

ELECTRONIC SPECTROSCOPY OF OZONE PART III. GROSS UV SPECTRUM IN THE FAR-UV REGION

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The first two parts of this review, which include general information concerning electronic spectra and levels and comprehensive information concerning energy region between the dissociation threshold and the near-ultraviolet (the Huggins bands) were published in the journals Atmospheric and Oceanic Optics, Nos. 5 and 8, 1993. In this paper they are referred to as Parts I and II. For convenience and continuity of this paper, I first repeat the references of Parts I and II and then add the new references.

1. UV ABSORPTION SPECTRUM IN THE 4.1–5.7 eV HARTLEY BAND (REGION V)

Roman numerals here correspond to the numeration of regions into which the gross ozone absorption spectrum, from the 1.05 eV dissociation threshold to the 30 eV ionization continuum, is divided (see Fig. 2 in Part I).

The Hartley 220–310 nm band, discovered in 1881 (see Ref. 2), is the most important ozone absorption band. The absorption cross section here attains its absolute maximum being equal to $1.1 \cdot 10^{-17} \text{ cm}^2$ at $\lambda = 255.3 \text{ nm}$. For $\lambda < 300 \text{ nm}$, O_3 is the basic atmospheric absorber of the biologically harmful UV radiation of the Sun, and attenuates the radiation in maximum by a factor of $\sim 10^{66}$. Moreover, O_3 dissociation in the Hartley band is a major natural source of chemically active excited oxygen $\text{O}(^1D)$. Therefore, after the function of ozone in the atmosphere had become clear, the most part of the papers was devoted to the study of the Hartley band in four basic lines:

- theoretical calculation of the absorption cross section,
- measurement of the cross section and its dependence on the temperature and O_3 state,
- determination of quantum yields of possible dissociation channels, and
- determination of energy states of dissociation products.

The detailed review concerning the two last items will be published somewhere else. Here we present only the main conclusions.

1.1. Measurements of absorption cross section

A list of papers dealing with the absorption cross section measurements in the Hartley band was given in Table I of Part II, the cross section at room temperature is shown in Fig. 1, and its temperature dependence is depicted in Fig. 2. As seen from the Table, the temperature dependence of absorption was measured in Refs. 92–93 (245–313 nm, 180–290 K), 107 (248.5 and 297.5 nm, 300–900 K), 109 (208–310 nm, 195–333 K), 111 (220–300 nm, 295–373 K), 114 (210–310 nm, 300–1050 K), 95, 117 (200–310 nm, 200–300 K), 125 (185–310 nm, 226–298 K), 124 (253.65 nm, 195–351 K), and 116 (mercury line; 195, 228, and 295 K). It is seen from Fig. 2 and papers concerning the UV absorption of

nonequilibrium vibration-excited ozone (Refs. 102, 103, 114, and 139) that at $\lambda = 272\text{--}275 \text{ nm}$ the sign of cross-section variation changes with temperature increase.

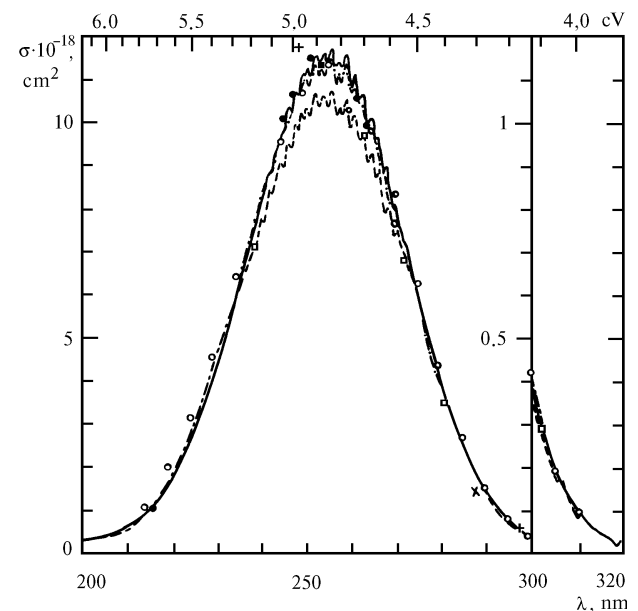


FIG. 1. Ozone absorption spectrum in the Hartley band at room temperatures: — — — 300 K, 1953 (Refs. 87 and 91); · · · · · 291 K, 1952–1953 (Refs. 92 and 93); × 292–295 K, 1961 (Ref. 94); + 298 K, 1962 (Ref. 107); ● ~300 K, 1964 (Ref. 108); ° ~300 K, 1982 (Ref. 114); ■ 297.5 K, 1986–1987 (Refs. 122 and 124); — 298 K, 1996 (Ref. 125), □ 295 K, 1988 (Ref. 116).

For $\lambda < 270 \text{ nm}$ the temperature dependence of the spectrum is insignificant ($\sim 1\%$ as T varies from 300 to 200 K). In the long-wave wing of the band this effect is more pronounced. As shown in Ref. 117, the temperature dependence at $\lambda = 270\text{--}350 \text{ nm}$ is satisfactorily approximated by a parabola. The parameters of fitting by the parabolic dependence $\sigma(\lambda, T)$ on T in the range between 275 and 350 nm, averaged over small intervals $\Delta\lambda \approx 5 \text{ nm}$, are given in Ref. 125.

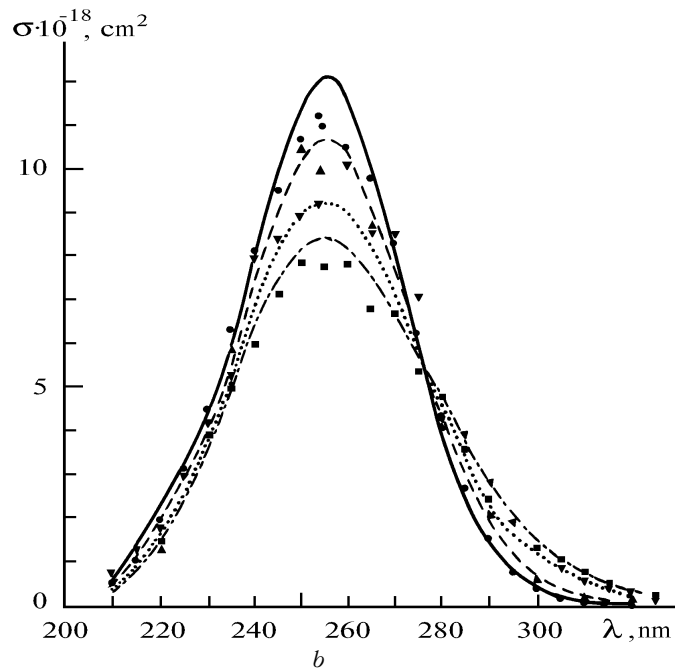
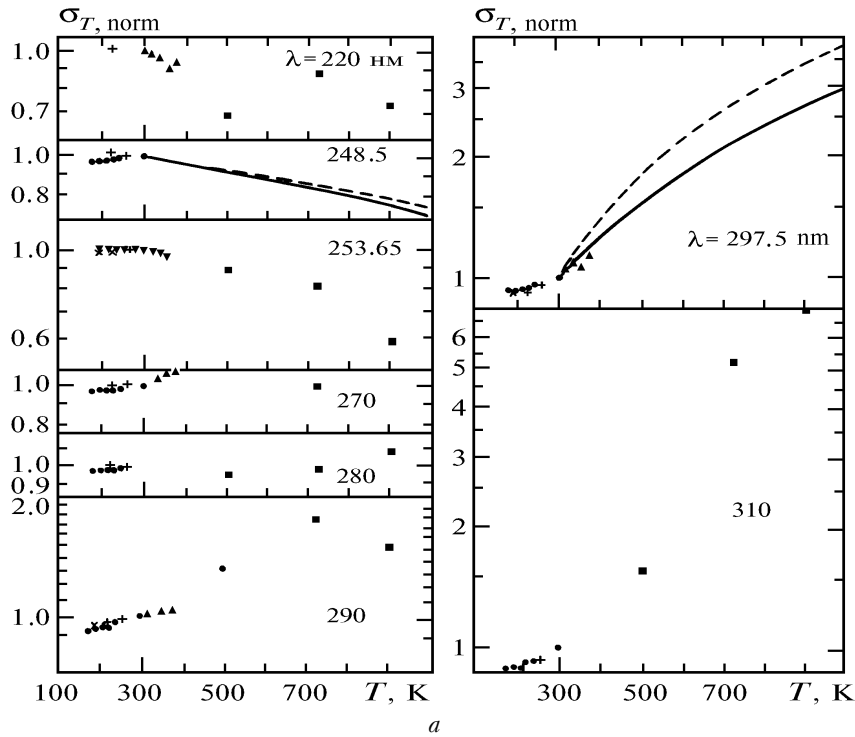


