

Analysis of temperature dependence of absorption cross section of the ozone molecule in the spectral region from 280 to 340 nm

O.N. Sulakshina and Yu.G. Borkov

*Institute of Atmospheric Optics,
Siberian Branch of the Russian Academy of Sciences, Tomsk*

Received November 12, 2004

We analyze the temperature dependence of the experimental data on the ozone absorption cross sections in the spectral region from 280 to 340 nm. It is shown that the temperature dependence of the absorption cross sections in the Huggins band system is well described by a second-order polynomial including three wavelength dependent parameters.

The important role of ozone in the radiation budget of the Earth's atmosphere and in photochemistry is well known. The knowledge of the ozone absorption cross sections and their temperature dependence is of great interest for atmospheric physics and chemistry and is necessary for determining the rate of the ozone photolysis and the ozone contribution to the heat balance of the atmosphere.

Recall that the ozone absorption bands associated with electronic transitions lie in a wide wavelength region from near-IR and deep into the UV range.

Today numerous experimental data have been collected on the ozone absorption cross sections in different temperature ranges, measured both under laboratory conditions and in the atmosphere from satellites. The critical review of these data can be found in Refs. 1 and 2. For atmospheric investigations, of interest is the wavelength range from 320 to 450 nm, because it is almost fully transparent for ozone.

A characteristic feature of the ozone spectrum is that in the atmospheric depth the absorption coefficient has, in addition to the ordinary temperature dependence, specific temperature dependence,^{3,4} associated with the redistribution of molecules over vibrational levels. The nature of this dependence is quite clear. If the temperature grows, the population of higher vibrational levels of the lower electronic state increases. However, the description of the temperature dependence for the Huggins band system still remains an open problem and requires careful analysis of the ozone spectrum in this region in order to develop a theoretical model.

The strongly diffuse Huggins band system, turning into the strongest Hartley absorption band, falls within the 300–390 nm range. The analysis of this band system is the only source of information about the excited states of the ozone in the UV region. The bands are discrete and have a vibrational structure with pronounced minima and maxima. To create theoretical models describing the temperature

dependence, correct assignment of the vibrational bands, forming the Huggins system, is needed. The assignment of this band system is still a subject of discussions, because the upper electronic state is not defined unambiguously.^{5–7} On the one hand, the Huggins bands may be a continuation of the Hartley continuum (${}^1\tilde{A}_2 \leftarrow \tilde{O}{}^1\tilde{A}_1$ electronic transition^{5,6}), but with weaker intensities due to the Frank–Condon factors. On the other hand, the low intensities may appear due to $2{}^1\tilde{A}_1 \leftarrow \tilde{O}{}^1\tilde{A}_1$ transitions, orbitally "forbidden" in the first approximation.⁷ The lack of reliable assignment of the bands makes one to use semiempiric and empiric models.^{8–10}

In this paper, all the known models, including the most appropriate empiric model, have been used for the interpolation of the temperature dependence in the Huggins band system.

The analysis was carried out for the spectral range from 280 to 340 nm, where the temperature dependence is most pronounced. The available experimental data on the absorption cross sections in the temperature range of 206–298 K [Refs. 3, 4, and 11] are summarized in Fig. 1.

Starting from 315 nm (Fig. 1b), at which the discrete structure of the vibrational bands in the system is clearly seen, the temperature dependence becomes very significant. As the temperature grows, the role of hot bands increases, and the changes in the absorption cross sections are associated with the redistribution of molecules over vibrational and rotational states. The contribution from hot bands due to the transitions from excited levels is especially pronounced in minima.

It should be noted that the temperature dependence in the Huggins band system is also complicated by the wing of the strongest Hartley band. For the detailed analysis, the known literature data have been used, and the temperature dependences of the absorption cross sections were calculated with the 5 nm wavelength step (Fig. 2a).

