Mean absorption coefficients of air plasmas

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Abstract. Mean absorption coefficients of air (both Planck and Rosseland mean) have been computed for different splitting procedures of the whole frequency interval (10^{13} – 6 \times 10^{15} \text{ s}^{-1}) and various temperatures (1 000 – 30 000 K). Results have been compared and discussed to find the optimal values of mean absorption coefficients for the multigroup method of solution of the equation of radiation transfer.

1. Introduction
The propagation of radiation through plasma is an integral part of the description of the plasma. In the description of radiation transfer, mathematical modeling is of great importance. However, the non-linearity of the equations describing the radiation field and the strong dependence of the parameters and coefficients on the radiation frequency makes mathematical plasma models very complicated. Therefore, various approximate methods are used (method of net emission coefficient [1-3], method of partial characteristics [4, 5]).

One of the procedures for handling the frequency dependence of the coefficients in the equation of transfer is the multigroup method, which assigns a given photon to one of G frequency groups. All photons within a given group are treated in the same way, assigning average properties, such as the absorption coefficient, to that group. In practice, the average absorption coefficient is generally taken as either a group Rosseland or group Planck mean (depending on the absorption properties of the medium for the given frequency group).

In this paper, attention has been given to the absorption properties of air at the pressure of 1 atm and in the temperature range (1 000 - 30 000 K). Both Rosseland and Planck averages have been computed for different splitting procedures of the whole frequency interval (10^{13} – 6 \times 10^{15} \text{ s}^{-1}).

2. Radiation transfer
The main quantity describing the radiation transfer is the radiation intensity \( I \). It is defined as the radiation power per unit solid angle and unit area of a surface that is placed normal to the rays. We distinguish between spectral and total intensity, \( I_\nu \) and \( I \), respectively:

\[
I(f, \Omega) = \int_0^\infty I_\nu(f, \Omega, \nu) d\nu .
\]

Here, \( f \) is a position vector fixing the location of a point in space, and \( \Omega \) a unit direction vector.

In case of thermodynamic equilibrium, the radiation intensity is direction-independent, and given by the Planck function.
\[ B_\nu (\nu, T) = \frac{2h \nu^3}{e^2 \left[ \exp \left( \frac{h \nu}{kT} \right) - 1 \right]} \]  

(2)

A light beam traveling through a gas layer of thickness \( ds \) loses intensity by absorption and by scattering of photons. The attenuation of radiation is proportional to the magnitude of the incident energy (intensity \( I_\nu \)) and to the length of the path

\[ dI_\nu = -\kappa_\nu I_\nu ds \]  

(3)

Because scattering of photons by molecules and atoms is always negligible for heat transfer, the proportionality constant \( \kappa_\nu \) represents the absorption coefficient.

In the local thermodynamic equilibrium the following relation holds between the emission and absorption coefficients

\[ \nu \kappa_\nu = \nu \varepsilon_\nu \]  

(4)

The complete stationary equation of radiation transfer for an absorbing and emitting medium is

\[ \frac{dI_\nu}{ds} = \tilde{\Omega} \cdot \text{grad} I_\nu = \kappa_\nu (B_\nu - I_\nu) \]  

(5)

3. Absorption properties of plasmas

Radiation in arc plasmas depends, besides others physical quantities, on the concentrations of all chemical species in the plasma. In the calculation of the plasma a dry air composition was assumed at the pressure of 1 atmosphere consisting of N\(_2\), O\(_2\), Ar, and CO\(_2\). The equilibrium composition of the air plasma was computed using Tmdgas code [6]. Atoms and up to the triple ions of N, O, Ar, C, and diatomic molecules O\(_2\), N\(_2\), N\(_2^+\), NO, NO\(^+\), CO, CO\(^+\), and CN were assumed to be present.

When a photon interacts with a gas molecule, atom, or ion, it may be absorbed raising the particle’s energy level. Conversely, a gas particle may spontaneously lower its energy level by the emission of an appropriate photon. There are three different types of radiative transitions that lead to a change in the energy level of a gas particle by photon emission or absorption:

- transition between non-dissociated (“bound“) atomic or molecular states, called bound-bound transitions (bb)
- transitions from a “bound“ state to a “free“ (dissociated) one (absorption) or from “free“ to “bound“ (emission), called bound-free transitions (bf)
- transitions between two different “free“ states, free-free transitions (ff)

The total absorption coefficient is given as the linear sum of all three processes mentioned above

\[ \kappa(\nu, T, p) = \kappa^{bb}(\nu, T, p) + \kappa^{bf}(\nu, T, p) + \kappa^{ff}(\nu, T, p) \]  