FIG. 2. Temperature dependence of the ozone absorption cross section in the Hartley band. a) Normalized temperature dependences for some wavelengths:

- $\sigma_T/\sigma_{291\text{ K}}$ (Refs 92 and 93); — — — $\sigma_T/\sigma_{298\text{ K}}$ (Ref. 107); Δ $\sigma_T/\sigma_{298\text{ K}}$ (Ref. 111);
- \square $\lambda \neq 248.5$ and 297.5 nm } $\sigma_T/\sigma_{300\text{ K}}$ (Ref. 114);
- \dots $\lambda = 248.5$ and 297.5 nm }
- + $\sigma_T/\sigma_{298\text{ K}}$ (Ref. 125);
- ∇ $\sigma_T/\sigma_{297.5\text{ K}}$ (Ref. 124);
- \times $\sigma_T/\sigma_{295\text{ K}}$ (Ref. 116).

b) Wavelength dependence at different temperatures from Ref. 114: 300 K (— theory, Δ experiment); 500 K (— — — theory, Δ experiment); 720 K (..... theory, ∇ experiment); 900 K (- · - · - theory, \square experiment).

1.2. Identification of an electron transition

The *ab initio* calculations^{22,41,71,72} showed that the Hartley band corresponds to the dipole allowed transition from the ground electronic state X^1A_1 to the 1^1B_2 state of the C_{2v} symmetry (or $3^1A'$ of the C_s symmetry, since the minimum energy of 1^1B_2 is attained with unequal lengths of side bonds^{22,41,60,140}) with the oscillator strength $f \approx 0.1$ (see Table III in Part I).

The 1^1B_2 state is a weakly bound (or unbound) state, and the O_3 predissociation is caused by interaction of at least three, except for X^1A_1 , intersecting surfaces: 1^1B_2 ,

2^1A_1 , and R , which are the surfaces $1A'$ along the dissociation coordinate v_3 (in the C_s geometry) and hence interact; moreover, 1^1B_2 and 2^1A_1 are correlated with the excited products $O^* + O_2^*$, while the repulsive surface R is correlated with the products in the ground states⁸³ $O + O_2$ (see Fig. 3 borrowed from Ref. 130). Hereafter the following designations of the O and O_2 electronic states are used: $O \equiv O(^3P)$, $O^* \equiv O(^1D)$, $O^{**} \equiv O(^1S)$, $O_2 \equiv O_2(X^3\Sigma_g^-)$, $O_2^* \equiv O_2(a^1\Delta_g)$, and $O_2^{**} \equiv O_2(b^1\Sigma_g^+)$. Therefore, photodissociation of O_3 in the Hartley band occurs through different channels.

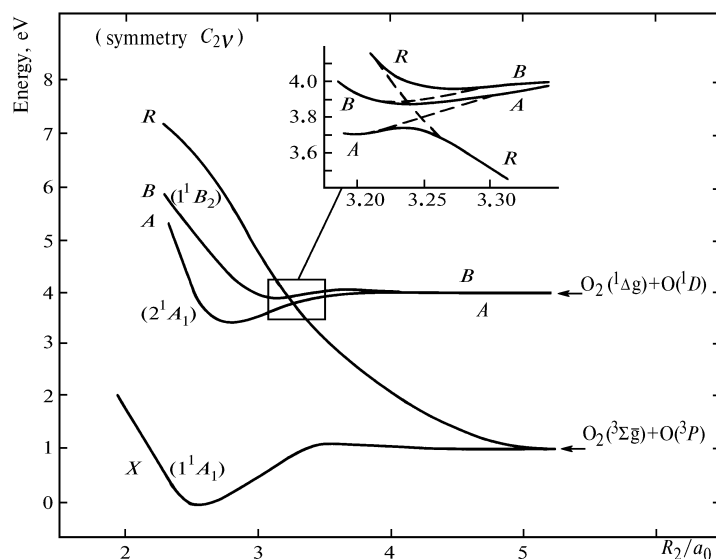


FIG. 3. Cross section in the C_s symmetry of the potential ozone surfaces 2^1A_1 , 1^1B_2 , and R ($1A'$ state in C_s) associated with absorption and dissociation in the Huggins and Hartley bands. The length of the second side bond of the molecule and the angle of bonding are fixed, $a_0 = 2.29 \cdot 10^{-9}$ cm, $R_1 = 2.5a_0$, and $\Delta = 110^\circ$.

Because of lower energy of the 1^1B_2 bond and due to intersection with R near the dissociation threshold (near a possible low potential barrier⁸³ 1^1B_2), the ozone dissociation in the Hartley band occurs within the time of a single vibration (several femtoseconds according to Ref. 140, ~ 3.6 ns according to Ref. 48, and ~ 130 fs according to Ref. 132). In this case the probability of molecular relaxation into the ground state is very small (no more than 10^{-6} according to Ref. 140). However, its observation is possible during short intervals considering probable existence of quasibound vibrational states 1^1B_2 . Such measurements were performed in Ref. 140, where not only O_3 luminescence with resolution of 0.035 nm was observed, produced by resonance Raman scattering of the fourth harmonic of a YAG:Nd³⁺ laser ($\lambda = 266$ nm) on O_3 , but also the positions were first recorded and the highly-excited (up to 6–7 quanta) vibrational levels of the ground state of the $(n\ 0\ 2m)$ type were identified with their upper levels being only 500 cm^{-1} lower than the dissociation threshold. It follows from the experiment of Imre et al.¹⁴⁰ that the excitation in 1^1B_2 does not noticeably change the O_3 bond angle since in the luminescence spectrum there are no bands with v_2 (it is also seen from the result of calculations, see

Table II in Part I), and in the region of vertical excitation 1^1B_2 has a repulsive character along the dissociation coordinate v_3 , in contrast to the calculations of Hay et al.⁸³

Though the experiment of Imre et al.¹⁴⁰ testifies the lack of a bound portion of 1^1B_2 , the final conclusion can be drawn only when luminescence is observed for scanning excitation frequency. But the luminescence itself counts in favor of successive consideration of radiation absorption processes between the two unperturbed surfaces and dissociation of molecules resulted from their motion over intersecting surfaces (Fig. 3). In support of this fact, in Ref. 80 it was shown by the example of an analysis of the $1.9\ \mu\text{m}$ IR-fluorescence band produced by laser-induced UV-photolysis that in the Hartley band a portion of molecules excited in 1^1B_2 does not dissociate and does not come back into vibrational state X^1A_1 . These molecules collide with O_2 or Xe and are stabilized into one of the lower unidentified triplets (singlet-triplet reactions of the type $O_3(^1B_2) + O_2(^3\Sigma_g^-)/\text{Xe} \rightarrow O_3(^3\beta) + O_2(^1\Delta_g, ^1\Sigma_g^+)/\text{Xe}$) with subsequent dissociation due to collision or fluorescence. A fraction of such molecules in the mixture 1000 Torr O_2 + small addition of O_3 estimated by Shi et al.⁸⁰, is $\sim 3 \cdot 10^{-4}$ and may depend on many factors.

