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Units and values for the ozone absorption cross section at 253.65 nm (air) with appropriate significant digits and rounding for use in documentary standards

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Abstract: This paper provides the recommended numerical values and uncertainties of the ozone absorption cross section, with appropriate significant digits and rounding, expressed in the different units commonly found in documentary standards. Use of these values in documentary standards will ensure consistency in reported values. The paper also gives guidance on how the quantity can be described to be most consistent with current written standards on quantities and expressed in SI units.

2. Introduction

The CCQM recommended in 2020 [1] that a new value for the ozone absorption cross section be used in the on-going key comparison, BIPM.QM-K1, of ozone photometers used for establishing metrological traceability for surface ozone measurements. The establishment of a date for the global implementation of the new value is being coordinated by the CCQM GAWG Task Group for Ozone Cross Section. A prerequisite for the change, is to ensure that developers of documentary standards and regulations that refer to ozone measurements are aware of the change and have sufficient time to update their documentation to the new value. The different documentary standards can report the value of ozone absorption cross section in different units. This paper provides the recommended numerical values and uncertainties of the ozone absorption cross section, with appropriate significant digits and rounding, expressed in the different units commonly found in documentary standards. Use of these values in documentary standards will ensure consistency in reported measurement results. The paper also gives guidance on how the quantity can be described to be most consistent with current written standards on quantities and expressed in SI units.

For an electromagnetic wave propagating along a given coordinate direction, z, through a medium containing C identical absorbing particles per-unit-volume, the particle-specific absorption cross section, σ, can be defined by

$$\sigma = -\frac{d\ln(N_{\mathrm{p}})}{dz}\frac{1}{C} \tag{1}$$

where N_{p} is the number of probing photons in the sample volume. Integration of this function leads to the well-known Beer-Lambert law. Based on this definition, σ has dimensions of length squared, with conventional units in the SI equal to cm^2 per absorbing particle. For documentary standards addressing absorption by ozone, it is common to refer to the measurand as the “absorption cross section of ozone”, although in many cases the quantity of interest is not consistent with the preceding definition. Unfortunately, historical choices of nomenclature have led to dimensional differences between various quantities sharing the same name. Furthermore, non-SI units are also often employed. To clarify these inconsistencies, we present the relevant relationships between various ozone-related measurands, as well as how these quantities can be described using the SI.

A change in cross section value will lead to an inverse change in the ozone amount fraction determined by an ozone photometer. In principle, correction factors to historically determined ozone amount fractions can be applied that would be consistent with the new ozone cross section values. The values of such conversion factors and the limitations of their application are discussed in Appendix 2.

3. Ozone absorption cross section per molecule at 253.65 nm (air) with appropriate significant digits and rounding

Table 1 below lists the CCQM recommended value of the ozone absorption cross section [2], which is referred to as the CCQM.O3.2019 value [3] and its standard uncertainty, both expressed in the unit cm^2. It also gives the values and uncertainties of three closely-related quantities often found in the literature. In each case the appropriate rounding and number of significant digits is used[a], which will avoid any significant biases being introduced when using different units or related quantities to report the absorption cross section.

Quantity	**symbol**	**Value / unit**	**Standard uncertainty/ unit**
absorption cross section per molecule	σ	1.1329×10^{-17} cm^2	0.0035×10^{-17} cm^2
mass absorption coefficient	α_{m}	1.4214×10^{-5} m^2 μg^{-1}	0.0044×10^{-5} m^2 μg^{-1}
linear absorption coefficient at standard temperature and pressure (0 °C and 101325 Pa)	α_x	304.39 cm^{-1}	0.94 cm^{-1}
absorption coefficient, at standard temperature and pressure (0 °C and 1 atm)	α_{O}	304.39 atm^{-1} cm^{-1}	0.94 atm^{-1} cm^{-1}

Table 1: CCQM recommended value of the ozone absorption cross section at 253.65 nm (air) and its standard uncertainty with appropriate significant digits and rounding for use in documentary standards, expressed in the unit cm^2, with values and uncertainties of three closely-related quantities often found in the literature.

[a] *Rounding follows the practice presented in NIST special publication 811, Appendix B: Conversion Factors https://doi.org/10.6028/NIST.SP.811e2008*

As defined above, the **absorption cross section per molecule** has the symbol σ, which is customary for ozone photometry. Its unit is often given in the literature as cm^2/molecule, but "molecule" is not an SI unit and therefore discussion of its use is deferred until section 5. The value and standard uncertainty of σ bear directly on the three remaining quantities given in the table. A basic summary of these quantities is presented in this section and in greater detail in sections 4 and 5. Note that the relative standard uncertainty of σ is 0.0035/1.1329 = 0.0031, or 0.31 %. This is the relative standard uncertainty of all entries in Table 1. A more expansive version of this table is provided in Appendix 1.