(6)

The calculation of the absorption coefficient represents a formidable task when experimental data is lacking, since the radial wave functions of all free and bound electronic states must be known. However, simplifications can be made by using various semi-empirical methods and hydrogenic approximations

3.1. Continuous radiation

The radiation continuum may be divided into photon emission from free-bound (recombination) radiation and free-free (bremsstrahlung) radiation.
Since the kinetic energy of free electron is not quantized, its recombination with positive ion of a chemical species \( \alpha \) leads to continuous radiation. Thus, for recombination radiation

\[
h \nu = \frac{1}{2} m v_e^2 + E_i^a - E_e^a.
\]

(7)

Here \( \nu \) is the frequency of recombination radiation, \( h \) Planck’s constant, \( v_e \) the velocity of free electron, \( E_i^a \) the ionization potential of the atom or ion, \( E_e^a \) the energy of the \( i \)-th electronic energy state, where the electron is captured.

The spectral absorption coefficient of process (7) is related to the photon absorption cross section \( \sigma_{\nu,j}^a \) by

\[
\kappa_{\nu,j}^{bf} = \sigma_{\nu,j}^a N_i^a
\]

(8)

where \( N_i^a \) is the population density of the \( i \)-th electronic state of the absorbing species \( \alpha \).

Neutral atoms and up to the triple ions of N, O, Ar, C elements were considered. Photo-ionization cross sections for the ground states of neutral atoms and ions of N, O, Ar, and C were calculated using analytic fits of theoretical cross sections from the “Opacity Project” [7]. The cross sections for excited levels of neutral atoms were calculated using the quantum defect method of Burges and Seaton [8]; this was applied to oxygen – 3s, 3p, 4s, and 4p states, nitrogen – 3s and 3p states, carbon – 3s, 3p, 4s, and 4p states. All other excited states of N, O, Ar, C were treated using the Coulomb approximation for hydrogen-like species [9]. The energy levels tabulated in [10] were used for all atoms and ions under consideration. We have taken into consideration almost 600 energy levels.

The hydrogen-like approximation was used for the treatment of free-free transitions, too. In contrast to bound electrons of a given level, free electrons contribute to the absorption coefficient at all frequencies. The relative importance of bound-free and free-free absorption depends on the state of ionization. At low temperatures, there are very few free electrons, and bound-free absorption dominates. At very high temperatures, most electrons are free, and free-free absorption is dominant.

3.2. Discrete radiation

Quantum mechanics postulates that the energy levels for atomic or molecular electron orbit as well as the energy levels for molecular rotation and vibration are quantized; i.e., electron orbits and rotational and vibrational frequencies can only change by certain discrete amounts. Therefore, in bound-bound transitions, photons must have a certain frequency (or wavelength) in order to be captured or released, resulting in discrete spectral lines for absorption and emission

\[
h \nu_{mn} = \frac{hc}{\lambda_{mn}} = E_m - E_n
\]

(9)

for the transition from the state \( m \) to the state \( n \).

However, no spectral line can be truly monochromatic; rather, absorption or emission occurs over a tiny but finite range of wavelengths. The results are broadened spectral lines that have their maxima at the wavelength predicted by equation (9).

Numerous phenomena cause broadening of spectral lines. The most important are natural line broadening, Doppler broadening, Stark broadening, resonance broadening, and Van der Waals broadening.

Absorption coefficient \( \kappa^{bb} \) for discrete spectrum must take account of all overlapping spectral lines of all atoms and ions of the plasma. The absorption coefficient of an isolated line “\( i \)” of species “\( \alpha \)” is [9]

\[
\kappa_{\nu,i}^{bb}(\nu, T, p) = \pi r_i \sigma_{\nu,i}^{\alpha,i} N_i^a(T, p) P_i^\alpha(\nu, T, p)
\]

(10)
where $r_0$ is the electron radius, $c$ the velocity of light, $f^{\alpha \delta}_{mn}$ the absorption oscillator strength of the spectral line for electronic transitions between the $m$ and $n$ energy states. $N^v_v(T, p)$ is the population density of the lower electronic energy state and $P^v_v(v, T, p)$ is the normalized line shape.