The structure of the upper surface of the bound–unbound electron transition in the Franck–Condon (F–C) region may also be investigated using the other conventional methods, among them the method of analyzing the temperature dependence of transition probability distribution moments. Such an analysis of the Hartley band was made in Ref. 141. The comparison between the temperature dependence of moments calculated from the experimental cross sections of O_3 and using the harmonic model of 1^1B_2 , taken from Refs. 142–143, enabled Ivanov et al.¹⁴¹ not only to detect pronounced vibrational interaction violating the Condon approximation of the constancy of electron moment of transition within the F–C region, but also to show inadequacy of harmonic approximation for description of the upper state. It was impossible to decrease the disagreement between the theory and the experiment adjusting the parameters of the harmonic model. This is an important point since the majority of the Hartley band calculations were made in the harmonic Condon approximation.

An interesting approach to the problem of absorption in the Hartley band is described elsewhere.¹⁴⁴ As shown below, the gross band spectrum can be described using rather approximate models. To reproduce satisfactorily its fine structure, one should consider a full variety of molecular properties: symmetry, three–dimensionality, and so forth. With these facts in mind, Tannor¹⁴⁴ considered the transition from the standpoint of general properties of $^{16}O_3$ symmetry. It is clear that any potential surface of the base isotope of O_3 must possess the symmetry of a threefold transposition of identical atoms. In the ground state these isomers can interact by tunnelling, but the estimated time of interaction in the ground vibrational state is astronomically large (10^{90} s). This enables one to consider isomers as being independent. However, the situation may change in other energy regions, e.g., for vibrational or electron excitation. It is the Tannor's opinion that the electron excitation is observed in the Hartley band.

The electron–excited molecule of O_3 is classified among so–called "floppy" molecules. It has large, far beyond harmonicity, oscillation amplitude. Such molecules must be considered not within the framework of point groups of symmetry, but within the transposition–inversion (TI) groups which are isomorphic to the point ones.

Investigating the Hartley band from this point of view, Tannor¹⁴⁴ showed that the lower and upper states of the transition (X^1A_1 and 1^1B_2) are the $1E'$ states in representation of the TI group, which is isomorphic to the point group D_{3h} . There occurs conic intersection of their surfaces for equilateral geometry of the molecule. The strong second–order Jahn–Teller effect of repulsion is known to appear in such molecules. Then the Hartley band can be associated with the transition from a lower to upper branch of the Jahn–Teller system. Such transitions are dipole–resolved for perpendicular polarized light and usually are very intensive.

To realize the aforementioned approach to the Hartley band, one should consider a transposition symmetry of the potential surfaces (Tannor and other researchers plan to do this for 1^1B_2) and impose some restrictions on the symmetry of vibrational–rotational states of O_3 concerning, in particular, the nature of "spikes" in the band and anomalous distribution over even and odd J in the O_2^* molecules formed by dissociation. As to the last problem, the effects of the $X^1A_1 \rightarrow 1^1B_2$ symmetry are in

contradiction with the experiments performed by Valentini^{129,130} that counts in favor of the anomaly model for J , proposed by him in Ref. 130, which is based on dissociation through the surfaces intersecting with 1^1B_2 in the Franck–Condon region rather than on the excitation process. The considerations of the spiky nature advance a very interesting hypothesis which must be verified.

1.3. Cross–section calculations

The theoretical *ab initio* and semiempirical adjustable surfaces of the upper state^{15,104,109,137,142,143,145,146} and primarily the harmonic approximation of the lower state were used to describe the absorption in the Hartley band between two unperturbed surfaces.

In the majority of papers the absorption was considered in the F–C approximation of constancy of the transition dipole moment. The contribution of rotation in the form of frequency shift of the spectrum $\Delta\nu = -0.055 T$ (approximation of equal centrifugal coefficients for both surfaces and the generalized single t rotational state) was considered by Ader–Golden.¹⁴² In Ref. 59 the *ab initio* calculations were made using the surfaces that consider rotation and vibration of O_3 , anharmonicity, and coupling of rotation with vibration assuming the dipole moment of transition to be constant. Direct two–dimensional (with a fixed angle)^{147,148} and three–dimensional^{137,149–151} quantum–mechanical calculations of cross section were made using the Heller formalism.¹⁵²

Finally the absorption cross sections of ozone $k_j(\nu)$ from different vibrational states (j) of the lower surface were obtained.^{15,83,104,109,139,142,143,145,146} Depicted in Fig. 4 are the results obtained by the method described in Refs. 109, 145, and 146, according to which $k_{000}(\nu)$ corresponds to the smoothed experimental spectrum at $T = 195$ K, $k_{010,001}(\nu) = k_{000}(\nu - \nu_{010,001})$, and $k_{100}(\nu)$ is found either by subtracting the components k_{000} , k_{010} , k_{001} from the experimental spectrum at $T = 333$ K (Ref. 109) or by quantum–mechanical calculation using the upper surface obtained from the assumption¹⁴⁵ $k_{000} = k(T = 195$ K). An analytical formula approximating k_{000} by a piecewise function of polynomials and exponents was used in Ref. 109. The following methods were also used:

- method of wave packets⁸³ using potential surfaces calculated *ab initio*,
- the Wigner method¹⁵ using two types of surfaces, namely, calculated (solid line) *ab initio*⁸³ (dashed line) and adjustable ones,
- method of quantum–mechanical calculation¹⁴² for three models of the parameters of the upper state calculated *ab initio*⁸³ and adjustable.

The absolute values of cross sections of the given spectra are close.¹⁴² The shifts of maxima k_{010} and k_{001} from k_{000} are equal to: $\Delta\nu_{010} \approx 700$ (Refs. 109, 145, and 146), 200 (Ref. 15), and 170 cm^{-1} (Ref. 142); $\Delta\nu_{001} \approx 1042$ (Refs. 109, 145, and 146), 970 (Ref. 15), and 2084 cm^{-1} (Ref. 142).

As seen from Fig. 4, the spectra from (000), (010), and (001) are similar in structure and differ only in the shift with λ and the width, while the spectrum from (100) differs strongly and has a bimodal structure. This is also related to vibrational states with a large quantum number: the states with the excited first mode ν_1 most noticeably change the spectrum.

We can also conclude (see Fig. 4) that the employed calculational methods, while providing satisfactory agreement with total cross sections (taking into account their spread) and assuming similar spectra for individual vibrational levels, give

pronounced differences in their widths and frequency shifts. This is indicative of indifference of the gross spectra to the calculational method. The more accurate models require the more detailed experiments.