It will be shown in section 4 that **the mass absorption coefficient** α_{m} is identical to the absorption cross section σ divided by the mass of a single ozone molecule, $m(\mathrm{O}_3)$:

$$\alpha_{\mathrm{m}} = \frac{\sigma}{m(\mathrm{O_3})}\,, \tag{2}$$

where it is customary to express σ in m^2 (instead of cm^2) and $m(\mathrm{O_3})$ in micrograms. The important point to note here is that the relative standard uncertainty of the mass absorption coefficient is also equal to 0.31 % because the relative standard uncertainty of $m(\mathrm{O_3})$ is negligible by comparison to that of σ, as shown in section 4. The mass absorption coefficient is defined in an equivalent way in ISO 80000-7-36.2 (2019) [4a]. However, the same quantity is often referred to in the literature as simply the absorption coefficient.

In this report, the **linear absorption coefficient** will be given the symbol α_x as is customary in ozone photometry. Other symbols for this coefficient are used in different disciplines or by different authors. The value of the linear absorption coefficient can be calculated from

$$\alpha_x = \sigma \frac{p_{\mathrm{std}}}{k_{\mathrm{B}} T_{\mathrm{std}}} = \sigma C_0\,, \tag{3}$$

where p_{std} is the standard atmospheric pressure, whose SI value is defined to be 101 325 Pa, T_{std} is the standard temperature, whose SI value is defined to be 273.15 K (0 °C), k_{B} is the Boltzmann constant, whose SI value was defined in October 2018 to be exactly 1.380 649 x 10^{-23} J/K, which is consistent with its previous experimental value [5].

Therefore the relative standard uncertainty of α_x, $0.31\ \%$, is completely due to σ.

It is made more obvious in section 4 that the unit of α_x is cm^{-1}. ISO 80000-7-35.2 (2019) [4a] defines the linear absorption coefficient, for which we use the symbol α_x. Physically, this quantity represents the absorption coefficient, α, of dimension inverse length, that would be observed at the standard temperature and pressure if the sample consisted solely of ozone with an ideal-gas-based number density equal to C_0. Using Eq. (3), we calculate $C_0 = \frac{p_{\mathrm{std}}}{k_{\mathrm{B}} T_{\mathrm{std}}}$ = 2.686 780 111… ×10^{19} cm^{-3}, which we show below is the well-known Loschmidt constant evaluated for an ideal gas at the same standard conditions.

Finally, we consider an older unit system still used by some practitioners to describe the ozone photometer. This system takes the standard atmosphere (atm) as its unit of pressure instead of the pascal, where 1 atm = 101 325 Pa.

We denote the **absorption coefficient** for the partial pressure of ozone by the symbol α_{O} and show in section 5 why it is that $\alpha_{\mathrm{O}} = \frac{\alpha_x}{1\ \mathrm{atm}}$ in a unit system where the standard atmosphere (atm) is used as the unit of pressure instead of the pascal (Pa).

This relation implies that the numerical value of α_{O} is identical to that of α_x in this system and that the uncertainties of both quantities are the same, but that the unit of α_{O} is atm^{-1}cm^{-1} as shown in Table 1. We show that the value of α_x is, and must be, the same in both systems of units.

If results in hand have been computed using a different cross section, call it σ_{old}, then for all calculations obtained using the quantities listed in column 1 of Table 1, multiply the quantity in question by the ratio $\sigma/\sigma_{\mathrm{old}}$ to incorporate the new value of σ. It is only required that both numerator and denominator are expressed in the same unit of area, cm^2 for example. However, due to rounding of historical values, this simple technique is only approximate. See Appendix 2 for more precise conversions of historical values.