To calculate the absorption coefficient $\kappa^{ab}_{ij}$ of the $i$-th spectral line it is necessary to determine its half-width $\delta$, spectral shift $d$, and the absorption oscillator strength $f^{\alpha \delta}_{mn}$. The values of absorption oscillator strength are tabulated for a lot of spectral lines of atoms and their ions in Kurucz Atomic Line Database [11]. The line shapes in our calculations are given by a convolution of Doppler and Lorentz profiles, resulting in simplified Voigt profiles. The fine multiplet structure and the possible overlap of lines have also been taken into account. For each spectral line we have calculated parameters defining their half-widths and shifts. Semi-empirical formulas given in [9] were used. We have taken into consideration more than 15 000 spectral lines.

3.3. Molecular absorption – diatomic molecules
Changing the orbit of an electron requires a relatively large amount of energy resulting in absorption-emission lines at short wavelengths between the ultraviolet and the near-infrared (between $3 \times 10^{15}$ s$^{-1}$ and $2 \times 10^{14}$ s$^{-1}$). Changes in vibrational energy level require somewhat less energy, so that their spectral lines are found in the infrared (between $2 \times 10^{14}$ s$^{-1}$ and $10^{13}$ s$^{-1}$), while changes in rotational energy levels call for the least amount of energy and rotational lines are found in the far infrared (beyond $10^{13}$ s$^{-1}$). Changes in vibrational energy levels are often accompanied by rotational transitions, leading to closely spaced groups of spectral lines that may partly overlap and lead to so-called vibration-rotational bands. Thus, the molecular spectrum is much more complicated than that of monatomic gases.

For electronic transitions no selection rules for vibration quantum numbers exist, i.e. transitions between arbitrary vibration levels of the upper and lower electronic states are possible. The theoretical background for the vibrational structure analysis is the Franck-Condon principle [12] that makes it possible to predict the distribution of vibrational band intensities. Relative line intensities in the electronic-vibrational spectra are determined by the Franck-Condon factors

$$\left| \int \psi\text{'}\psi\text{'} d\tau \right|^2 \equiv q_{\nu\nu} .$$

(11)

Here, $\psi\text{'}$ and $\psi\text{'}$ are the vibrational wave functions of the lower and higher electronic states, respectively. The bound-bound absorption coefficient for a transition between two vibrational levels $\nu\text{'}$, $\nu$ of two electronic states can be expressed in the form

$$\kappa^{\nu\nu} = \pi r_0 c N^v_v f_{\nu\nu} .$$

(12)

where $r_0$ denotes the electron radius, $c$ the speed of light, $N^v_v$ the number density of the lower vibrational state, and $f_{\nu\nu}$ the band oscillator strength defined by [13]

$$f_{\nu\nu} = \frac{\nu_{\nu\nu}}{2R_\infty c} \frac{R^2}{g^\nu} q_{\nu\nu} .$$

(13)

where $R_\infty$ is the Rydberg constant, $g^\nu$ the weighting factor of the lower level, $\nu_{\nu\nu}$ the frequency at which the transition occurs, and $R^2$ gives the intensity distribution in electronic structure. For approximate calculation of radiative properties, it is useful to define the spectral absorption coefficient for the band system averaged over the rotational spectrum, and also partially smeared out over the vibrational structure

$$\bar{\kappa}_v = N\sigma(v, T) = N\pi r_0 \frac{\nu}{3R_\infty} \frac{R^2}{g^\nu} \frac{1}{\Delta \nu} \sum_{\nu\nu} q_{\nu\nu} w_{\nu\nu} .$$

(14)
Here, \( N \) is the molecular number density, \( \nu \) the radiation frequency of absorbed photon, and \( w_{v^\prime} \) denotes the Boltzman probability of the occupation of the lower vibrational level. The sum of Franck-Condon factors is performed for all transitions \( \nu^{\prime\prime} \rightarrow \nu^{\prime} \) with

\[
\nu_{\nu^{\prime\prime}} = \left( \nu - \frac{\Delta \nu}{2}, \nu + \frac{\Delta \nu}{2} \right)
\]

where \( \Delta \nu \) is interval of averaging around \( \nu \). The Franck-Condon factors are tabulated for many molecular transitions in [14], or they can be calculated by computer code [15]. Molecular photo-absorption was taken into account for selected electronic transitions of the following diatomic molecules and electronic transitions: \( \text{O}_2, \text{O}_2^+, \text{N}_2, \text{N}_2^+, \text{NO}, \text{NO}^+, \text{CO}, \text{CO}^+, \) and \( \text{CN} \).

Calculated total absorption coefficients of radiation as a function of radiation frequency for plasma temperatures of 6 000 K and 20 000 K are plotted in figure 1. Molecular species (electronic transitions) contribute to the total absorption coefficients slightly at lower temperatures below 10 000 K at radiation frequencies up to \( 2.5 \times 10^{15} \text{ s}^{-1} \). Due to the frequency interval under consideration, radiation transitions between rotational levels were not taken into account. With increasing temperature the contribution of discrete radiation to the absorption coefficient increases.