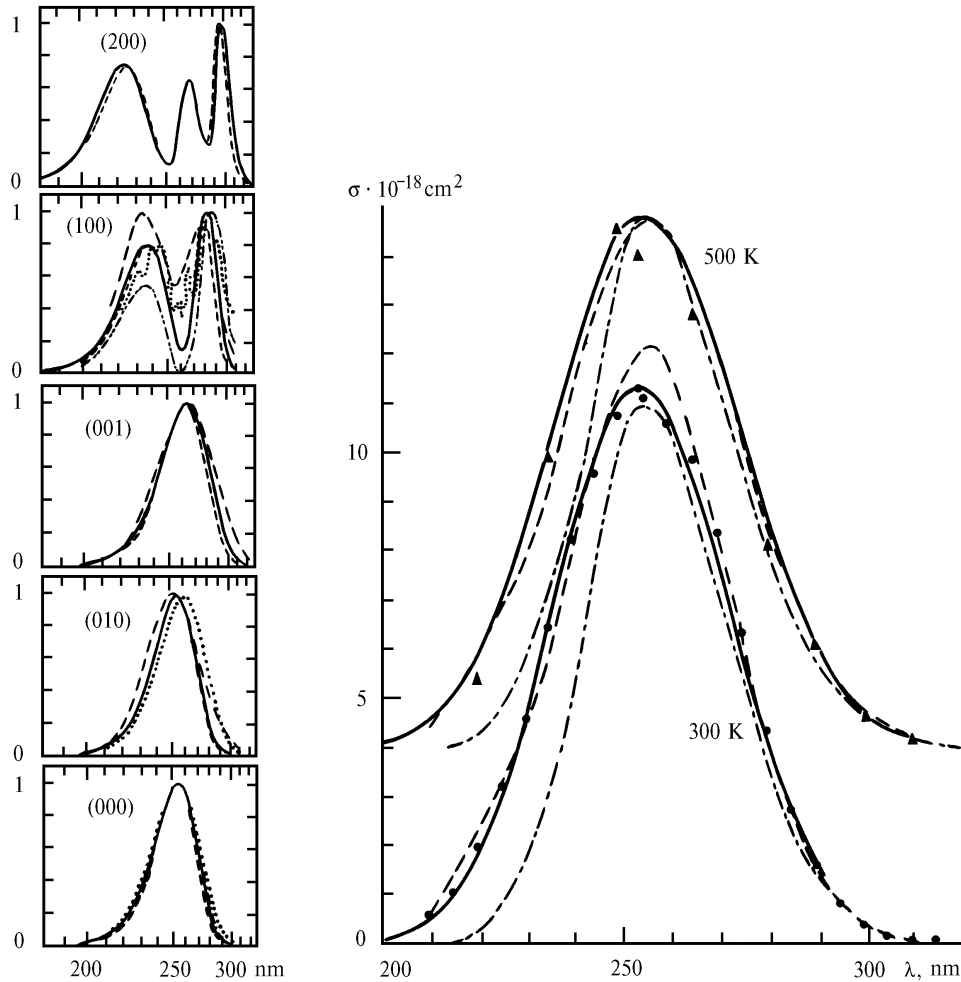


FIG. 4. Calculation of absorption cross section in the Hartley band corresponding to the $X^1A_1 \rightarrow 1^1B_2$ transition. The normalized cross sections from different vibrational levels X^1A_1 (at the left): $\dots\dots$ Ref. 109; $-\cdot-\cdot-\cdot-$ Refs. 145 and 146; $-\cdot-\cdot-\cdot-$ Ref. 83; $—$ Ref. 15; $---$ Ref. 142. Total cross section at $T = 300$ and 500 K (at the right): $-\cdot-\cdot-$ Ref. 153, $---$ Ref. 114, $---$ Ref. 142. For vivid presentation, the curves of total cross sections at $T = 500$ K are shifted upward along the ordinate axis by $4 \cdot 10^{18} \text{ cm}^2$. The experimental data for comparison (\bullet 300 K, Δ 500 K) were borrowed from Ref. 114.

The observed UV spectrum of O_3 is represented by a sum of spectra of different vibrational levels X^1A_1 with weights being equal to their population densities. Some of the spectra calculated by this method are represented by analytical expressions which conveniently approximate the Hartley band without spikes in a wide temperature range.^{114,132,142,153} Some of them are also given in Fig. 4. Here the formulas¹⁵³

$$\sigma(\nu, T) = \sum_{ijk} \sigma_{ijk}(\nu) Z_{ijk} / \sum_{ijk} Z_{ijk}, \quad (1)$$

are used, where T is expressed in K and ν — in cm^{-1} ; $Z_{ijk} = \exp(-h \omega_{ijk} / k T)$ is the Boltzmann factor; ω_{ijk} is

the vibrational frequency (ijk), in cm^{-1} , and σ_{ijk} is calculated by the formula

$$\sigma_{ijk} = [C / (3200 + \beta \omega_{ijk})] \exp[-((39200 - \nu - \omega_{ijk}) / (3200 + \beta \omega_{ijk}))^2]$$

with the parameter $C = 3.53 \cdot 10^{-4} \text{ cm}$; 39200 and 3200 are the band center and its width, in cm^{-1} ; $\beta = 0.8$ is the adjustable parameter.^{87,91,92,107} The simple approximation of the spectrum by Gaussian functions was used in derivation of Eq. (1). It is assumed to be applicable over the temperature range $T = 200-1000 \text{ K}$. The empirical formula

$$\sigma(\nu, T) = \sigma_a(\nu, T) + \sigma_b(\nu, T) \quad [114], \quad (2)$$

where $\sigma_a = s_{a0}^m [\tan h(\theta_{ae}/2T)]^{1/2} \exp[-\tan h(\theta_{ae}/2T) \times ((v - v_{a0})/\Delta v_{a0})^2]$ and $\sigma_b = s_{b0}^m \exp[-(T/\theta_{be}) - ((v - v_{b0})/\Delta v_{b0})]$, was derived in the Sulzer–Wieland approximation¹⁵⁴ developed for diatomic molecules. Eight adjustable parameters of formula (2): $s_{a0}^m = 1.187 \cdot 10^{-17} \text{ cm}^2$, $v_{a0} = 38800 \text{ cm}^{-1}$, $\Delta v_{a0} = 2900 \text{ cm}^{-1}$, $\theta_{ae} = 900 \text{ K}$, $s_{b0}^m = 6.21 \cdot 10^{-18} \text{ cm}^2$, $v_{b0} = 43000 \text{ cm}^{-1}$, $\Delta v_{b0} = 3300 \text{ cm}^{-1}$, and $\theta_{be} = 660 \text{ K}$ were found from the experimental data presented in Ref. 114. The formula (2) with the above-indicated parameters was derived for $220 \text{ nm} \leq \lambda \leq 320 \text{ nm}$ and $300 \text{ K} \leq T \leq 900 \text{ K}$. The third formula¹⁴²

$$\sigma(v, T) = (Cv / f(n)) (\sigma / \omega_1)^{2n} \exp[-(\sigma / \omega_1)^2] \quad (\text{Ref. 142}), \quad (3)$$

where

$$\langle v \rangle = \langle v_{000} \rangle + \sum_{j=1}^3 0.5 \omega_j (R_j - 1) (Z_j / (1 - Z_j)),$$

$$Z_j = \exp(-h\omega_j/kT), \quad f(n) = n! \approx \sqrt{2\pi n} \left(\frac{n}{e}\right)^n \left(1 + \frac{1}{12n}\right)$$

for $n = (v - \langle v \rangle + \sigma^2 / \omega_1 + 0.055 T) / \omega_1 \gg 1$,

$$\sigma^2 = \sum_{j=1}^3 \omega_j^2 \left[(R_j \delta_j)^2 \left(\frac{1}{2} + \frac{Z_j}{1 - Z_j} \right) + \frac{1}{8} (R_j - 1)^2 \left(1 + \frac{2Z_j}{(1 - Z_j)^2} \right) \right],$$

with $v_{000} = 39750 \text{ cm}^{-1}$; $C = 1.83 \cdot 10^{-21} \text{ cm}^3$; $\omega_1 = 1103$, $\omega_2 = 701$, and $\omega_3 = 1042 \text{ cm}^{-1}$ being the fundamental vibrational frequencies of ozone; $R_1 = 1.21$, $R_2 = 0.509$, and $R_3 = 3.0$ and $\delta_1 = 2.32$, $\delta_2 = 3.50$, and $\delta_3 = 0$ being the parameters of the upper surface.

