

## EXTINCTION OF THE UV RADIATION ALONG THE ATMOSPHERIC PATHS

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*The paper presents the scheme for calculating the transmission function of the atmosphere along arbitrary paths in the range of 170–1200 nm based on the modern spectroscopic databases. A comparison of the calculated results with the data of field experiments is made. No anomalous spectral dependence of the aerosol extinction in the range of 310–400 nm<sup>1</sup> is shown to occur. The contribution of absorption by H<sub>2</sub>O vapor to the UV radiation extinction is refined.*

The problems of studies in ecology, gas analysis, laser detection and ranging have caused the necessity of achieving the task of determining the atmospheric transmission, in the UV spectral range, along arbitrary paths. As opposed to the IR range, no reliable methods for calculating spectral transmission in this spectral region are available, and so the interpretation of the results of a few field measurements is very troublesome.<sup>1,2</sup> In the majority of cases the molecular absorption bands in the UV range have diffuse structure due to overlapping of a great number of unresolved and very often unidentified transitions. Therefore the precise methods of molecular absorption developed for the IR range and based on the database of the fine spectral structure parameters (HITRAN,<sup>3</sup> GEISA<sup>4</sup>) do not work in the UV region. Besides, the influence of the aerosol extinction and strong temporal instability of the spectra make the interpretation of field experiments very difficult.<sup>1</sup>

The primary goal of this study was to develop a scheme for calculating the atmospheric transmission in the UV region, along arbitrary paths, that would suit calculations of the atmospheric extinction for laser radiation while, at the same time, being based on modern spectroscopic databases.

Complex structure of the molecular absorption spectra in the range of 0.17–1.2 μm, owing to the diffuse and structured absorption bands, results in the necessity of using combined calculation procedures that assume using approximate expressions for the continuous absorption based on the exact line-by-line method of determining the transmission in the structured absorption bands.

The expression for the transmission function of atmospheric path along the trajectory  $l$  may be written as

$$\tau(\Delta\lambda, l) = \frac{1}{\Delta\lambda} \int_{\Delta\lambda} \exp\left(-\int_l K(\lambda, l) dl\right) d\lambda, \quad (1)$$

where  $K = K_A^m + K_R^m + K_A^a + K_R^a$  is the sum of molecular absorption ( $K_A^m$ ) and scattering, ( $K_R^m$ ), coefficients as well as of the aerosol absorption ( $K_A^a$ ) and scattering ( $K_R^a$ ) coefficients. Since the molecular absorption alone may be essentially selective, the expression (1) can be written as follows:

$$\begin{aligned} \tau(\Delta\lambda, l) = & \exp\left(-\int_l (K_R^m(\Delta\lambda, l) + \right. \\ & \left. + K_A^a(\Delta\lambda, l) + K_R^a(\Delta\lambda, l)) dl\right) \times \\ & \times \frac{1}{\Delta\lambda} \int_{\Delta\lambda} \exp\left(-\int_l K_A^m(\lambda, l) dl\right) d\lambda. \end{aligned} \quad (2)$$

When deriving Eq. (2) it is believed that the integration interval  $\Delta\lambda$  is rather small, so for low selective components  $K^j$  the following condition:

$$\frac{1}{\Delta\lambda} \int_{\Delta\lambda} \exp\left(-\int_l K^j(\lambda, l) dl\right) \approx \exp\left(-\int_l K^j(\Delta\lambda, l) dl\right). \quad (3)$$

is fulfilled.