4. Photometer measurements of ozone concentrations and amount fraction in SI units Summary results tabulated in Appendix 1

SI units will be needed for the following quantities:

length, ℓ: metre (m), centimetre (cm)
energy, E: joule (J)
pressure, p: pascal (Pa)
temperature, T: kelvin (K)
mass, m: kilogram (kg)

Pressure is usually thought of as the quotient of a uniform force applied to an area.
It therefore follows that $1\ \mathrm{Pa} = 1\ \mathrm{m}^{-3}\ \mathrm{J}$ by the following logic: $1\ \mathrm{Pa} = 1\ \frac{\mathrm{N}}{\mathrm{m}^2} = 1\ \frac{\mathrm{N{\cdot}m}}{\mathrm{m}^3} = 1\ \frac{\mathrm{J}}{\mathrm{m}^3}$, where N is the symbol for the newton, the SI unit of force. The newton-metre is equivalent to the joule (J), the SI unit of energy. Therefore, $1\ \mathrm{J} = 1\ \mathrm{m}^3\ \mathrm{Pa}$. This is a useful identity which will be exploited in this report.

The amount fraction x_{O_3} is the ratio of two quantities measured in the same unit. Therefore the ratio itself has no measurement unit, or more precisely, its measurement unit is 1 [5,6]. To avoid ambiguity in reporting measurements of x_{O_3}, amount fractions should be reported in nmol/mol to indicate the ratio that has been determined. The term “parts per billion” (ppb), or sometimes ppbv, is still used by some practitioners [7,8] despite being deprecated for its ambiguity (section 3.10.2 of [6]).

Constants used in this report (in SI units)

Boltzmann constant, k_B = 1.380 649 x 10^{-23} J K^{-1} (m^3 Pa K^{-1}) : SI defining constant
Avogadro constant, N_A = 6.022 140 76 x 10^{23} mol^{-1} : SI defining constant
molar gas constant, $R = N_\mathrm{A} k_\mathrm{B}$, R = 8.314 462 618… J K^{-1} mol^{-1}
standard atmospheric pressure, p_std = 101 325 Pa
standard temperature, T_std = 273.15 K

All these numerical values are exactly defined [9] but the numerical value of R has been truncated. Only k_B and N_A are in the set of seven defining physical constants of the SI [5], but any constant defined by combinations of the defining constants is itself exact. In addition, we will use the recommended value of the absorption cross section per molecule as given in Table 1 as our starting point for discussing different concentration quantities.

Ideal gas equation

Taking dry air to be an ideal gas, and air with tropospheric ozone to be an ideal gas as well [7,8], ozone in air will have a number density C_{O_3} (number of ozone molecules N_{O_3} per volume V; $C_{\mathrm{O}_3} = N_{\mathrm{O}_3}/V$), and a partial pressure $p_{\mathrm{O}_3} = x_{\mathrm{O}_3} p$. The sum of amount fractions of all gas components equals 1 and the sum of all partial pressures equals the total pressure, p. The ideal gas equations for ozone in air become [2]:

$$x_{\mathrm{O}_3}\, p = C_{\mathrm{O}_3}\, k_\mathrm{B} T, \tag{4}$$

or

$$C_{\mathrm{O}_3} = x_{\mathrm{O}_3} \frac{p}{k_{\mathrm{B}} T}, \tag{5}$$

where p and T are the measured pressure and temperature and k_{B} is the Boltzmann constant.

Mass absorption coefficient

The mass absorption coefficient α_{m} is calculated from the following equation:

$$\alpha_{\mathrm{m}} = \frac{\sigma}{M_{\mathrm{r}}(\mathrm{O}_3) \cdot m_{\mathrm{u}}} \tag{6}$$

where m_{u} is the atomic mass constant [10], whose value is 1.660539… x 10^{-27} kg (relative standard uncertainty 3 x 10^{-10} [9]), and $M_{\mathrm{r}}(\mathrm{O}_3)$ is the relative molecular mass of ozone: 47.9982 [10,11] with a relative standard uncertainty of only 0.0014 %. The dominant uncertainty component of this result is clearly that of the ozone cross section in the numerator of eq. (6).

The term "relative molecular mass" means relative to m_{u}. The latter is defined as 1/12 the mass of a ^{12}C atom. The denominator of the quotient is simply the average mass of an ozone molecule, which takes account of the relative abundances of the three stable isotopes of oxygen, ^{16}O, ^{17}O and ^{18}O, comprising the various isotopologues of O_3. Oxygen-16 has by far the greatest relative abundance of these, more than 99 % [2].

To obtain the result in Table 1, the unit of σ must be m^2 and the unit of m_{u} must be µg, i.e. σ = 1.1329 x 10^{-21} m^2; m_{u} = 1.660539… x 10^{-18} µg.