Formula (3), analogous to formula (2), was obtained from the Sulzer–Wieland approximation for the model of a diatomic molecule at the frequency ω_1 with the Poisson functions in place of the Gaussian functions used in Eq. (2). The first ($\langle v \rangle$) and second (σ^2) moments of the spectrum were obtained from the rule of sums following from the F–C approximations. The term $0.055 T$ takes into account the contribution from the O_3 rotational degrees of freedom. The formula (3) is valid for $\lambda \leq 280 \text{ nm}$. Three models of the parameters R and σ were considered in Ref. 142.

Using such simple models, the more complicated analytical formulas of cross sections were also obtained, e.g., the integral expression¹³² for a one-dimensional model with adjustable parameters or the spectrum represented by Atabek et al.¹⁴³ as a weighted sum of spectra of different vibrational states, each being an integral of overlap expressed as a sum of hypergeometric functions ${}_2F_1$ of complex arguments. The harmonic surfaces were used, and the Dushinskii effect relating bending to stretching was taken into account in this model. In numerical calculations, these formulas are no less convenient than those given above.

The models described yield spectra which adequately approximate the thermal spectrum of the Hartley band averaged over a spiky structure near the extreme and its temperature dependence,^{83,109,114,142,143} which are in good agreement with the experiments analyzing the O_3 spectrum formed by recombination^{145,146} and double IR and UV resonance,^{102–104,139,142,155} and can be used in many applied problems of UV and IR–UV photochemistry,^{104,149}

although, as has been already noted, the harmonic model of 1^1B_2 and the F–C approximation are inadequate for the Hartley band.¹⁴¹

These calculations approximate the Hartley band without small but clearly pronounced spikes near the extreme that are observed in the experimental spectrum. These spikes were attributed either to the neglected contribution of the bound portion of 1^1B_2 (Ref. 22), or to the contribution of high vibrational levels X^1A_1 (Refs. 109, 145, and 146), or to the contribution of perturbations caused by interaction with the other upper states, e.g. with 2^1A_1 , determining the most pronounced vibrational structure in the longer-wavelength Huggins bands. As early as 1976 Pack¹⁵⁶ showed using a simple model that the vibrational (spiky) structure of the diffuse UV spectra of the XY_2 -type molecules can be observed for molecules directly excited into a simple dissociating state and in the majority of cases it is not necessary to use the model of bound upper state or intersection of bound state with dissociating one to account for the diffuse vibrational structure superimposed on the continuum. Some spikes obtained in theoretical calculations⁵⁹ and attributed to the vibrational contribution of 1^1B_2 reflect only in general the presence of spiky structure, though the gross spectrum in this case is in good agreement with the experimental one including its temperature dependence.

In the last few years some direct efforts were made to reproduce theoretically the spikes in the Hartley band.^{59,137,148–151,157} These calculation, though they demonstrate only qualitative agreement with the experiments, have revealed two important points. First, the spikes may be reconstructed only for a three-dimensional model; quenching of bending motion either yields no spikes, even if large anharmonic amplitudes of asymmetric and symmetric stretching are taken into account (quantum-mechanical calculations in Ref. 147 and quasiclassical ones in Ref. 148) or calls for some supplementary assumptions about the nature of quasiperiodic orbits (quantum-mechanical calculations performed in Ref. 148). Second, the quantitative description of spikes depends strongly on the model of the upper surface 1^1B_2 . The Sheppard–Walker surface¹⁵ taken by the authors of Ref. 149, 150, and 157 has some disadvantages that may be significant in calculating the spikes (e.g., it has a minimum C_{2v} symmetry rather than C_s , as the *ab initio* calculations predict, and has been fitted in the standard Sorbi–Murrell form to the surface *ab initio* from Ref. 83 which is in bad agreement with the experimental energy parameters: depth of well, height of energy barrier, etc.), while the quadratic model of 1^1B_2 (Ref. 151) does not provide quantitative agreement even with an account of anharmonicity to the fourth order of the perturbation theory. The only available calculations with a better *ab initio* surface than that proposed in Ref. 83, being also fitted to an analytical form of Sorbi–Murrell (Ref. 137), provide better reconstruction of the gross spectrum of the Hartley band and its spikes (as well as the Huggins bands,^{137,138} see Part II).

In Refs. 132 and 158 Johnson and Kinsey analyzed, using the Heller formalism,¹⁵² not the O_3 photodissociation spectrum, but the dipole–dipole autocorrelation function $\langle \phi_0 | \phi_j(t) \rangle$ derived from it. The spectrum was represented in the form of the Fourier transform

$$\sigma(\omega) \sim \omega \int_{-\infty}^{+\infty} \langle \phi_0 | \phi_j(t) \rangle e^{i\omega t} dt, \quad (4)$$

They showed that the spikes in the Hartley band are accounted for by several successive peaks of the time dependence of $\langle \phi_0 | \phi_j \rangle$ [at 19, 41, 68, 99, and 128 fs, followed by the plateau to ~ 250 fs (see Fig. 5 borrowed from Ref. 132)] appearing due to unstable quasiperiodic trajectories of motion over the surface 1^1B_2 in the F–C region during the first 200 fs after the light absorption. Here $\langle \phi_0 = \hat{\mu} | \phi_0 \rangle$ is the state produced by the action of the dipole–moment operator $\hat{\mu}$ of the transition $X^1A_1 \rightarrow 1^1B_2$ on the found vibrational state $|\psi_0\rangle$ of the lower surface, and $|\phi_j\rangle = \exp[-i\hat{H}(1^1B_2)t/\hbar]|\phi_0\rangle$ described its temporal evolution governed by the upper–state Hamiltonian. The gross wide spectrum of the band, on account of the correspondence between frequency and time Fourier transforms in Eq. (4), is caused by rapid (≤ 6 fs) dissociation of overlapping wave–packet states due to primary motion of the excited molecule from the F–C region in the direction of symmetric stretching.