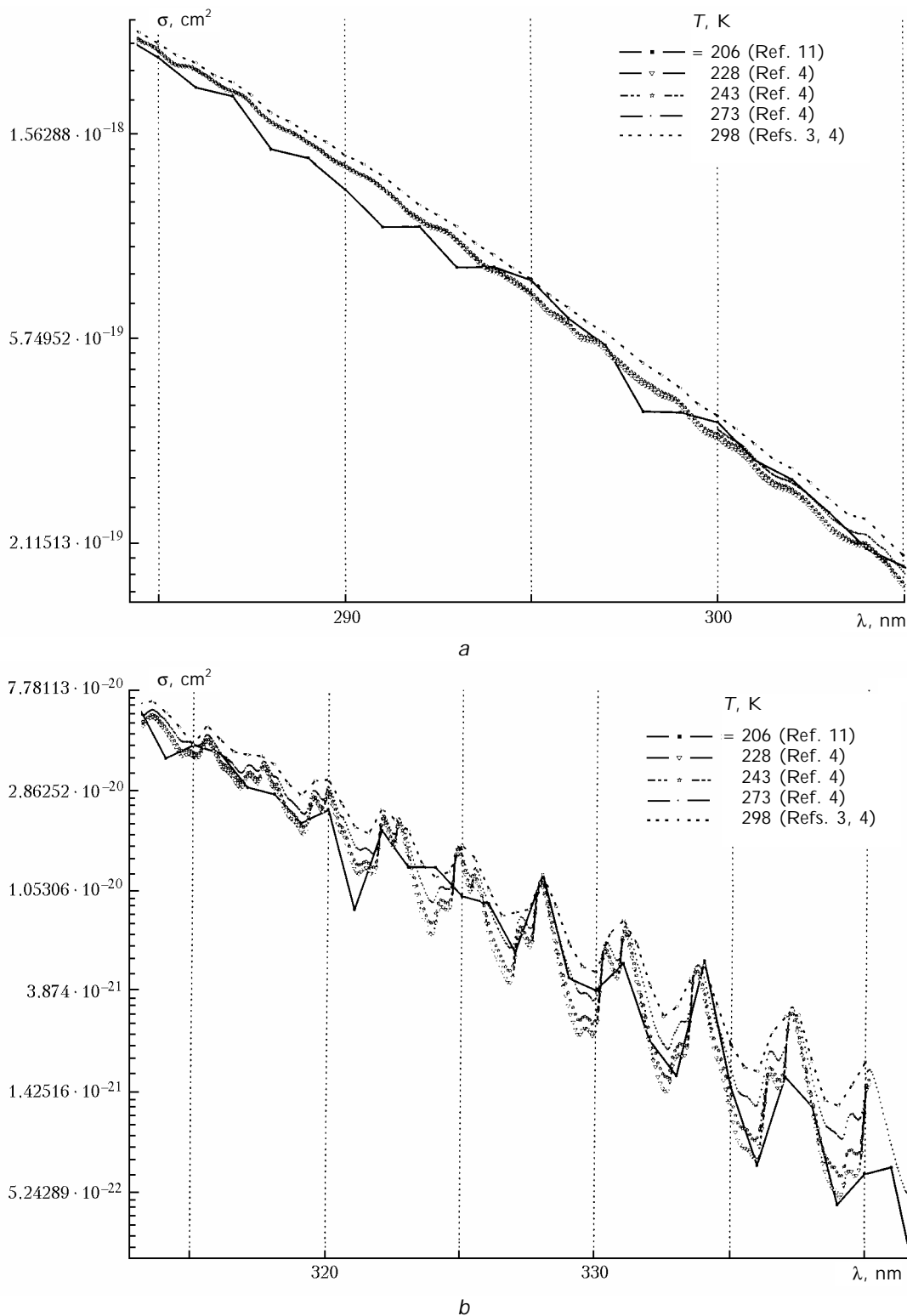


Fig. 1. Absorption cross sections of the ozone molecule in the Huggins band system.