Derivation of equation (6)

The transmittance of an ozone photometer cell follows the Beer-Lambert law, which for a sample that is uniform in molecular composition, temperature and pressure, can be derived by integration of eq. (1). We first state this law for the number density of ozone molecules, $C_{\mathrm{O}_3}(T, p)$, at the sample pressure and temperature. In this case, $C_{\mathrm{O}_3}(T, p)$ is to be determined by photometry and σ is the absorption cross section of ozone, which is the appropriate coefficient for this concentration [2,8]:

$$Tr = \frac{I}{I_0} = e^{-\sigma C_{\mathrm{O}_3} \ell_{\mathrm{o}}}, \tag{7}$$

where Tr is the transmittance of a photometer cell of optical path length ℓ_{o}, I is the power of ultraviolet radiation of wavelength 253.65 nm transmitted through the cell with ozone present and I_0 is the transmitted power in the absence of ozone ($C_{\mathrm{O}_3} = 0$). The number density may vary over several orders of magnitude but its coefficient is treated as a constant.

Here and below, an ozone concentration (number density C_{O_3} in this case) is associated with an absorption coefficient (σ in this case). The term "concentration" is reserved for quotients whose denominator is volume ([4b],[6]).

The concentrations discussed in this report are: number concentration (number density of ozone molecules), C_{O_3} [SI coherent unit = m^{-3}] and mass concentration (mass density), γ_{O_3} [SI coherent unit = kg m^{-3}]. Two other quantities are closely related to the number concentration: amount fraction of ozone in air, x_{O_3} [SI coherent unit = 1] and the partial pressure of ozone in air, p_{O_3} [SI coherent unit = Pa]. See [4b] and Table 2.10 of [6].

In terms of $\ln(Tr)$,

$$C_{O_3}(T,p) = \frac{-1}{\sigma \ell_o}\ln(Tr)\ . \tag{8}$$

To adjust the measured value of $C_{O_3}(T,p)$ to standard conditions, $C_{O_3}(T_{std}, p_{std})$, the former must be multiplied by the factor $F(T,p) = \frac{T}{T_{std}}\frac{p_{std}}{p}$, to give $C_{O_3}(T_{std}, p_{std}) = F(T,p)C_{O_3}(T,p)$ [8]. The function F is derived from the ideal gas law. At standard conditions of temperature and pressure, $F = 1$.

We now consider the mass concentration, γ_{O_3}, and note that $\gamma_{O_3} = C_{O_3} m(O_3)$. Its associated absorption coefficient is denoted as α_m . Thus the Beer-Lambert law for these parameters is:

$$\gamma_{O_3}(T,p) = \frac{-1}{\alpha_m \ell_o}\ln(Tr)\ , \tag{9}$$

which is eq. (1) of ISO 13964:1998 [12], when allowance is made for our use of recommended symbols in [4b]. When α_m is given in m^2 µg^{-1} and ℓ_0 in m, γ has units of µg/m^3 (see Appendix 1).

Multiplying both sides of eq. (8) by $m(O_3)$ leads to the following definition of α_m :

$$\alpha_m = \frac{\sigma}{m(O_3)} = \frac{\sigma}{M_r(O_3)\cdot m_u}. \tag{10}$$

The mass of the ozone molecule can also be written as $M_r(O_3)\cdot M_u/N_A$ where M_u is the molar mass constant, whose value for all practical purposes is 1 g/mol [13].

Multiplication of the measured $\gamma_{O_3}(T,p)$ determined from eq. (9) by $F(T,p)$ adjusts its value to standard conditions of temperature and pressure so that $\gamma_{O_3}(T_{std}, p_{std}) = F(T,p)\gamma_{O_3}(T,p)$ [12].

Linear absorption coefficient at standard conditions

Substituting the right-side of eq. (5) for $C_{O_3}(T,p)$ in eq. (8) and rearranging terms,

$$x_{O_3}(T,p) = \frac{-1}{\sigma \ell_o}\frac{k_B T}{p}\ln(Tr). \tag{11}$$

Multiplying the right-side of eq. (11) by unity in the form of $\frac{p_{\mathrm{std}}}{k_{\mathrm{B}}T_{\mathrm{std}}}/\frac{p_{\mathrm{std}}}{k_{\mathrm{B}}T_{\mathrm{std}}} = 1$, leads to

$$x_{\mathrm{O_3}}(T,p) = \frac{-1}{\left(\sigma\cdot\frac{p_{\mathrm{std}}}{k_{\mathrm{B}}T_{\mathrm{std}}}\right)\ell_{\mathrm{o}}} F\,\ln(Tr). \tag{12}$$

The right sides of eqs. (11) and (12) differ by a factor of unity. The two equations are therefore identical and thus equally valid.