The quasiclassical calculations showed that recurrence of spiky movement over 1^1B_2 is stipulated by several quasivibrations of a short O–O bond accompanying the dissociative motion of a long one. Quantum^{137,149,150} (in Ref. 149 in the Jacobi coordinates and in Ref. 150 in the hyperspherical Pack coordinates, being more suitable for the A_3 –type molecules and substantially reducing the time of calculations) and classical¹⁵⁷ three–dimensional calculations of the autocorrelation function and its classical analog indicate good qualitative agreement with the Johnson–Kinsey function calculated from the experimental spectrum.^{115,125} The spectra derived using the aforementioned calculations and the formula (4) were in good agreement with the initial spectrum.^{115,125}

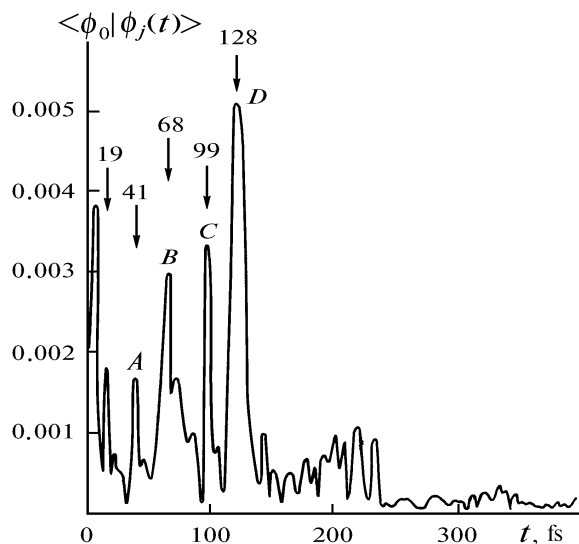


FIG. 5. Autocorrelation functions in the Hartley band obtained from the experimental spectrum¹¹⁵ in Ref. 132. The figure is reproduced from Ref. 132. The initial peak corresponding to the gross spectrum of the band has been subtracted from the plot. A, B, C, and D denote the fundamental recurrent peaks.¹³²

Analogous result was also obtained in the two–dimensional quantum calculations with a quenched bending mode.¹⁴⁸ However, it became necessary to consider quasiperiodic orbits above the barriers of isomerization and dissociation of the upper surface (see below). Since such orbits are highly sensitive to the surface quality and the Sheppard–Walker surface, used for calculations, was of low quality, the calculation by Farantos¹⁴⁸ should be considered as preliminary, especially due to the facts that classical two–dimensional calculation¹⁴⁸ yielded no spikes, and the reason for their absence in quantum calculations¹⁴⁷ remained unknown.

To explain the nature of spikes further, one should improve the quality of calculations based on the scheme proposed in Ref. 137, 149–150, and 157, in particular, develop more adequate models of potential surfaces, take into account interaction with the other surfaces, variable dipole moment of transition, and so on. Some of these improvements have been already made. The autocorrelation function and the Hartley band were calculated in Ref. 137 with a more realistic surface 1^1B_2 than that borrowed from Ref. 15 and used for calculation in Refs. 149, 150, and 157. This surface, calculated and approximated in Ref. 137, was closer, by its parameters, to the experiment than that introduced in Ref. 15. It had steeper slope in the F–C region, minimum in the C_s symmetry, etc. As a result, both the gross spectrum of the band and spikes found in Ref. 137 agreed with the experiment much better than in Refs. 149, 150, and 157. The estimates performed in Ref. 137 showed that the neglected effects of variable dipole moment and rotation affected the spectrum insignificantly, while the effect of 1^1B_2 intersection with the other surfaces should be taken into account.

Some interesting considerations have been applied to spikes by Tannor.¹⁴⁴ The most complicated point in explaining the recurrent motion of molecules in the 1^1B_2 state is the density of the trajectories, whose temporal structure correspond to the peaks in $\langle \phi_0 | \phi_j \rangle$: whether they can provide the observed pronounced spiky structure or not. Tannor suggested that the contribution to spikes came not only from a recurrent motion in the strict sense of the word (with quasirecursion to the initial state), but also from the transitions from three locally symmetric regions of the surface (caused by transposition symmetry due to the identical atoms of O_3) to the other isometric region.

The density of such trajectories for the excited 1^1B_2 –type states can be much higher than that of strictly recurrent trajectories.¹⁴⁸ To test this hypothesis, one should symmetrically consider the motions described in Refs. 132, 137, 149, 150, 157, and 158 which is planned by Tannor¹⁴⁴ and has been partially shown in two–dimensional calculations.¹⁴⁸ It might also be of great interest to compare the Hartley band spectra of ozone isotopes of three types: with the same transposition symmetry as in $^{16}O_3$, lower symmetry, e.g., for $^{16}O_2^{18}O$, and entirely absent symmetry for $^{16}O^{17}O^{18}O$. Such experiments are yet to be made.

The analogous comments can be applied to the calculations of the resonance Raman spectrum (RRS) in the Hartley band to compare them with the experiment of Imre et al.¹⁴⁰ The RRS was calculated in Refs. 143, 147, and 151. In Ref. 143 the analytical three–dimensional calculations of a sum of overlap integrals were performed for quadratic surfaces in the F–C approximation; in Refs. 147 and 151 the numerical calculations were performed using the Fourier transforms of autocorrelation

functions in analogy with calculations of the absorption spectrum (in Ref. 151 a three-dimensional calculation was performed for harmonic surfaces with an account of anharmonicity to the fourth order of the perturbation theory, while in Ref. 147 two-dimensional calculation with quenched bending vibration, but for a more realistic Sheppard-Walker surface¹⁵ and with an account of arbitrary large amplitudes of vibrations was performed).

All calculations indicated good agreement with the RRS spectrum and slightly poorer agreement with the spectrum intensity. This shown an important role of all the three modes of vibrations, anharmonicity, the 1^1B_2 surface shape, and the account of large amplitudes of vibrations being outside the scope of the perturbation theory. Of particular importance (as in the absorption cross section) is the bending vibration ν_2 , which is not immediately evident from the spectrum.

1.4. Conclusions

Thus the strongest ozone absorption band, i.e., the Hartley band (220–310 nm, $\sigma_{\max} \approx 1.1 \cdot 10^{-17} \text{ cm}^2$ at $\lambda = 255.3 \text{ nm}$) corresponds to the dipole-resolved transition ($f \approx 0.1$) between the electron states X^1A_1 and 1^1B_2 . The absorption spectrum (smoothed over weak spikes near maximum) and its temperature dependence are well described in Refs. 15, 83, 104, 109, 114, 132, 139, 142, 145, 146, and 153 by simple models of transition between these two states (a harmonic surface is assumed for the lower state and a repulsive one –for the upper state) taking into account the F–C principle, though there is some evidence on inadequacy of the F–C approximation and harmonic representation of the upper surface.¹⁴¹ Some more exact calculations of the smoothed spectrum are also available.^{59,143} The spectrum is represented as a sum of continuous spectra from different vibrational levels X^1A_1 ; it should be noted that for the lower levels of the modes ν_2 and ν_3 (000, 010, 001, etc.) these spectra are similar in shape and differ only in shift and width, while for ν_1 (100, 200, etc) the spectrum differs strongly and has a bimodal and more complicated character. A fine structure of the spectrum, i.e., spikes that are caused by unstable quasiperiodicity of motion over the surface 1^1B_2 (Refs. 132, 137, 148, 157, and 158), are described qualitatively well by a sequence of peaks in temporal dependence of the dipole-dipole autocorrelation function or its classical analog in the form of a Fourier transform of the spectrum. A quantitative description of spikes requires a three-dimensional model (in spite of the lack of bending vibration in the RRS), an account of transposition symmetry of O_3 , and is very sensitive to quality of the potential surfaces being used.

The estimated time of dissociation (predissociation) of 1^1B_2 is of the order of 1 ps (several femtoseconds – 3.6 ps, see Refs. 48, 80, 132, and 140). Imre et al.¹⁴⁰ observed a weak luminescence spectrum (RRS) of nondissociated molecules in 1^1B_2 , consisting of overtones X^1A_1 of the type ($k \ 0 \ 2 \ m$) up to the levels being $\sim 0.06 \text{ eV}$ lower than the dissociation threshold. Shi and Barker⁸⁰ observed the possible collisional transition from 1^1B_2 to one of the lower triplet states. The RRS was satisfactorily reproduced in two-dimensional¹⁴⁷ and three-dimensional¹⁵¹ quantum-mechanical calculations by the method of the Fourier

transform of the corresponding autocorrelation function and in three-dimensional analytical calculations¹⁴³ of the overlap integrals within the framework of the harmonic F–C model.

