Photoabsorption of diatomic molecules

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Radiative transport of energy plays an important role in many plasma processing devices. Jets of thermal plasma are produced in plasma generators with electric arcs. The experimental observation of radiation transfer is very difficult due to experimental conditions. In such cases, the mathematical modeling is of great importance. Several approximate methods have been described; one of them is the method of partial characteristics.

The preliminary task for computation of partial characteristics is the knowledge of absorption coefficients of the plasma. In addition to atomic and atomic ions species, molecules play an important role in re–absorption of radiation in colder arc regions.

In the present paper, attention is given to the calculation of photoabsorption cross sections of diatomic molecules. The cross sections of O_2, N_2, H_2, NO, OH, N_2^+, NO^+ have been calculated using an approximate method. Results of the calculation are compared with the data available in literature.

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1 Introduction

Thermal radiation in arc plasmas provides a significant contribution to an energy transfer. Any quantitative study of the radiation transport requires knowledge of the frequency–dependent absorption properties.

In previous paper [1] we have calculated the spectral coefficients of absorption for various kinds of arc plasmas. Only atomic and atomic ions bound–bound, bound–free, and free–free transitions were considered. Molecular band contributions must be taken into account for plasma when the temperature is below 8 000 K. This paper is dedicated to the preparation of diatomic line data base for all the electronic systems of the O_2, N_2, NO, N_2^+, NO^+, H_2, and OH molecules which significantly contribute to the radiative transfer inside air and water vapor plasma.

2 Electronic transitions of diatomic molecules

According to Franck–Condon principle, the bound–bound absorption coefficient for transition between two vibrational levels v'', v' of two electronic states (single primed letter refer to the upper electronic state, the double primed letter to the lower one) can be expressed in the form [2]

$$\kappa^{v''v'} = \pi r_0 c N_{v''} f_{v''v'}, \tag{1}$$

where r_0 denotes the electron radius, c is speed of light, $N_{v''}$ the number density of the lower vibrational state, and $f_{v''v'}$ the band oscillator strength defined by

$$f_{v''v'} = \frac{\nu_{v''v'}}{3R_\infty c}\frac{1}{g''}\left|R^{v''v'}\right|^2. \tag{2}$$

It depends on the transition matrix element

$$\left|R^{v''v'}\right|^2 = R_{\mathrm{e}}^2\left(\overline{r}_{\mathrm{e}}\right) q_{v''v'}. \tag{3}$$

The square of the integral over the product of the vibrational eigenfunctions of the two states involved

$$\left|\int \psi_{v''}\psi_{v'}\mathrm{d}\tau\right|^2 \equiv q_{v''v'}, \tag{4}$$

is called Franck–Condon factor (the overlap integral). These factors represent "selecting rules" for electronic–vibrational transitions.

$R_{\mathrm{e}}^2\left(\overline{r}_{\mathrm{e}}\right) \equiv \overline{R}_{\mathrm{e}}^2$ is the average value of the electronic transition moment, it gives the intensity distribution in the electronic structure.

In (2) R_∞ is the Rydberg constant, g'' the weighting factor of the lower level, and $\nu_{v''v'}$ the frequency at which the transition occurs.

For approximate calculation of radiative properties, it is useful to define the spectral absorption coefficient for the band system averaged through the rotational spectrum, and also partially smeared through the vibrational structure [2]

$$\overline{\kappa}_\nu = N\sigma\left(\nu, T\right) = N\pi r_0 \frac{\nu}{3R_\infty c}\frac{\overline{R}_{\mathrm{e}}^2}{g''}\frac{1}{\mathit{\Delta}\omega}\sum_{v'',v'} q_{v''v'}w_{v'}. \tag{5}$$

Here N is the molecular number density, and $w_{v''}$ denotes the Boltzmann probability of the occupation of the lower vibrational level. The summation in (5) is over all transitions $\nu'' \to \nu'$ having energy levels such that

$$\omega_{v'} - \omega_{v''} \equiv \omega_{v''v'} \in \left\langle \omega - \frac{\mathit{\Delta}\omega}{2}, \omega + \frac{\mathit{\Delta}\omega}{2}\right\rangle, \tag{6}$$