At standard temperature and pressure, F =1 and eqs. (11) and (12) become

$$x_{\mathrm{O_3}}(T_{\mathrm{std}},p_{\mathrm{std}}) = \frac{-1}{\left(\sigma\cdot\frac{p_{\mathrm{std}}}{k_{\mathrm{B}}T_{\mathrm{std}}}\right)\ell_{\mathrm{o}}} \ln(Tr). \tag{12'}$$

Equation (12) can be compared to eq. (5) of [8], which we cite here, simplified for a photometer with a single cell:

$$x_{\mathrm{O_3}}(T,p) = \frac{-1}{\alpha_x \ell_{\mathrm{o}}} F\,\ln(Tr). \tag{13}$$

The more elaborate equation in [8] is appropriate to the NIST Standard Reference Photometer (SRP [14]), which achieves enhanced performance by using two optical cells in tandem. However, the generic photometer model used throughout this Report leads to the same absorption coefficients as do the equations used to model the SRP.

Equation (13) introduces the parameter α_x , defined as: "the linear absorption coefficient under standard conditions [i.e., F =1], expressed in cm^{-1}" [8]. Equating the right-sides of eqs. (12') and (13) with F =1 leads to the desired result:

$$\alpha_x = \sigma \frac{p_{\mathrm{std}}}{k_{\mathrm{B}}T_{\mathrm{std}}} = \sigma \cdot n_0. \tag{14}$$

The same relation is also shown in [8], but here we have used the identity $k_{\mathrm{B}} = R/N_{\mathrm{A}}$ to simplify that equation and to take advantage of the value of k_{B} now being a defining constant of the SI with only seven digits. We also note that the multiplier of σ in eq. (14) is identified by CODATA [9] as the Loschmidt constant[1], with symbol n_0. This constant is the number density of an ideal gas at standard conditions. Its value is 2.686 780 111… x 10^{25} m^{-3}, which is equivalent to 2.686 780 111… x 10^{19} cm^{-3}. (Since the cross section is reported in the unit cm^{2}, we convert the unit of n_0 to cm^{-3}). The value of the Loschmidt constant is exact [9], but trailing digits have been truncated (as in [9]) for convenience.

Using the recommended value of σ [1-3], the value of α_x is readily found to be the linear absorption coefficient in Table 1. The relative uncertainty of σ, which is given above, is also the relative uncertainty

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[1] The Loschmidt constant can also be defined in terms of a different reference pressure (10^5 Pa) [9], in which case its value would be different from that required in this Report. In addition, in some countries the constant N_{A} is referred to as the Loschmidt constant and given the symbol L.

of α_x because the value of n_0 is exact. As mentioned above, some practitioners still adopt the non-SI unit "molecule", symbol: molecule. In the SI, which we have used in this section, "molecule" is simply replaced by the number 1. The molecule is introduced as a unit in the next section.

5. Photometer measurements of ozone concentrations, partial pressure and volume fraction in atm-system units. Summary results tabulated in Appendix 1

The "atm" unit system was used initially to describe the operation of ozone photometers and, though antiquated, remains in use by many practitioners. In this section we compare the atm system to the SI. We again emphasize that amount fractions are ratios of quantities having the same unit and these ratios are therefore numbers with unit 1 that must be identical in both unit systems discussed in this Report.

The SI and the atm system have many units in common–
length, ℓ: metre (m), centimetre (cm)
temperature, T: kelvin (K)

Most importantly, however, the system uses the standard atmosphere as its unit of pressure–
pressure, p: fractions or multiples of 1 standard atmosphere (atm)
energy, E: cubic centimetre-atmosphere (cm^3 atm)

It is also customary to use "molecule" as a measurement unit, whose symbol is also "molecule".

Here are the exact conversion factors to the corresponding SI units:
1 atm = 101 325 Pa
1 cm^3 atm = 0.101 325 m^3 Pa = 0.101 325 J
N molecule[s] = N

Values of physical quantities in the atm system:
Boltzmann constant, k_B = 1.362 5946… x 10^{-22} cm^3 atm K^{-1} molecule^{-1} (exact, but truncated here)

> This value of k_B has been converted from the SI value, which is given in section 4.
> To be consistent with atm-system conventions, the "unit" molecule^{-1} is added because the units of the atm system and the SI both parallel the equations of science. In this case, the relevant equation is the ideal gas equation: $k_B = \frac{V}{N}\frac{p}{T}$. The units on the left and right of the equals sign must be identical.