Since in the general case the molecular absorption coefficient is, in the spectral range considered, a sum of absorption coefficients of the selectively absorbing molecular species having a resolved rotational structure ( $K_A^{mj}$ ) and these of low selective components with unresolved structure ( $K_A^{mi}$ ), the latter factor in equation (2) may be written in the following form

$$\begin{aligned} \tau_A^m = & \exp\left(-\int_l \sum_j K_A^{mj}(\Delta\lambda, l) dl\right) \frac{1}{\Delta\lambda} \times \\ & \times \int_{\Delta\lambda} \exp\left(-\int_l \sum_i K_A^{mi}(\lambda, l) dl\right) d\lambda. \end{aligned} \quad (4)$$

When passing from integration over the path  $l$  to the summation over layers and expressing  $K_A^{mj}$  in terms of the absorption cross-sections  $\sigma^j$ , we obtain that the total transmission function is as follows:

$$\begin{aligned} \tau(\Delta\lambda, l) = & \exp\left(-\sum_n \Delta l_n [K_R^m(\Delta\lambda, l_n) + \right. \\ & \left. + K_A^a(\Delta\lambda, l_n) + K_R^a(\Delta\lambda, l_n)]\right) \times \\ & \times \exp\left(-\sum_n \sum_j \Delta l_{nj} N_L \sigma_n^j(\Delta\lambda, l_n)\right) \times \\ & \times \frac{1}{\Delta\lambda} \int_{\Delta\lambda} \exp\left(-\sum_n \sum_i \Delta l_{ni} K_A^{mi}(\lambda, l_n)\right) d\lambda. \quad (5) \end{aligned}$$

Here  $N_L = 2.69 \cdot 10^{19} \text{ (cm}^{-3}\text{)}$  is the Loschmidt number,  $\Delta l_{nj} = C_{nj} l_n P_n$  is the reduced thickness of the  $j$ th-component in the layer of length  $l_n$  at the volume concentration  $C_{nj}$  and the pressure  $P_n$ ;  $K(\Delta\lambda, l_n)$  is the absorption or scattering coefficient in the layer  $l_n$  averaged over the interval  $\Delta\lambda$ .

Equation (5) allows the construction of the calculating algorithm of the transmission function of arbitrarily oriented atmospheric path to be done with an arbitrarily high spectral resolution  $\Delta\lambda$ . For the broad intervals  $\Delta\lambda$  the accuracy of Eq. (5) is limited by the condition (3).

Let us note some details of the calculation procedure developed. As known the calculation of molecular scattering coefficient  $K_R^m(\Delta\lambda, l)$  is an easy task. To calculate the value of aerosol absorption and scattering  $K_A^a$  and  $K_R^a$  we use in this program the known procedure from LOWTRAN-7.<sup>5</sup> For brevity this calculation procedure is not described here. The most complicated problem is to calculate the molecular absorption. The difficulties in estimating the components due to continuous absorption  $K_A^m$ , presented in Eq. (5) by the absorption cross-sections  $\sigma_n^j$ , are caused by the lack of data available on the absorption cross-sections. It should be noted first that the accuracy of the majority of the data available<sup>6</sup> is insufficient and spectral resolution low. Besides only little data on the dependence of  $\sigma_n^j$  on the pressure and temperature may be found in literature. To overcome this difficulty the data bank has been compiled of the absorption cross-sections of basic and contaminating components of the atmosphere. The first version of this data bank (bank UVACS – Ultraviolet Absorption Cross-Section) may be found in Ref. 7. At present the data bank contains the data on the absorption cross-sections of 69 gas components in the range of 160–720 nm. The data bank structure is identical to that of the known data banks (HITRAN, GEISA) of the parameters of spectral lines in the IR range. That means that the absorption cross-sections are listed in the order of the wavelength increase and not according to types of molecules that better suits the calculation of the atmospheric transmission. For some molecules ( $O_3$ ,

$NO$ ,  $SO_2$ ,  $N_2O$ ) the data bank includes the experimental and theoretical data on temperature dependence of the absorption cross-section. The Table I gives the list of gases presented in the UVACS data bank, along with the spectral ranges and spectral resolution of data on the absorption cross-sections.