$$\omega_{v''v'} = T_{\mathrm{e}}' - T_{\mathrm{e}}'' + \omega_{\mathrm{e}}'\left(v' + \frac{1}{2}\right) - \omega_{\mathrm{e}}'x_{\mathrm{e}}'\left(v' + \frac{1}{2}\right)^2 - \omega_{\mathrm{e}}''\left(v'' + \frac{1}{2}\right) + \omega_{\mathrm{e}}''x_{\mathrm{e}}''\left(v'' + \frac{1}{2}\right)^2,$$

where T_{e}', T_{e}'', ω_{e}', ω_{e}'', $\omega_{\mathrm{e}}'x_{\mathrm{e}}'$, $\omega_{\mathrm{e}}''x_{\mathrm{e}}''$ are molecular constants of selected electronic states. The value of the interval provides the degree of the "smearing" of the vibrational structure. For $\mathit{\Delta}\omega < \min(\omega_{\mathrm{e}}', \omega_{\mathrm{e}}'')$, the vibrational structure of the spectra is accepted in the calculation, if $\mathit{\Delta}\omega > \max(\omega_{\mathrm{e}}', \omega_{\mathrm{e}}'')$ then the detailed vibrational structure is smeared. ω_{e}', and ω_{e}'' are the vibrational constants of the upper, and lower electronic state, respectively. $R_{\mathrm{e}}^2\left(\overline{r}_{\mathrm{e}}\right)$ dependence on the internuclear distance can be replaced by an approximate dependence on the wavelength [3]

$$\frac{\overline{R}_\mathrm{e}^2}{g''} = A\left(1 + B\lambda + C\lambda^2 + D\lambda^3\right)^2 , \qquad (7)$$

where A, B, C, D are parameters of the molecular electronic transition.

3 Selected molecular bands

Main goal of this paper is to prepare molecular input data for the calculation of the radiative transfer inside air and water vapor plasma. For these reasons, we have prepared data for following significant molecular bands of O_2, N_2, NO, N_2^+, NO^+, H_2, and OH molecules:

1. **O_2 molecule:** Schuman–Runge system $B^3\Sigma_u^- \rightarrow X^3\Sigma_g^-$
2. **N_2 molecule:** First positive system $B^3\Pi_g \rightarrow A^3\Sigma_u$
   Second positive system $C^3\Pi_u \rightarrow B^3\Pi_g$
3. **N_2^+ molecule:** First negative system $B^2\Sigma_u^+ \rightarrow X^2\Sigma_g^+$
   Meinel system $A^2\Pi_u \rightarrow X^2\Sigma_g^+$
4. **NO molecule:** Beta system $B^2\Pi_r \rightarrow X^2\Pi_r$
   Gama system $A^2\Sigma^+ \rightarrow X^2\Pi_r$
5. **NO^+ molecule:** Transition $A^1\Pi \rightarrow X^1\Sigma^+$
6. **H_2 molecule:** Lyman system $B^1\Sigma_u^+ \rightarrow X^1\Sigma_g^+$
   Verner system $C^1\Pi_u \rightarrow X^1\Sigma_g^+$
7. **OH molecule:** Transition $A^2\Sigma^+ \rightarrow X^2\Pi_i$

Molecular constants for selected terms are given in Tables 1–3. In the calculation Franck–Condon factors published in [4] were used.

Table 1. Molecular parameters for selected electronic transitions of O_2, OH, NO^+ [5]

	O_2		**OH**		**NO^+**	
	$X^3\Sigma_g^-$	$B^3\Sigma_u^-$	$X^2\Pi_i$	$A^2\Sigma^+$	$X^1\Sigma^+$	$A^1\Pi$
$T_\mathrm{e}(\mathrm{cm}^{-1})$	0	49793.3	0	32684	0	73471.7
$\omega_\mathrm{e}(\mathrm{cm}^{-1})$	1580.2	709.3	3737.8	3178.9	2376.4	1601.9
$\omega_\mathrm{e}x_\mathrm{e}(\mathrm{cm}^{-1})$	12	10.7	84.9	92.9	16.3	20
$\Delta\omega$ (cm^{-1})	-	500	-	2500	-	2000
A (a.u.)	-	5.5	-	468.9	-	0.023
B (nm^{-1})	-	$-3.09(-3)$	-	$-9.041(-3)$	-	$44.2(-3)$
C (nm^{-2})	-	$6.18(-6)$	-	$28.02(-6)$	-	$-266(-6)$
D (nm^{-3})	-	$-4.99(-9)$	-	$-29.57(-9)$	-	0

Table 2. Molecular parameters for selected electronic transitions of N_2, N_2^+ [5]