Avogadro constant, N_A = 6.022 140 76 x 10^{23} molecule/mol (exact)

molar gas constant $R = N_A k_B$, R = 82.057 366… cm^3 atm mol^{-1} K^{-1} (exact, but truncated here)
standard pressure, p_{std} = 1 atm (exact)
standard temperature, T_{std} = 273.15 K (exact)
Loschmidt constant, n_0 = 2.686 780 111… x 10^{19} molecule/cm^3 (exact, but truncated here)

ozone cross section (see section 3), σ = 1.1329 x 10^{-17} cm^2/molecule

Absorption coefficients in atm units

Historically, measurements made by photometry were analyzed in terms of the partial pressure of ozone expressed in atmospheres. This section provides a link to the past. Appendix 1 compares SI absorption coefficients where the unit of pressure is the pascal (Pa), with the same coefficients where the unit of pressure is the atmosphere (atm).

As a preliminary step, we first consider the amount fraction x_{O_3}. Because x_{O_3} has the unit 1, its numerical value must be the same in either system of units discussed in this Report.

We therefore begin with a restatement of eqs. (12) and (13):

$$x_{\mathrm{O}_3}(T_{\mathrm{std}}, p_{\mathrm{std}}) = \frac{-1}{\left(\sigma \cdot \frac{p_{\mathrm{std}}}{k_{\mathrm{B}} T_{\mathrm{std}}}\right)\ell_{\mathrm{o}}} \ln(Tr) = \frac{-1}{\alpha_x \ell_{\mathrm{o}}} \ln(Tr) \,.$$

Note that we have set $F = 1$ for standard conditions of temperature and pressure.

Whenever the Boltzmann constant k_{B} is required, it must be expressed in the units of the system in use: either J K^{-1} (1 J K^{-1} = 1 m^3 Pa K^{-1} = 10^6 cm^3 Pa K^{-1}) for the SI or cm^3 atm K^{-1} molecule^{-1} for the atm system discussed in this section. As for the unit "molecule", it cancels out from σ/k_{B} wherever this quotient occurs in our Report. The reader may verify that the value of the linear absorption coefficient, α_x = 304.39 cm^{-1}, is independent of whether the standard pressure is expressed as 1 atm or 101325 Pa.

The absorption coefficient α_{O} , which corresponds to a measure of the partial pressure of ozone, $p_{\mathrm{O}_3}\ (= x_{\mathrm{O}_3} p)$ played a prominent role in the first descriptions of the SRP. The Beer-Lambert law for this concentration at standard temperature and pressure is

$$x_{\mathrm{O}_3}(T_{\mathrm{std}}, p_{\mathrm{std}}) p_{\mathrm{std}} = p_{\mathrm{O}_3,\mathrm{std}} = \frac{-1}{\frac{\sigma}{k_{\mathrm{B}} T_{\mathrm{std}}} \ell_{\mathrm{o}}} \ln(Tr) \quad , \tag{15}$$

and

$$\alpha_{\mathrm{O}} = \frac{\sigma}{k_{\mathrm{B}} T_{\mathrm{std}}} \,. \tag{16}$$

In the atm system of units, α_{O} = 304.39 atm^{-1} cm^{-1}, as shown in the Table of section 3.
(The corresponding value of α_{O} in the SI is α_{O} = 3.0041 x 10^{-3} Pa^{-1} cm^{-1} but this coefficient is less used in SI treatments of tropospheric ozone. It is not discussed in [8] or listed in the Table of section 3, but does appear in Appendix 1 for the sake of comparison to the SI.)

By comparing eqs. (14) and (16), it is evident that $\alpha_x = \alpha_{\mathrm{O}} p_{\mathrm{std}}$ for both unit systems discussed in this Report. If p_{std} takes the value 1 atm, then $\alpha_{\mathrm{O}} = \frac{\alpha_x}{1\ \mathrm{atm}}$, as asserted in section 3. If p_{std} takes the value 101325 Pa, then $\alpha_{\mathrm{O}} = \frac{\alpha_x}{101325\ \mathrm{Pa}}$ = 3.0041 x 10^{-3} Pa^{-1} cm^{-1}. Recall that measurements of x_{O_3} were originally reported in ppbv (e.g. footnote 1 of [14]) and more recently in nmol/mol [7,8], but that a result reported in either nmol/mol or in ppbv is equal to the same pure number–provided that the ideal gas law is applicable [7,8]. We repeat in this section that the use of nmol/mol is encouraged by IUPAC and the use of ppbv and ppb is deprecated, as seen in section 3.10.2 of [6]. See also [7] and entries 9-13 and 9-14 in [4b] for more on the conceptual difference between amount fraction and volume fraction.