In the dependences shown in Fig. 2a for different wavelengths, we can separate three characteristic types of the curves (Figs. 2b–d), which represent the dependences at the three parts of the studied range. Figure 2b depicts the temperature dependence at the part of the spectrum, where the

vibrational structure is practically invisible. Figure 2c characterizes the temperature dependence at the minima of vibrational bands, while Fig. 2d shows the dependence at the maxima. As can be seen from the figures, the temperature dependence is nonlinear and different for different parts of the spectrum.

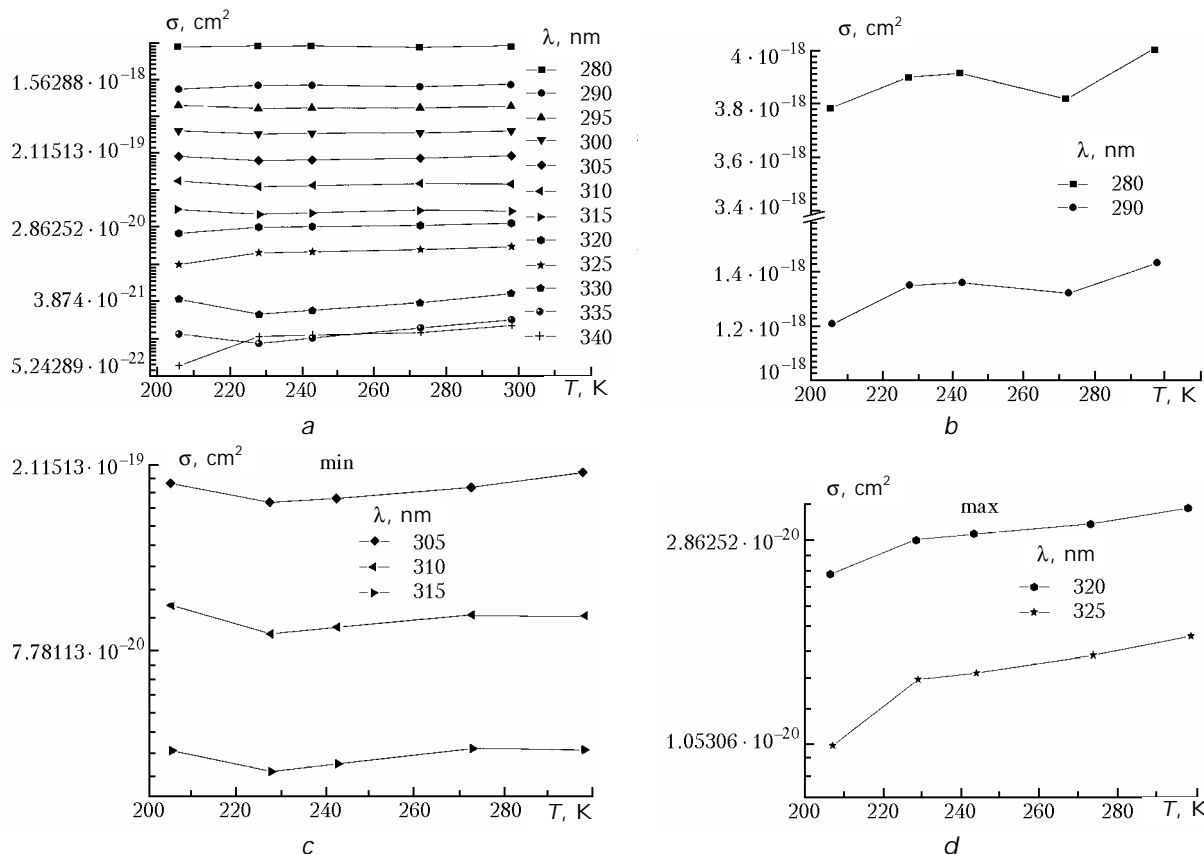


Fig. 2. Temperature dependence of absorption cross sections in the range of 280–340 nm.