The difficulties in calculating components of the selective molecular absorption are connected both with the lack of data on the parameters of the absorption fine structure and with purely computational problems of taking integral from the fast oscillating functions. The latter problem has successfully been solved for the IR spectral range. In this program the data bank of the parameters of spectral lines of  $O_2$  and  $H_2O$ , in the range of 0.6–1.2  $\mu\text{m}$ , was formed on the basis of the latest versions of the HITRAN bank,<sup>3</sup> and for calculations of the transmission functions we use the line-by-line version of the method developed for the IR range.<sup>8</sup>

As the standard atmospheric models to set the altitude variation of concentration of the absorbing gases, as well as of temperature and pressure<sup>9,10</sup> we use the AFGL atmospheric models.

The program developed was used for quantitative interpretation of the results of laboratory and field measurements of the atmospheric transmission in the UV spectral range.<sup>11</sup> As an illustration, below we present some results of the quantitative interpretation of field measurements of solar radiation extinction, conducted by the authors of Ref. 2 at the "Pik Terskol" mountain observatory of the MAO AN of Ukraine.

These data are of particular interest since the information is obtained under conditions of a highly stable atmosphere at 3100 m altitude, the rms error  $\Delta\tau \leq 1\%$  in the range of 310 nm and 0.2% in the range of 400 nm. Use of the above program along with the latest spectroscopic data on the UV absorption by  $O_3$  and  $H_2O$  enabled us to explain the problems discussed in the literature on the strong spectral dependence of the aerosol extinction in the wavelength range  $\lambda < 325 \text{ nm}$ ,<sup>11</sup> as well as on the relative role of absorption by  $H_2O$  vapor in the wavelength range  $\lambda < 330 \text{ nm}$ .<sup>12–14</sup>

The absorption spectrum of the atmosphere for solar radiation in the 310–400 nm range, investigated in Ref. 2, is mainly due to absorption by the ozone in the Huggins band. This band, whose upper electronic state identification is still being debated (see Ref. 15), is the progression (over the mode  $\nu_1$ ) of the vibrational transitions with unresolved, because of the pre-dissociation, rotational structure. The weaker absorption by other atmospheric molecules ( $H_2O$ ,  $NO_2$ ) forms a weak continuum superposed on the continuous extinction by aerosols. When calculating the molecular absorption the  $O_3$  absorption cross-sections from the UVACS bank measured by the authors of Ref. 16 as well as the data on the  $H_2O$  absorption cross-sections published in Refs. 12 and 13 were used. To account for the temperature

dependence of  $O_3$  absorption cross-sections, we used the linear interpolation of the experimental data on the  $O_3$  absorption cross-sections,  $\sigma(\lambda, T) = k(\lambda)\sigma(\lambda, 300 \text{ K})$ . The coefficient of temperature dependence  $k(\lambda)$  was determined using the measurement data from Refs. 17 and 18 for the temperature range from 195 to 300 K with the spectral step  $\Delta\lambda = 1 \text{ nm}$ . In the intervals between the wavelength grid nodes the values of  $k(\lambda)$  were determined by linear interpolation as well. The remaining components of the extinction coefficient have been

calculated using the above-mentioned methods. Note that the ozone profile was set according to the model from Ref. 9, and the total ozone content in the layer above 3100 m presented was  $0.35 \text{ cm-atm}_{\text{STP}}$ , that is close to the column density in this layer of  $U_{O_3} = 0.343 \text{ cm-atm}_{\text{STP}}$  used in Ref. 2. According to the LOWTRAN-7 method the aerosol model was set the assuming that the humidity was 70%, the visible range was 23 km and aerosols were of the background type.

TABLE I.