	N_2			**N_2^+**		
	$B^3\Pi_g$	$A^3\Sigma_u$	$C^3\Pi_u$	$X^2\Sigma_g^+$	$B^2\Sigma_u^+$	$A^2\Pi_u$
$T_\mathrm{e}(\mathrm{cm}^{-1})$	59618.4	50203.6	89136.9	0	25461.5	9167
$\omega_\mathrm{e}(\mathrm{cm}^{-1})$	1733.4	1460.6	2047.2	2207	2419.8	1903.7
$\omega_\mathrm{e}x_\mathrm{e}(\mathrm{cm}^{-1})$	14.1	13.87	28.4	16.1	23.2	15
$\Delta\omega$ (cm^{-1})	-	1500	2000	-	2000	2000
A (a.u.)	-	0.355	457.6	-	380.1	0.516
B (nm^{-1})	-	$3.7(-4)$	$-8.05(-3)$	-	$-6.7(-3)$	$-4.6(-4)$
C (nm^{-2})	-	$-3.2(-8)$	$19.7(-6)$	-	$15.6(-6)$	$1.96(-7)$
D (nm^{-3})	-	0	$-1.6(-8)$	-	$-1.2(-8)$	$-2.6(-11)$

Table 3. Molecular parameters for selected electronic transitions of NO, H_2 [5]

	NO			**H_2**		
	$X^2\Pi_r$	$B^2\Pi_r$	$A^2\Sigma^+$	$X^1\Sigma_g^+$	$B^1\Sigma_u^+$	$C^1\Pi_u$
$T_\mathrm{e}(\mathrm{cm}^{-1})$	0	45913.6	43965.7	0	91700	100089.8
$\omega_\mathrm{e}(\mathrm{cm}^{-1})$	1904.2	1037.2	2374.3	4401.2	1358.1	2443.8
$\omega_\mathrm{e}x_\mathrm{e}(\mathrm{cm}^{-1})$	14.1	7.7	16.1	121.3	20.9	69.5
$\Delta\omega$ (cm^{-1})	-	1500	2000	-	1000	2000
A (a.u.)	-	0.75	60.9	-	2.36	0.024
B (nm^{-1})	-	$-9.94(-3)$	$-12.55(-3)$	-	$-23.9(-3)$	$55(-3)$
C (nm^{-2})	-	$41.6(-6)$	$52.7(-6)$	-	$71.8(-6)$	0
D (nm^{-3})	-	$-47.4(-9)$	$-71.1(-9)$	-	0	0

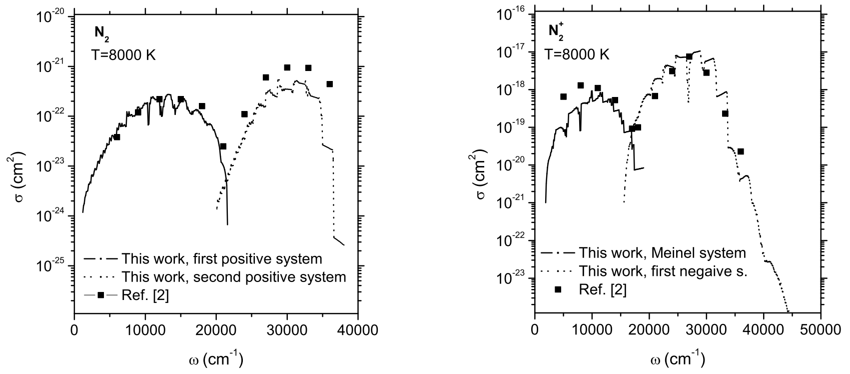
4 Results

Photoabsorption cross sections for above mentioned molecular electronic transitions were computed. Examples for molecules N_2, N_2^+, NO, NO^+, OH, H_2, and O_2 are given in Figs. 1–5. In Figs. 1 and 2 comparison is made for molecules N_2, N_2^+, and NO with the results of [2]. Good agreement is due to the same approximation method. Small discrepancies occur due to the different sources of the Franck–Condon factors. Photoabsorption cross section of the H_2 molecule at the temperature of 4000 K is presented in Fig. 3. The effect of various temperatures can be seen in Fig. 4 for molecules OH and NO^+. For molecules NO^+, OH, and H_2 no data for comparison were available. In Fig. 5 the influence of the choice of the interval $\Delta\omega$ on the photoabsorption cross section of the molecule O_2 is demonstrated.