In the literature, we can find three models describing the temperature dependence of the ozone absorption cross sections in the UV. The first model, proposed in Ref. 8, uses the exponential function

$$\frac{\sigma(\lambda, T)}{\sigma(\lambda, T_0)} = c_1(\lambda) \exp\left[\frac{-1300}{T}\right] + c_2(\lambda), \quad (1)$$

where \hat{O} is the temperature, in K; $\hat{O}_0 = 295$ K; $\bar{n}_1(\lambda)$, $\bar{n}_2(\lambda)$ are the parameters depending on wavelength. The constant equal to 1300 appears in the exponent from the Boltzmann factor for the vibrational energy of 900 cm^{-1} , corresponding to the mean energy of the ozone vibrations ν_1 , ν_2 , and ν_3 in the ground state. This model was used to describe the temperature dependence of the absorption cross sections in the Hartley continuum.⁸

The second model⁹ is a quadratic polynomial

$$\frac{\sigma(\lambda, T)}{\sigma(\lambda, T_0)} = c_0(\lambda) + c_1(\lambda)T + c_2(\lambda)T^2, \quad (2)$$

including three wavelength dependent parameters $\bar{n}_0(\lambda)$, $\bar{n}_1(\lambda)$, and $\bar{n}_2(\lambda)$. Despite the model (2) has no physical interpretation, nevertheless, as was mentioned in Ref. 2, it can be used for the reconstruction of the temperature dependence of ozone absorption cross sections in different spectral ranges² and even in the Huggins band system.

The third model includes a two-parameter exponential function¹⁰:

$$\frac{\sigma(\lambda, T)}{\sigma(\lambda, T_0)} = \frac{c_0(\lambda)}{\lambda} \exp\left[\frac{-c_1(\lambda)}{T} + c_2(\lambda)T\right]. \quad (3)$$

The wavelength dependent parameters $\bar{n}_0(\lambda)$, $\bar{n}_1(\lambda)$, and $\bar{n}_2(\lambda)$ in the model (3) bear the information about transition moments and the Boltzmann factor of the lower vibrational states, involved in the transition. Such an empirical model was used for processing of the high-accuracy data on the absorption cross sections in the 230–362 nm range, measured with a Fourier transform spectrometer (spectral resolution of 5 cm^{-1}) for five temperature values. The investigation of the temperature dependence based on the data array obtained by the GOME satellite spectrometer¹² in the region of 240–790 nm was carried out in Ref. 2. All the three models were used in the processing. It has been found² that, in the absence of theoretical models, a quadratic polynomial is the best for interpolation of the temperature dependence of absorption cross sections in this region.

Based on the results of Ref. 2, we also tested all the three known models for the description of the temperature dependence in the Huggins band system. The results of interpolation for the first two models are shown in Fig. 3.

The results obtained for the third model are omitted, because they virtually coincide with those for the first model, and the parameters $\bar{n}_1(\lambda)$ and $\bar{n}_2(\lambda)$ correlate. Figure 3a demonstrates the reconstructed temperature dependence obtained in the part of

spectrum, where the structure of vibrational bands is invisible and the wing of the Hartley continuum is pronounced. As can be seen (Fig. 3a), both of the models adequately reconstruct the temperature dependence within the experimental accuracy of 3% for this part of the spectrum. In the two other characteristic parts, denoted as min and max, the quadratic polynomial provides for a better description of the temperature dependence than the exponential model does.

