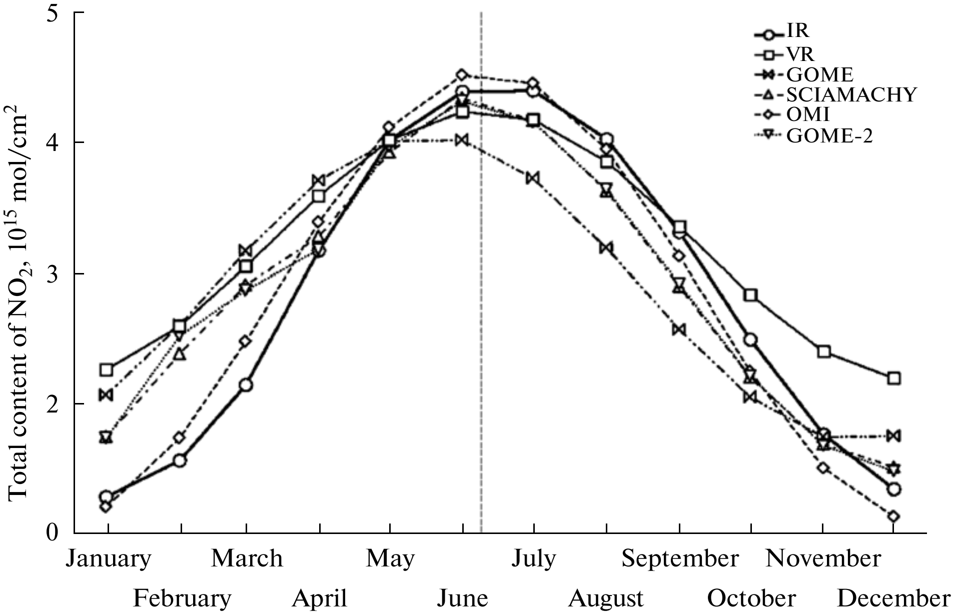

Fig. 5. Seasonal cycle of the total content of NO_2 according to IR measurements at the RIP SPbSU (IR); ground-based twilight measurements in the visible spectral region (VR); and daytime satellite measurements with the GOME, SCIAMACHY, OMI, and GOME-2 instruments. The IR-measurement data were adjusted (decreased) by a tropospheric NO_2 content of 0.4×10^{15} mol/cm^2. The vertical line marks the time of the summer solstice on June 22.

mum with respect to each other due to the local Gaussian disturbance of width σ and intensity c on the day x_p.

Figure 5 gives the results of an approximation of the mean daytime contents of NO_2 obtained from these different measurements, which were reduced to its monthly means (IR-measurement data were adjusted (decreased) by a tropospheric NO_2 content value of 0.4×10^{15} mol/cm^2). On the whole, the curves are close to the sinusoids with a maximum on June 22, which corresponds to the maximum length of daylight (summer solstice). At the same time, the NO_2 content maximum is somewhat shifted to an earlier point of time according to the SCIAMACHY, GOME-2, and (very noticeably) GOME data. This effect may be associated with the anthropogenic tropospheric contribution to the measured NO_2 content: on the one hand, this contribution is maximal in winter (heating season, surface temperature inversions) and, on the other hand, the sensitivity of satellite measurements to the tropospheric NO_2 content increases with the sun's height, i.e., with the onset of spring. The effect of the tropospheric contribution apparently causes a reduction in the seasonal-cycle amplitude (a decrease in the depth of winter minimum) according to the GOME, SCIAMACHY, and GOME-2 data when compared, for example, with OMI data and ground-based IR measurement data. These latter demonstrate a symmetric (with respect to the summer solstice) seasonal variability, which basically supports the stratospheric origin of the total NO_2 content measured by these instruments. The data obtained from the ground-based twilight measurements (VR) are also symmetric with respect to the summer maximum, although they are partially affected by winter tropospheric pollution,

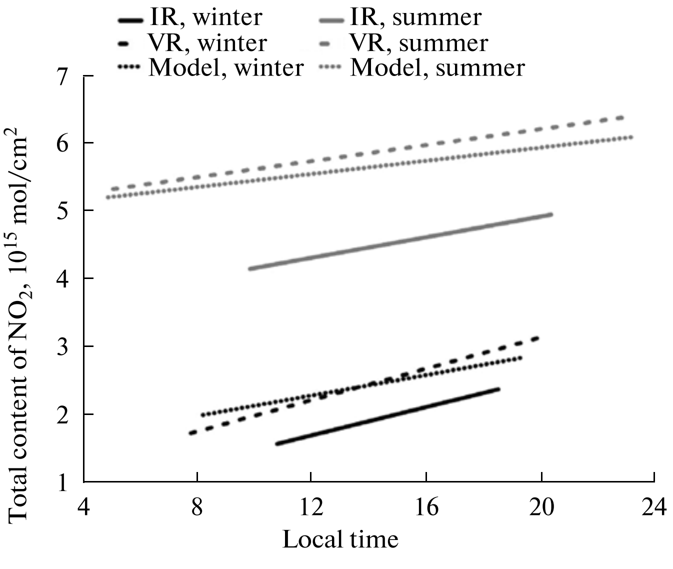

Fig. 6. Linear approximation of the daytime NO_2 variations averaged over different periods (winter and summer) according to data obtained from ground-based IR measurements, twilight measurements in the visible spectral region (VR), and calculations based on a photochemical model.

which is manifested in a decrease in the amplitude of the NO_2 seasonal cycle. In this case, unlike the GOME, SCIAMACHY, and GOME-2 data, according to data from the ground-based twilight measurements (VR), the indicated tropospheric contribution does not result in a seasonal-cycle asymmetry, because the geometry of these measurements is independent of season. It should be noted that, unlike other data under consideration, in the ground-based IR measurement data, the maximum of the NO_2 content is somewhat shifted to July. The reasons for this shift are not clear.