We conclude by showing a "shortcut" that has been used in the past to convert the partial pressure of ozone at standard conditions of temperature and pressure, as shown in eq. (15), to the amount fraction of ozone in air, expressed as nmol/mol in section 4 and as ppbv in this section. This shortcut can be traced back at least to 1979 [15] and has vestiges in [14], published decades later. Using our notation, we can rewrite two relevant equations in Appendix A of [15]. The first equation is essentially our eq. (15),

$$p_{\mathrm{O_3,std}} = \frac{-1}{\frac{\sigma}{k_{\mathrm{B}} T_{\mathrm{std}}} \ell_{\mathrm{o}}} \ln(Tr) \ . \tag{a}$$

The second, for $x_{\mathrm{O_3}}$ expressed in parts per million (ppm), is

$$x_{\mathrm{O_3}}(T_{\mathrm{std}}, p_{\mathrm{std}}) = 10^6 \cdot p_{\mathrm{O_3,std}} \ . \tag{b}$$

The calculation of $x_{\mathrm{O_3}}(T_{\mathrm{std}}, p_{\mathrm{std}})$ in eq. (b) is numerically correct in the atm system of units but, even in this system, the units on either side of the equals sign are not the same. Simply put, an amount fraction is not a partial pressure. Nevertheless, amount fraction calculated from eq. (b) does yield the correct numerical result, as can be verified below in Appendix 1. If one is concerned about such rigor, the value of $x_{\mathrm{O_3}}(T_{\mathrm{std}}, p_{\mathrm{std}})$ is best determined from eq. (12'), which is valid in the atm system of units.

Turning now to [14], eq. (1) of this reference shows how a generic "concentration", denoted by *c*, is measured using the Beer-Lambert law with coefficient equal to the absorption cross section of ozone "(or equivalently 308.32 atm^{-1} cm^{-1}, base e)". The choice of the former coefficient is appropriate if *c* is defined as the number density of ozone and the latter, if *c* is defined as the partial pressure of ozone. It is then noted in [14] that software "converts the concentration to ppbv". Although the ozone amount fraction in units of ppbv is referred to in [14] (for ideal gases, 1 ppbv is equivalent to 1 nmol/mol), the authors did not give the coefficient to be used for amount fraction in the Beer-Lambert law. To clarify this omission, their evaluation of the ozone amount fraction in units of nmol/mol required the following operations. First, the partial pressure of ozone in atmospheres was evaluated as described in [14]. Next, this result was divided by the standard pressure (1 atm) to give the dimensionless ratio *r* of the two pressures. Finally, value of *r* was expressed as *r* × (10^9 ppbv) [14] and, following IUPAC guidance [6], is expressed as *r* × (10^9 nmol/mol). From the ideal gas law, the ratio of pressures, *r*, equals the amount fraction, $x_{\mathrm{O_3}}$.

References

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Revision History:

Date	Revision
10 March 2022	First Publication
16 January 2023	1. Correction of references in the table in Annex 2, and corrections to conversion factors in the table (changes at the level of the last decimal place from the initial values published). 2. Correction of the values of the absorption coefficient when expressed in units of Pa^{-1} cm^{-1} (change at the level of the last decimal place from initial value published)

Appendix 1

Summary of ozone quantities and their corresponding coefficient equations; SI and atm-system values of each coefficient.

type of ozone quantity	quantity symbol, Q	symbol of associated coefficient, α	α in terms of σ	SI value of α	atm-system value of α
number density*	$C_{\mathrm{O_3}}$ at T and p	$\boldsymbol{\sigma}$	$\boldsymbol{\sigma}$	1.1329 x 10^{-17} cm^2	1.1329 x 10^{-17} cm^2/molecule
mass density	$\gamma_{\mathrm{O_3}}$ at T and p	α_{m}	$\frac{\boldsymbol{\sigma}}{M_{\mathrm{r}}(\mathrm{O_3})m_u}$	1.4214 x 10^{-5} m^2 µg^{-1}	1.4214 x 10^{-5} m^2 µg^{-1}
amount fraction (mole fraction)	$x_{\mathrm{O_3}}$ at T_{std} and p_{std}	α_x	$\boldsymbol{\sigma}\frac{p_{\mathrm{std}}}{k_{\mathrm{B}}T_{\mathrm{std}}}$	304.39 cm^{-1}	304.39 cm^{-1}
Partial pressure	$p_{\mathrm{O_3}}$ at T_{std} and p_{std}	α_{O}	$\frac{\boldsymbol{\sigma}}{k_{\mathrm{B}}T_{\mathrm{std}}}$	3.0040 x 10^{-3} Pa^{-1} cm^{-1}	304.39 atm^{-1} cm^{-1}