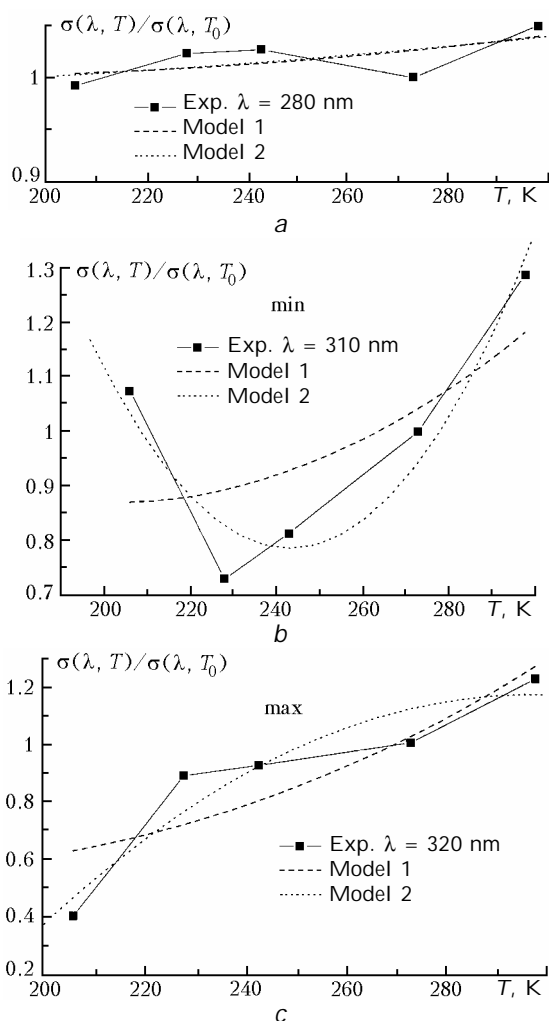


Fig. 3. Interpolation of the temperature dependence of absorption cross sections by different models.

The analysis of the experimental curves (see Fig. 3) shows that the quadratic polynomial allows the temperature dependence of the absorption cross sections within all parts of the Huggins band system to be reconstructed with the experimental accuracy.

Thus, we have succeeded in describing the temperature dependence of the absorption cross sections in the Huggins band system by the quadratic polynomial, including three wavelength dependent parameters. It should be noted that it is very important to take into account the temperature dependence when analyzing the Huggins band system. Thus, at a 2% measurement error for the absorption cross sections at $T_0 = 295$ K, the temperature-induced changes of the absorption cross sections can achieve 15–50%, depending on the temperature and wavelength. The temperature dependence of absorption in the region of Hartley and Huggins bands is also important in the practical aspect, because it should be taken into account in the analysis of the ozone concentration.

In conclusion, it should be noted that the empiric model has no physical meaning, and it is still needed to construct a theoretical model for the description of the temperature dependence of the absorption cross sections in the Huggins band system of the ozone molecule.

Acknowledgments

The authors are grateful to B.D. Belan for his interest in this study.

References

1. R. Basis, A.J. Bouvier, and J.M. Flaud, *Spectrochim. Acta A* 54, No. 1, 17–34 (1998).
2. J. Orphal, *J. Photochem. Photobiol. A Chemistry* 2–3, No. 157, 185–209 (2003).
3. L.T. Molina and M.J. Molina, *J. Geophys. Res. D* 91, No. 13, 14500–14508 (1986).
4. J. Malicet, D. Daumont, J. Charbonnier, C. Parisse, A. Chakir, and J. Brion, *J. Atmos. Chem.* 21, 263–273 (1995).
5. J.C.D. Brand, K.J. Cross, and A.R. Hoy, *Can. J. Phys.* 56, No. 3, 327–333 (1978).
6. D.H. Katayama, *J. Chem. Phys.* 71, No. 2, 815–820 (1979).
7. A. Joens Jeffrey, *J. Chem. Phys.* 101, No. 7, 5431–5437 (1994).
8. S.M. Adler-Golden, *J. Quant. Spectrosc. Radiat. Transfer* 30, No. 2, 175–185 (1983).
9. A.M. Bass and R.J. Paur, *J. Photochem.* 17, No. 1, 141 (1981).
10. S. Voigt, J. Orphal, K. Bogumil, and J.P. Burrows, *J. Photochem. Photobiol. A Chemistry* 143, No. 1, 1–9 (2001).
11. J.E. Davenport, *Parameters for Ozone Photolysis as a Function of Temperature at 280–330 nm*, Federal Aviation Administration (FAA) Report FAA-EE-80-44R (1982).
12. J.P. Burrows, A. Richter, A. Dehn, B. Deters, S. Himmelmann, S. Voigt, and J. Orphal, *J. Quant. Spectrosc. Radiat. Transfer* 61, No. 4, 509–517 (1999).