The O_3 dissociation in the Hartley band is caused by interaction (intersection) of four-electron surfaces, namely, the lower X^1A_1 and upper 1^1B_2 , 2^1A_1 , and repulsive surface R . It should be noted that X^1A_1 and R dissociate into $O + O_2$ and 1^1B_2 and 2^1A_1 dissociate into $O^* + O_2^*$. Interaction among these surface determines the presence of two channels of O_3 dissociation with quantum yield of the excited channel ϕ^* in the form of a ~ 0.8 – 0.9 smooth step (Steinfeld et al.⁶³ recommended 0.92) for $\lambda < 300 \text{ nm}$ vanishing near the threshold (~ 308 – 310 nm) or possibly having a "tail" up to $\lambda \approx 325 \text{ nm}$, which depends on temperature and vibrational excitation of O_3 . No other channels of dissociation were observed.^{113,159–163}

The experimental investigations of ϕ^* and the dissociation product states (which have specific nonequilibrium vibrational-rotational distribution^{97,107,129,130,164,165}) are indicative of a complicated mechanism of dissociation which cannot be described adequately without regard for surface interaction,^{15,104,130,166} their symmetry, and, correspondingly, isotopic dependence $\phi^* [(1 - \phi^*)$ for $^{16}O^{18}O$ is twice as large as that for $^{16}O_2$ (Ref. 130)] which can be associated with anomalous isotopic enrichment of O_3 under laboratory conditions and in the atmosphere,¹⁶⁷ whose mechanism leaves unexplained.

The vibrational-rotational distribution of O_2^* in the Hartley band appeared to be very similar to the O_2 distribution obtained by the analogous methods in the visible Chappuis is band^{98–100} (see Part II) and explained within the framework of the same models of "vibrational adiabatic transition" (see Ref. 130) and "modified angular momentum" (Refs. 128 and 165), as well as to the rotational distribution of O_2 in the Hartley band.¹⁶⁵ The more adequate models ϕ^* have not been developed yet, though the empirical analytical formulas for $\phi^*(\lambda, T)$ have been proposed by Moortgat and Kudzus¹⁶⁸ and satisfactory qualitative explanations of experimental data has been also given.

In the experiments the pressure dependence of the Hartley band spectrum was not observed since the total pressure of a gas did not exceed 1 atm.

2. ABSORPTION REGION TO THE IONIZATION THRESHOLD (5.7–12.75 eV) (REGION VI)

2.1. Measurements of the absorption spectrum

The O_3 absorption spectrum at wavelengths shorter than 220 nm was measured only in a few papers^{21,88,105,106,125,169} mainly in the 1950's. These results, shown in Fig. 2 of Part I and in Fig. 6, are in good agreement; the agreement is observed among the cross-section values obtained forty years ago^{88,106} and among them and the spectrum of electron losses at small angles obtained in Ref. 21 in 1974. Then the measurements were made only at individual wavelengths λ (Ref. 169) and in the long-wavelength wing of the region for $\lambda \geq 185 \text{ nm}$ (Ref. 125). The temperature dependence was investigated only in the temperature range from range 226 to 298 K for $\lambda \geq 185 \text{ nm}$ (Ref. 125), where the temperature variations did not exceed 1%.

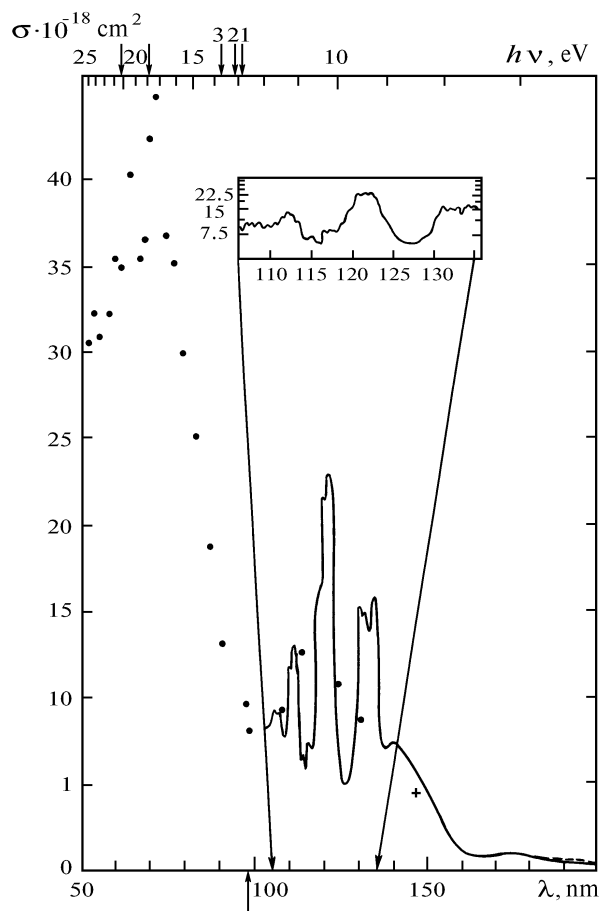


FIG. 6. The ozone absorption spectrum in the vacuum UV at room temperature: — 1953 (Refs. 88 and 105); • 1958 (Ref. 106); + 1986 (Ref. 169); - - - - 1986 (Ref. 125). The cross section borrowed from Ref. 106 was normalized to the cross section for the L_{α} line (121.6 nm) reported in Refs. 88 and 105. At the top of the figure a fine structure of the spectrum near the first IP is shown in the logarithmic scale.⁸⁸ The arrows denote the first IP of O_3 .

2.2. Identification of the spectrum

The spectrum to the first ionization potential (IP), extended from 100 to 220 eV, represents a set of pronounced wide extrema at ~ 7.2 (172.5), ~ 8.5 (145), ~ 9.3 (133), ~ 10.2 (122), and 11.3 eV (110 nm). The most pronounced structure between 9 (139) and 13 eV (95 nm) (see Fig. 6) is interpreted²¹ as ns and np Rydberg series reaching their peaks at 9.24, 10.20, 11.12, and 11.48 eV that can be reduced to the first IP at 12.75 eV (97.24 nm). Narrower and frequent small spikes that correspond to the Rydberg states that can be reduced to higher IP are superimposed on these peaks.²¹

Above the first IP the spectrum shape changes and ionization continuum is observed with wide maximum near 16.5 eV (75 nm). It is still possible to separate out some individual sharp peaks on it,¹⁰⁶ but above 19 eV ($\lambda < 65$ nm) the continuum becomes structureless.²¹

As of the present, there are no experimental data on the spectrum and its dependence on temperature and pressure in the far — UV. There are also few theoretical papers on this subject. The excitation energies calculated in them are in good agreement with salient features of the experimental spectrum. An attempt of Tanaka et al.⁸⁸ to identify the spectrum cannot be considered successful since it was based on incorrect data on the O_3 molecule shape and structure of electron levels.

2.3. Analysis of dissociation products

The O_3 photolysis products in the entire UV region will be analyzed at length in separate paper. Let us briefly run through the results obtained.