5 Conclusion

Calculation have been made of the photoabsorption cross sections for various electronic transitions of selected diatomic molecules. General agreement with other sources of similar data has been reached.

The presented cross sections have been used for computation of total spectral



a) N_2 molecule

b) N_2^+ molecule

Fig. 1. Photoabsorption cross section of molecules N_2 and N_2^+ as a function of radiation wavenumber for temperature of 8 000 K.

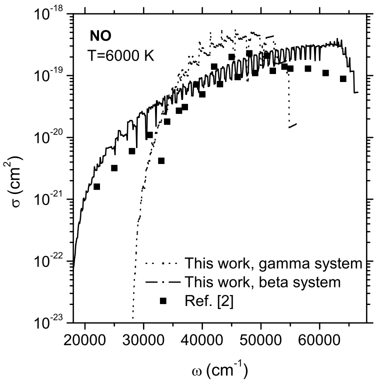


Fig. 2. Photoabsorption cross section of NO molecule as a function of radiation wavenumber for temperature of 6 000 K.

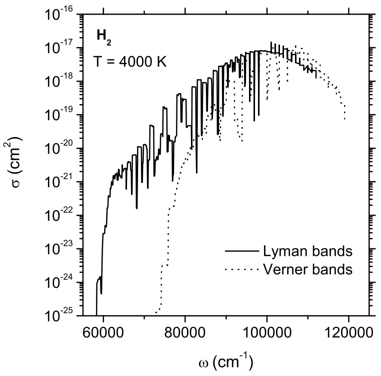


Fig. 3. Photoabsorption cross section of H_2 molecule as a function of radiation wavenumber for temperature of 4 000 K.

absorption coefficients of air and water vapor arc plasmas. These coefficients are the input data for computation of tables of partial characteristics and net emission coefficient of radiation which are widely used for a prediction of the radiative heat transfer.

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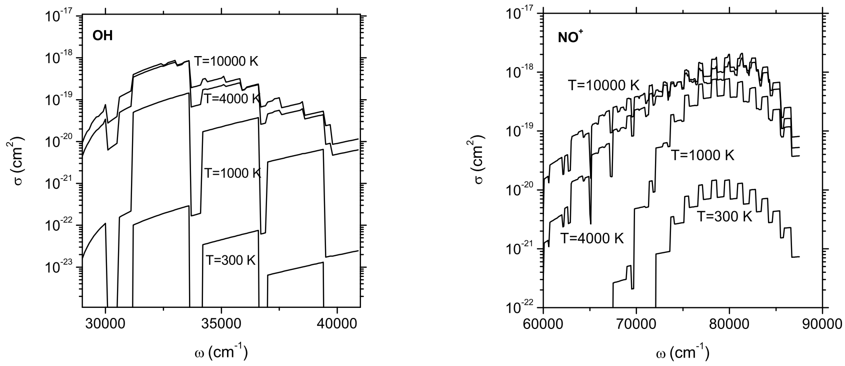
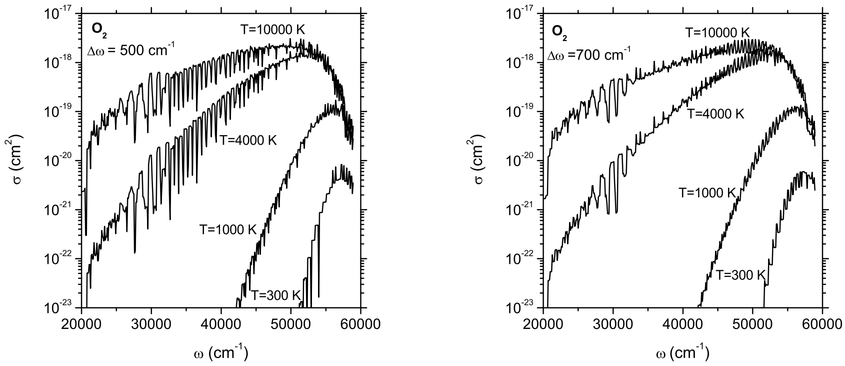


a) OH molecule b) NO$^+$ molecule

Fig. 4. Photoabsorption cross section of OH and NO$^+$ molecules at various temperatures.



a) $\Delta\omega = 500\ \mathrm{cm}^{-1}$ b) $\Delta\omega = 700\ \mathrm{cm}^{-1}$

Fig. 5. Photoabsorption cross section of O_2 molecule at various temperatures for two different values of $\Delta\omega$.

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