![Figure 1](image)

**Figure 1.** The total absorption coefficient as a function of frequency for thermal air plasmas at temperature of 6 000 K and 20 000 K. Doted lines represent boundaries between specific frequency groups for non-uniform splitting (see table 1).
4. Multigroup method – mean absorption coefficients
One of the methods for handling the frequency dependence in radiation transfer is the multigroup method [16]. One assigns a given photon to one of $G$ frequency groups, and all photons within a given group are treated the same from the point of view of the absorption properties of the medium, the absorption coefficient for given frequency group $k$ is supposed to be constant with certain average value

$$\kappa_k(\vec{r}, \nu, T) = \kappa_k(\vec{r}, T), \quad \nu_k \leq \nu \leq \nu_{k+1}, \quad k = 1, \ldots, G.$$  

(15)

The values of total intensity are then given by

$$I(\vec{r}, \vec{\Omega}) = \sum_{k=1}^{G} I_k(\vec{r}, \vec{\Omega}), \quad I_k(\vec{r}, \vec{\Omega}) = \int_{\nu_k}^{\nu_{k+1}} I_{\nu}(\vec{r}, \nu, \vec{\Omega}) d\nu$$  

(16)

The equation of transfer for the given frequency group can be treated as equation for grey medium:

$$\vec{\Omega} \cdot \text{grad} I_k(\vec{r}, \vec{\Omega}) = \overline{\kappa_k} (b_k \frac{\sigma}{\pi} T^4 - I_k(\vec{r}, \vec{\Omega})), \quad 1 \leq k \leq G$$  

(17)

where $\sigma$ is the Stefan-Boltzmann constant, $b_k$ the fraction of $\frac{\sigma}{\pi} T^4$ lying within the $k$-th group, i.e.

$$b_k = \frac{\int_{\nu_k}^{\nu_{k+1}} B(\nu) d\nu}{\int_{0}^{\nu_{k+1}} B(\nu) d\nu} = \frac{\nu_{k+1} - \nu_k}{\nu_{k+1} - \nu_1}.$$  

(18)

For the multigroup method to be useful, one must be able to compute or estimate the mean values of absorption coefficients. Generally, $\overline{\kappa_k}$ is taken as either Rosseland or Planck mean.

4.1. The Rosseland mean
The Rosseland mean, also called the mean free path of radiation is appropriate when the system approaches equilibrium (almost all radiation is reabsorbed). The Rosseland mean absorption coefficient is given by

$$\overline{\kappa_R^{-1}} = \frac{\int_{\nu_k}^{\nu_{k+1}} \frac{dB(\nu, T)}{dT} d\nu}{\nu_{k+1} - \nu_k}.$$  

(19)

4.2. The Planck mean
The Planck mean is appropriate in the case of optically thin system. The Planck mean absorption coefficient is given by

$$\overline{\kappa_P} = \frac{\int_{\nu_k}^{\nu_{k+1}} \kappa_\nu B(\nu, T) d\nu}{\int_{\nu_k}^{\nu_{k+1}} B(\nu, T) d\nu}.$$  

(20)
The values of mean absorption coefficients depend on the choice of the frequency interval splitting. As example, results for two different splitting of frequency interval \((0.01 - 6) \times 10^{15} \text{ s}^{-1}\) are presented. Boundaries between 12 specific frequency groups of a non-uniform splitting are given in table 1 and shown in figure 1, boundaries between 7 frequency groups of a quasi-uniform splitting are given in table 2. Values of Planck mean absorption coefficients for two different splitting (non-uniform and quasi-uniform) are shown in figures 2 and 3, respectively.

**Table 1.** Boundaries between specific frequency groups \((\nu_k \times 10^{15} \text{ s}^{-1})\), non-uniform splitting.

| \(\nu_1\) | \(\nu_2\) | \(\nu_3\) | \(\nu_4\) | \(\nu_5\) | \(\nu_6\) | \(\nu_7\) | \(\nu_8\) | \(\nu_9\) | \(\nu_{10}\) | \(\nu_{11}\) | \(\nu_{12}\) | \(\nu_{13}\) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 0.01 | 0.03 | 0.057 | 0.296 | 0.386 | 0.746 | 0.986 | 1.71 | 2.098 | 2.64 | 2.997 | 4.49 | 6.00 |