Though for $\lambda < 200$ nm there appears a spin-resolved channel of dissociation with O^{**} formation, the O^{**} formation was not observed in the experiments.^{163,172} It follows from the experiments at three wavelengths: 222 (a KrCl laser), 193 (an ArF laser) (Ref. 51), and 157.6 nm (F_2 -laser) (Ref. 173) that as λ decreases in the UV region, $O^* + O_2^*$ yield also decreases, the channel $O^* + O_2^{**}$ appears (its threshold is 260 nm), and the $O + O_2$ yield increases. In this case the contribution of reactions with O_2 formation with large internal energy sufficient for collisionless dissociation of the molecule into atoms increases (i.e., there occurs a two-step dissociation of O_3 into three O atoms). It is clear that to obtain a complete pattern in the vacuum UV, one needs further experiments at more than three wavelengths.

TABLE I.

Authors, years, references	Serial number of IP	1	2	3	4	5	6	7	8	9	10	
1	2	3	4	5	6	7	8	9	10	11	12	
	Excited orbit by the Koopmans theorem (H-F method)	1 a_2	6 a_1	4 b_2								
Radwan, Turner 1966 Ref. 174	Excited orbit	Unidentified										
	Symmetry of state	Unidentified										
	Energy, eV	12.3±0.1	12.52±0.05	13.52±0.05	16.4 – 17.4	19.24±0.10						
Frost, Lee, McDowell 1974 Ref. 24	Excited orbit	6 a_1	1 a_2	4 b_2								
	Symmetry of state	$1^2 A_1$	$1^2 A_2$	$1^2 B_2$	$1^2 B_1$; $2^2 B_2$							
	Energy, eV	12.75±0.01 (adiabatic 12.53±0.01)	13.03±0.02	13.57±0.01	20.3 ± 0.1							
Brundle 1974 Ref. 23	Excited orbit	6 a_1	1 a_2 ; 4 b_2									
	Symmetry of state	$1^2 A_1$	$1^2 A_2$; $1^2 B_2$		$1^2 B_1$; $2^2 B_2$							
	Energy, eV	12.75 (12.56)	13.02	13.57	16.0 – 18.5 (three lines, center at 17.7)		18.7 – 21.5 (center at 20.1)					
Dyke, Golob, Jonathan, Morris, Okuda 1974 Ref. 175	Excited orbit	6 a_1	4 b_2	1 a_2								
	Symmetry of state	$1^2 A_1$	$1^2 B_2$	$1^2 A_2$								
	Energy, eV	12.75 (12.44±0.01)	13.02	13.57	16.54	17.45	~ 20 wide band	~ 24.5				
Weiss, Berkowitz, Appelman 1977 Ref. 54	Excited orbit											
	Symmetry of state											
	Energy, eV	adiabatic 12.519±0.004										
Moseley, Ozenne, Cosby 1981 Ref. 176	Excited orbit											
	Symmetry of state											
	Energy, eV	adiabatic 12.52±0.04	13.03	13.52	15.57	16.54	17.45	19.99				
Katsumata, Shiromaru, Kimura 1984 Ref. 177	Symmetry of state	6 a_1	4 b_2	1 a_2								
	Symmetry of state	$1^2 A_1$	$1^2 B_2$	$1^2 A_2$	$2^2 B_2$ Refs. 170, 171 $2^2 B_1$ Ref. 183	$2^2 B_1$ Refs. 170, 171 $3^2 A_1$ Ref. 183	$3^2 A_1$, $4^2 B_2$ Refs. 170, 171 $3^2 B_1$, $3^2 B_2$ Ref. 183	$5^2 B_1$, $5-7^2 A_1$, $5-7^2 B_2$ Refs. 170, 171				
	Energy, eV	12.73 (12.43)	13.00	13.54	15.6	16.5 (16.09)	17.6 (17.1)	19.4–20.8 (center at 20.00)	22.7	24.1	26.8	

3. OZONE IONIZATION POTENTIALS (IPs): $h\nu > 12.75$ eV (REGION VII)

3.1. Measurements of the IPs

The ozone IPs were repeatedly measured^{23,24,54,174–180} and calculated (see Refs. 7, 8, 30, 170, 171, and 180–183 and the references therein). The experimental results are summarized in Table I and are shown in Fig. 6 with arrows.

3.2. Identification of the IPs

By the Koopmans theorem¹⁸⁴ (based on the Hartree–Fock single–configurational method) the three lower IP should correspond to electron detachment from the orbits $1a_2$, $6a_1$, and $4b_2$, respectively. However, as is well known,¹⁸⁵ the ozone electron levels are poorly described by the Hartree–Fock single–particle theory. This also concerns the IP.

Almost all studies identify the first IP as an electron detachment from the $6a_1$ orbit. There is some disagreement on the second and third IPs. These potentials correspond to the transitions from $1a_2$ and $4b_2$, their sequence in the experiments and calculations is different. The majority of calculations^{7,8,170,171,182} in agreement with the experiments^{175,177} gave the second IP occurring from the $4b_2$ orbit (dual violation of the Koopmans theorem). However, in some calculations^{30,170,181} and in the experiment,²⁴ $4b_2$ is related to the third, and $1a_2$ —to the second IP. The summary results concerning the first ten IPs of O_3 are given in Table I where the experiments starting from the 1960's are described. Only the first IP was measured earlier: in 1954 (Ref. 178) it was found to be 12.8, in 1956 (Ref. 179) -12.8 ± 0.05 , and in 1957 (Ref. 180) -11.7 eV.

The higher ozone IPs were studied only in some papers (theoretically in Refs. 8, 170, 171, 182, and 183 and experimentally in Refs. 23, 24, 175, and 177). They were not identified, and their location remained uncertain. The so–called "shake–up" effect when the detachment of one electron is accompanied by excitation of the other¹⁷⁰ is typical of them. This is experimentally manifested in satellite bands of the ionization spectrum and makes the IP identification more difficult. There appears to be one IP of O_3 in the 15.5 eV region,^{170,171,177} 1–3 potentials in the 16–18 eV region (Refs. 21, 23, 170, 171, and 174–177), as well as one or several potentials in the 20–21 eV region (Refs. 23, 24, 170, 171, 174–177, and 182). Further up to 28 eV the IPs were not observed^{21,23} or very weak IPs were observed¹⁷⁷ but were not calculated. Above 28 eV, according to the calculations of Padiál et al.,¹⁸² there must be weak ionization transitions that merge into the ionization continuum and do not possess a pronounced structure of the spectrum in the region of a few tens of eV. In Ref. 182 the IP from inner shells in the 550 eV region were also calculated.

In Ref. 54 the yields of ionization products were investigated up to 60 nm (21 eV). The main product over the entire region above the first IP is the O_3^+ ion. Above 13.08 eV, there appears a poor yield of the O_2^+ ions (the threshold of the reaction $O_3 + h\nu \rightarrow O_2^+ + O + e$ is 13.125 ± 0.004 eV). The O_2^+ yield increases for $h\nu \geq 13.432$ eV, which is close to the adiabatic energy of the third IP and probably indicates a predissociation mechanism of O_2^+ formation. The atomic O^+ ion appears for

$h\nu \geq 15.21 \pm 0.01$ eV (being 0.57 eV higher than the threshold of the reaction $O_3 + h\nu \rightarrow O^{++} + O_2 + e$), and its quantum yield increases gradually with λ decrease. The 15.21 eV energy is close to the fourth IP of O_3 . It is probable that the start of O^+ formation may be associated with the band of this potential, as well as the further periodic variations of the O^+ yield increase may be associated with the fifth and sixth IPs. The relative quantum yields of O_3^+ , O_2^+ , and O^+ are equal to 1.00, 0.36, and 0.05 at 60 nm (Ref. 54).

The energies of the two lower vibrational states of the v_1 mode were measured in Ref. 176 for the first ion of ozone O_3^+ .

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