Molecule	Spectral resolution, nm	Spectral range, nm	Molecule	Spectral resolution, nm	Spectral range, nm
$m_2n$	0.1–1	150–205, 260–330	OCIO	3–5	242–476
$q n_2$	0.04–0.4	169–300	COCl <sub>2</sub>	1–5	185–280
$n_3$	0.003–0.07	240–724	COFCl	0.2–3.0	186–226
N <sub>2</sub> O	0.3	160–250	CH <sub>3</sub> Br	5	190–260
CO	0.006	120–261	CF <sub>2</sub> Br <sub>2</sub>	2	190–308
O <sub>2</sub>	0.04	60–102, 141–245	CF <sub>3</sub> Br	5	190–286
NO	0.2–0.5	186–227	CHF <sub>2</sub> Br	5	210–255
SO <sub>2</sub>	0.003	290–320	HClO <sub>4</sub>	5	190–280
NO <sub>2</sub>	0.04	200–725	N <sub>2</sub> O <sub>4</sub>	0.1	185–410
NH <sub>3</sub>	0.5	185–230	HO <sub>2</sub> NO <sub>2</sub>	1	190–330
HNO <sub>3</sub>	0.3–0.7	190–330	CS <sub>2</sub>	0.4	295–355
OH		282	CH <sub>3</sub> OOH	5	210–365
HCl	0.03	140–220	ClO <sub>3</sub>	5	200–350
HBr	1	170–221	NO <sub>3</sub>	1	400–695
HI	1	170–228	CCl <sub>3</sub> F	2	174–260
ClO	0.03–0.3	240–310	CCl <sub>2</sub> F <sub>2</sub>	2	160–240
OCS	0.01	185–300	CClF <sub>3</sub>	0.3	160–220
H <sub>2</sub> CO	0.01	224–376	CHCl <sub>2</sub> F	5	160–235
HOCl	0.3–1.0	215–375	CHClF <sub>2</sub>	2	160–220
CH <sub>3</sub> Cl	2	174–216	CCl <sub>2</sub> F–CClF <sub>2</sub>	2	160–250
H <sub>2</sub> O <sub>2</sub>	0.3–0.5	190–350	CClF <sub>2</sub> –CClF <sub>2</sub>	0.3	160–235
ClONO <sub>2</sub>	0.2	190–450	CF <sub>3</sub> –CClF <sub>2</sub>	2	160–230
COF <sub>2</sub>	2	186–224	CF <sub>3</sub> –CH <sub>2</sub> Cl	5	160–245
CH <sub>2</sub> Cl <sub>2</sub>	0.3	160–190	CH <sub>3</sub> –CClF <sub>2</sub>	2	160–230
CHCl <sub>3</sub>	0.3	160–255	BrO	0.2–0.4	300–388
CCl <sub>4</sub>	5	174–275	BrCl	10	220–540
C <sub>2</sub> H <sub>5</sub> Cl	0.03	160–240	Br <sub>2</sub>	10	220–510
CH <sub>3</sub> CCl <sub>3</sub>	5	160–240	Cl <sub>2</sub>	10	240–450
ClONO	5	235–400	Cl <sub>2</sub> O <sub>2</sub>	2	200–410
BrONO <sub>2</sub>	5	186–390	JBr	10	220–540
HONO	0.9	190–399	JCl	10	220–540
ClNO <sub>2</sub>	5	190–400	CH <sub>3</sub> CHO	10	200–345
ClNO	2	190–400	Cl <sub>2</sub> O	10	200–500
N <sub>2</sub> O <sub>5</sub>	5	200–380	–	–	–

The calculated values of the transmission functions (curve 1 in the Figure 1) strongly differ from the results of experimental measurements (dashed curve 2). Analysis of the data available from the literature and the results of laboratory and field

measurements of the absorption by  $O_3$ , in this spectral range, has made it possible to establish that the discrepancy is due to a considerable overestimation of the H<sub>2</sub>O contribution to the value of molecular absorption that was set according to data.<sup>12,13</sup>