6. ESTIMATING A DAYTIME PHOTOCHEMICAL INCREASE IN THE NO_2 CONTENT

The important advantage of ground-based IR measurements over both satellite and ground-based twilight measurements is that the former can be taken repeatedly during daylight hours at one observation point. This allows one to use such measurement results in analyzing variations in the NO_2 content in the daytime. Because the number of IR measurements is different in different seasons, the data collected over the entire observation period were grouped into four periods: October–March, June–July, April and September, and May and August. These periods correspond to the features of the evolution of the NO_2 content in accordance with its seasonal cycle rather than to the astronomical seasons (see Fig. 5). The dependence of the results of IR measurements of the total NO_2 content on the time of recording the IR spectrum was approximated by a straight line individually of each of the four periods.

The daytime variations in the NO_2 content for both winter and summer periods are shown in Fig. 6. For comparison, similar estimates were obtained using the results of ground-based twilight measurements and photochemical simulation. In these estimates, only the morning and evening contents of NO_2 (at sunrise and sunset) were used for approximation. The twilight-measurement (VR) data and the results of model calculations systematically exceed the IR-measurement data, because the twilight contents of NO_2 are higher than its daytime contents. It follows from Fig. 6 that all data demonstrate a daytime increase in the NO_2 content; however, the estimates of the rate of increase (inclination of line) according to different data differ slightly. These estimates for all four averaging periods are given in Table 2. All of them are positive and amount to $\sim 1 \times 10^{14}$ mol/cm^2 per hour (varying from $\sim 0.5 \times 10^{14}$ to $\sim 1.2 \times 10^{14}$ mol/cm^2 per hour), which approximately corresponds to the results obtained earlier by other authors from measurements in the middle latitudes of the Northern Hemisphere [4, 18, 39]. Taking into account errors in the estimates, one cannot find any regularity in their seasonal differences with the exception of slightly lower rates of increase during summer (noticeable in twilight (VR) data; model-calculation results; and, to a lesser degree, IR-measurement data). On the whole, this daytime increase is a slow component of the diurnal cycle of the stratospheric NO_2 content, which is caused by N_2O_5 photolysis [1].

Table 2. Linear estimates of the rate of daytime increase in the total content of NO_2 according to data obtained from ground-based IR measurements, twilight measurements in the visible spectral region (VR), and calculations based on a photochemical model and their rms deviations in units of 10^{14} mol/cm^2 per hour in different seasons

Period	IR	VR	Model
October–March	1.04 ± 0.29	1.16 ± 0.06	0.75 ± 0.44
June–July	0.76 ± 0.09	0.59 ± 0.03	0.48 ± 0.07
April, September	0.75 ± 0.13	1.17 ± 0.04	0.78 ± 0.22
May, August	0.85 ± 0.13	1.02 ± 0.04	0.66 ± 0.15

7. CONCLUSIONS

Determining the total content of NO_2 from the results of ground-based measurements of solar IR radiation is based on the use of spectrometers with a high spectral resolution, which allow a very slight molecular absorption in the centers of spectral lines to be recorded. This complex and bulky instrumentation hampers the automation of such measurements, and the need for direct solar radiation significantly restricts the period of observations of clear-sky conditions. At the same time, this method has a number of advantages over the methods of both ground-based and satellite measurements of scattered radiation in the visible range. First and foremost, the IR-measurement results are low-sensitive to variations in the tropospheric content of NO_2 and, thus, they can be used in determining its stratospheric content even under conditions of severe anthropogenic tropospheric pollution (as, for example, in the St. Petersburg region). Moreover, unlike one–two measurement runs a day in the case of both twilight ground-based and daytime satellite observations, several runs of IR measurements (under favorable weather conditions) make it possible to isolate the daytime component from diurnal variations in the stratospheric content of NO_2.

Interpreting the results of regular measurements of direct solar IR radiation in the vicinity of ~3.4 μm with a high-resolution spectrometer in the St. Petersburg region showed their fairly good accuracy: the rms disagreements with data obtained from independent measurements amount to about 10%. With consideration for the inaccuracy of independent measurements, the random component of error in the IR measurements of the stratospheric content of NO_2 amounts to less than 10%. According to the 2009–2011 measurement data, in the St. Petersburg region, the daytime stratospheric content of NO_2 varies, on average, from approximately 1.3×10^{15} mol/cm^2 in winter to 4.4×10^{15} mol/cm^2 in summer. A daytime photochemical increase in the NO_2 content with a mean rate of $\sim 1 \times 10^{14}$ mol/cm^2 per hour is observed during all the seasons.

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