*the value of σ is known from [1-3]. Thus the generalized Beer-Lambert law for $C_{\mathrm{O_3}}$ is the logical starting point for deriving the coefficients of the three other types of ozone quantities listed in column 1. The relative standard uncertainties of all values in the last two columns of the table are 0.31 %, which is the relative standard uncertainty of σ. This is because uncertainties in the multipliers of σ are either negligible (in the case of mass density) or zero.

Generalized Beer-Lambert law:

$$Q = \frac{-1}{\alpha \ell_{\mathrm{o}}} \ln(Tr)$$

where ℓ_{o} is the optical path length of an ozone photometer cell with transmittance Tr at the specified UV wavelength, 253.65 nm in air. Q is always measured in reciprocal units of $\alpha \ell_{\mathrm{o}}$.

Appendix 2

Conversion factors for ozone amount fractions measured using different values of the Ozone absorption Cross section

Modifying the ozone cross section value in the measurement equation for an ozone photometer will lead to an inverse change in the measured ozone amount fraction, and in principle corrections factors to historically determined ozone amount fractions can be applied to correct to values that would be consistent with the new ozone cross section value.

As the CCQM.O3.2019 value of the ozone absorption cross section is smaller than historically applied values, this means that corrected ozone amount fractions, corrected to what they would be when measured using the new absorption coefficient, will be larger in magnitude than historically reported values by a factor that is inversely proportional to the change in value of the zone absorption cross section. Caution should however be applied in applying such correction factors, as it requires knowledge of the exact value of the absorption cross section value used for historical data. Also, recalibration of field-based ozone photometers with primary photometers that use the new cross section value will automatically correct for the change in absorption cross section values, and correction factors should then not be reapplied to newly measured data, as this would lead to a double correction.

Examples of commonly used historical values for ozone absorption cross section at 253.65 nm (air) are given in the table below, as well as correction factors that can be applied to ozone amount fractions measured using these historical values, to correct them ozone amount fractions that would have been measured using the new CCQM.O3.2019 value of the ozone absorption cross section.

Label	Quantity used to express ozone cross section	Historical value and unit used for the ozone absorption cross section	To convert from ozone amount fraction (nmol/mol) measured using a historical cross section value to ozone amount fraction (nmol/mol) that would be measured using the CCQM.O3.2019 value of the ozone absorption cross section, **multiply by*:**	Comments on historical value of ozone absorption correction
1	absorption cross section per molecule	1.147×10^{-17} cm^2	1.01245	Hearn-61 value reported in [2]
2	absorption cross	1.1476×10^{-17} cm^2	1.01298	Value reported in

	section per molecule			the WMO guidance document [8]
3	mass absorption coefficient	1.44 x 10^{-5} m^2 μg^{-1}	1.01308	Value used in ISO 13964:1998
4	linear absorption coefficient at standard temperature and pressure (0 °C and 101325 Pa)	308.32 cm^{-1}	1.01293	Value reported in the WMO guidance document [8]
5	absorption coefficient, at standard temperature and pressure (0 °C and 1 atm)	308.32 atm^{-1} cm^{-1}	1.01293	Value reported for NIST SRP [14]
6	absorption coefficient, at standard temperature and pressure (0 °C and 1 atm)	308.3 atm^{-1} cm^{-1}	1.01286	Value from EPA-600-4/4-79-057, page 3-9
7	absorption coefficient, at standard temperature and pressure (0 °C and 1 atm)	308 atm^{-1} cm^{-1}	1.01188	Value given in EPA 40 Code of Federal Regulations (CFR) part 50, appendix D

*Conversion factors are quoted to 6 significant digits, which maintains the correct relationship, without rounding errors, between historically used and the newly adopted cross section value at the level of significant digits reported in Table 1.

Historical conversions between the cross section and absorption coefficient have led to some variation in reported values due to slight difference in the choice of standard pressure used for the conversions. The magnitude of these differences is in the order of 0.025%.