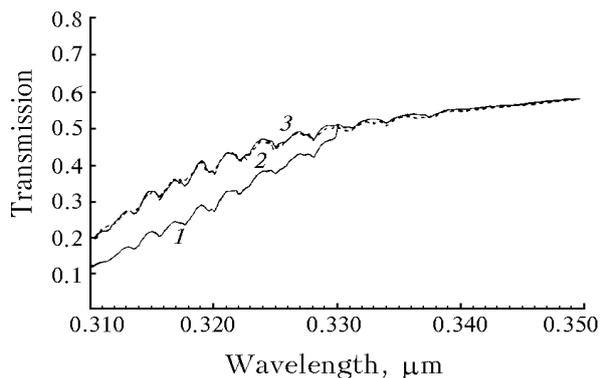


FIG. 1. Calculated values of the atmospheric transmission (solid curves 1 and 3) and experimental data (dashed line 2) obtained at the station "Pik Terskol, B Ref. 2.

Actually, as the calculations show, the account for the temperature dependence of the ozone absorption cross-sections results in an increase of the total spectral transmission of the path, by no more than 3% in some portions of the range from 310 to 330 nm. Because the data from Ref. 17 indicate a nearly linear dependence of the ozone absorption cross-sections on temperature in the range of 200–300 K, possible errors of linear interpolation of the absorption cross-sections cannot result in a noticeable ( $> 1\%$ ) error, when calculating the total path transmission, and especially in its essential decrease. The experimental fact that no pressure dependence of the ozone absorption cross-section occurs in the Huggins band enables us to neglect possible errors of calculations of the transmission along an inhomogeneous path using the approximate method, Eq. (2). The contribution due to absorption by the  $\text{NO}_2$  molecule does not exceed 0.3% of the transmission value.

On the other hand, the range and time resolved measurements of the  $\text{H}_2\text{O}$  vapor absorption coefficient, performed in Ref. 4 using an optoacoustic detector at the fourth harmonic of a pulsed Nd:YAG laser ( $\lambda = 266$  nm), gave the value of  $(1.3 \pm 0.2) \cdot 10^{-7} \text{ cm}^{-1} \text{ Torr}^{-1}$  that is 20 times higher than the value of  $2.6 \cdot 10^{-6} \text{ cm}^{-1} \text{ Torr}^{-1}$  measured at the same frequency in Ref. 13. We used the coefficient  $k = 1/20$  to re-normalize the spectral dependence  $\sigma^{\text{H}_2\text{O}}(\lambda)$  measured in the Refs. 12 and 13. Because in the papers 13 and 19 the conclusions were drawn on the lack of fine structure of the water vapor band studied and thus on the negligible influence of the instrumental function on measurement results<sup>13</sup> (measurements, Refs. 12 and 14, were made using lasers in the relevant spectral ranges), such re-normalization seems to be quite reasonable.

In this case the  $\text{H}_2\text{O}$  contribution to the UV radiation extinction is much less and for our conditions, at  $\lambda = 310$  nm, this contribution is about 3% of the total value of the extinction coefficient. The calculated

transmission values are presented by curve 3 in the figure. Its deviations from the mean values of the spectral transmission are presented in the table in Ref. 2.

A good agreement between calculated and measured spectral dependences of the transmission in the range of 310–400 nm makes it possible to draw the following conclusions:

1. The strong spectral dependence of residual aerosol extinction in the range of  $\lambda < 325$  nm that was revealed in Ref. 2 is mainly due to the errors in the initial data used on the value of the ozone molecular absorption or the errors in calculations of the transmission function of the atmospheric path.

2. The values of water vapor absorption coefficient, presented in Refs. 12 and 13, do not agree with the results of field measurements.<sup>2</sup> These values, in accordance with the results from Ref. 14, should be reduced by approximately 20 times.

3. The use of the calculation scheme proposed, in combination with the latest spectroscopic information, makes it possible to achieve good agreement with the results of field measurements performed under steady state atmospheric conditions. Thus, in the spectral range studied there is no need in a hypothesis of "anomalous atmospheric transmittance"<sup>1</sup> to interpret the data of field experiments.

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