**Table 2.** Boundaries between specific frequency groups \((\nu_k' \times 10^{15} \text{ s}^{-1})\), quasi-uniform splitting.

| \(\nu_1\) | \(\nu_2\) | \(\nu_3\) | \(\nu_4\) | \(\nu_5\) | \(\nu_6\) | \(\nu_7\) | \(\nu_8\) |
|---|---|---|---|---|---|---|---|
| 0.01 | 0.1 | 1.00 | 2.00 | 3.00 | 4.00 | 5.00 | 6.00 |

**Figure 2.** Mean absorption coefficients for 12 specific frequency groups, non-uniform splitting.
Figure 3. Planck mean absorption coefficient for 7 specific frequency groups, the quasi-uniform splitting.

The Rosseland and Planck mean absorption coefficients can differ by an order of magnitude or more, as can be seen in figure 4 where comparisons of Planck and Rosseland means for two different frequency groups of the non-uniform interval splitting are shown. For the group $\nu_7 - \nu_8 = (0.986 - 1.71) \times 10^{15}$ s$^{-1}$ both means differ only slightly up to the temperature 25 000 K. Great difference for the group $\nu_9 - \nu_{10} = (2.098 - 2.64) \times 10^{15}$ s$^{-1}$ appears due to strong discrete radiation in this frequency group which makes the Planck mean by several orders of magnitude greater than Rosseland mean. Comparisons of Planck and Rosseland means for all 12 groups of the non-uniform interval splitting are shown in figure 2.

The use of Rosseland and Planck mean absorption coefficients is only strictly appropriate in limiting circumstances (absorption dominated, or emission dominated system, respectively). As can be seen in figures 2 and 4, these two means can differ very strongly, and thus the results of the multigroup method can vary widely depending upon which mean is used. In reality, neither mean is correct in general. Anyway, the splitting of the whole frequency interval has to be made according to the frequency dependence of the absorption coefficients. The simplest procedure is then to use the Planck mean for frequency groups with low values of absorption coefficients; for groups with high values of absorption coefficients the Rosseland mean is more suitable. More accurate results brings the new multigroup method [16] which involves generalization of the Planck and Rosseland means which occur together in the multigroup equations.
5. Conclusions
Calculations of the absorption coefficients for thermal plasma of air have been performed as a function of temperature in frequency interval \((10^{13} - 6 \times 10^{15})\) s\(^{-1}\) at the pressure of 1 atm. Both Planck and Rosseland means have been computed for different frequency interval splitting procedures. Results for 12 groups of the non-uniform splitting and 7 groups of the quasi-uniform splitting have been presented. The use of Planck or Rosseland means in the multigroup method of solution of the equation of radiation transfer depends on values of absorption coefficients.

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References
[1] Lowke J J 1974 \textit{JQSRT} 14 111-122
[2] Naghizadeh-Kashani Y, Cressault Y and Gleizes A 2002 \textit{J.Phys. D: Appl. Phys.} 35 2925-2934
[3] Aubrecht V and Bartlova M 2009 \textit{Plasma Chem Plasma Process} 29 131-147
[4] Aubrecht V and Lowke J J 1994 \textit{J.Phys. D: Appl. Phys.} 27 2066-2073
[5] Raynal G and Gleizes A 1995 \textit{Plasma Sources Sci. Technol.} 4 152-160
[6] Coufal O, Sezemsky P and Zivny O 2005 \textit{J.Phys. D: Appl. Phys.} 38 1265-1274
[7] Verner D A, Ferland G J and Korista K T 1996 \textit{Astrophysical Journal} 465 487/-492
[8] Burges A and Seaton M 1958 *Rev. Mod. Phys.* **30** 992/-1003
[9] Liebermann R W and Lowke J J 1976 *JQSRT* **16** 253-264
[10] NIST scientific and technical database [http://physics.nist.gov/]
[11] Kurucz Atomic Database [http://www.cfa.harvard.edu/amp/ampdata/kurucz23/sekur.html]
[12] Herzberg G 1950 *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (New York: D. Van Nostrand Co)
[13] Mnacakanjan A Ch 1968 *TVT* **6** 236-241
[14] Kuzmenko N E, Kuznecova L A and Kuzjakov J J 1994 *Faktory Franka-Kondona dvuchatomnych molekul* (Moskva: Izd. Moskovskogo universiteta)
[15] Stakhursky V L [http://www.chemistry.ohio-state.edu/vstakhur]
[16] Pomraning G C 1973 *The Equations of Radiation Hydrodynamics* (New York: Dover Publications)