DIAGNOSTICS OF PLASMA PROCESSES AND MODELLING

APPROXIMATE CALCULATIONS OF CONTINUOUS SPECTRA OF DIATOMIC MOLECULES

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1. Introduction

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 extreme experimental conditions. In such cases, the mathematical modeling is of great importance. However, the nonlinearity of equations describing the radiation field and strong dependency of input parameters on the radiative frequency and properties of the medium make mathematical plasma models very complicated. Exact calculations are hardly possible, even with modern computers, due to the large computation times required; therefore, several approximate methods have been developed (method of partial characteristics, net emission coefficient, etc.).

Any quantitative study of the radiative transport of energy requires knowledge of the frequency-dependent absorption properties of the arc plasma. Theoretical calculations of radiation field are based on the knowledge of the plasma composition and subsequently absorption coefficients. The total spectral absorption coefficient (spectral absorptivity) needs to be calculated as a function of wavelength, temperature and pressure with radiation wavelengths spanning from the infrared to the far ultraviolet region of the spectrum.

Intensive radiation is irradiated from the hot central part of the arc and reabsorbed in cold edge of the plasma. Therefore, besides of continuous and discrete radiation of atoms and atomic ions the influence of molecular species on the absorption properties of the plasma has to be taken into account. Recently, we have studied discrete band spectra of diatomic molecules[1]. In this paper two radiation processes leading to the continuous absorption molecular spectra are studied. Simple approximate formulas for photodissociation and photoionization cross sections of diatomic molecules are presented. Results obtained for selected diatomic molecules are compared with available experimental and other theoretical data from literature.

2. Absorption coefficients

A light beam traveling through a participating gas layer of thickness *dx* loses energy by absorption and by scattering away from the direction of travel. The attenuation of radiation in non-scattering medium is proportional to the magnitude of the incident energy (intensity I_n) and to the length of the path

$$dI_\nu = -\kappa_\nu I_\nu dx \qquad (1)$$

The proportionality constant k_n is known as an absorption coefficient. 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. Three different types of radiative transitions can be distinguished: *i*) transition between bound atomic or molecular states, called bound-bound transitions (*bb*), *ii*) transitions from a bound state to a "free" (dissociated) one (absorption) or from "free" to bound (emission), called bound-free transitions (*bf*), and *iii*) transitions between two different "free" states, free-free transitions (*ff*).

Total absorption coefficient is given as a linear sum of all three processes

$$\kappa(\nu, T, p) = \kappa^{bb} + \kappa^{bf} + \kappa^{ff} \qquad (2)$$

The spectral absorption coefficient of any process is related to the photo-absorption cross section s_n (T) by

$$\kappa^a_{\nu,i}(T, p) = \sigma^a_{\nu,i}(T) N^a_i(T, p) \qquad (3)$$

where N_i^a is the population density of the *i*-th electronic state E_i^a of the absorbing species "*a* ". Thus, at a given spectral frequency, plasma temperature and pressure, the total spectral absorption coefficient is

$$\kappa_\nu = \sum_a \sum_i \sigma^a_{\nu,i} N^a_i \qquad (4)$$

Calculation of absorption coefficients represents a complex task, since the radial wave functions of all free and bound atomic and molecular states must be known. However, simplifications can be made by using various semi-empirical methods.

3. Photodissociation

The process of photodissociation can proceed in various ways. Photodissociation can occur by line and by continuous absorption. The most important case of dissociation absorption continua is the direct photodissociation, in which a transition takes place from a stable lower state to a

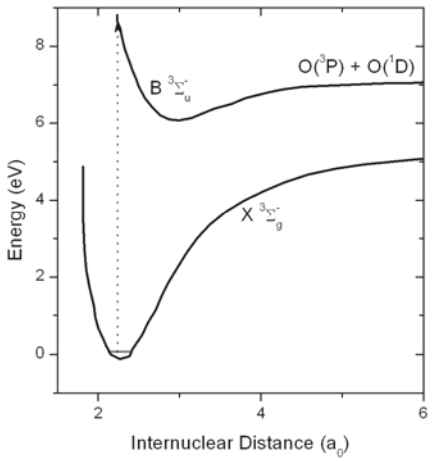

Fig. 1. **Relevant potential curves for O_2 illustrating direct photo-dissociation (Schumann-Runge continuum) from Jarmain at all[2]**

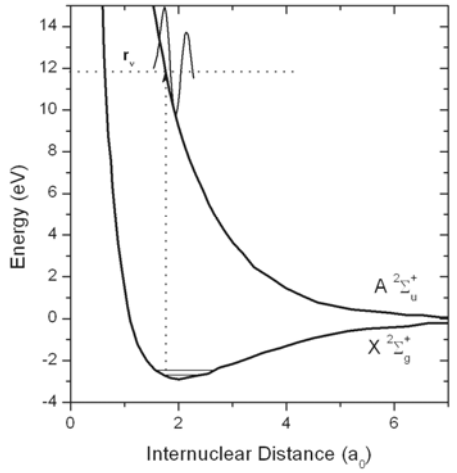

Fig. 2. **Relevant potential curves for H_2^+ illustrating direct photo-dissociation from Dunn[3]**. Also shown are a typical continuum wave function and turning radius r_c

continuous upper state.

Continuous spectra join onto the series of vibrational levels of the upper electronic state (see Fig. 1 for Schumann-Runge continuum of molecule O_2), and are the only feature present if the electronic state under consideration has no discrete vibrational levels at all (unstable state – see Fig. 2 for molecule H_2^+).

According to the Franck-Condon principle, the most probable transition in absorption is that going vertically upward (see Fig.1 and Fig.2). The probability of the transition between two states ψ' and ψ'' is proportional to the square of the dipole transition moment

$$\left|\int \psi'^{*} D \psi'' d\tau\right|^2 \qquad (5)$$

where D is the vector of electric dipole moment and dt is the element of volume of the space of nuclear and electronic coordinates. Neglecting the molecular rotation we obtain

$$\left|\int \psi_E R_e(r) \psi_{v'} dr\right|^2 \qquad (6)$$

where $\psi_{v''}$ and ψ_E are the vibrational wave function for the lower bound molecular state and the repulsive wave function of continuum state, respectively, and

$$R_e(r) = \int \psi_{e'}(r, \tau_e) D \psi_{e''}(r, \tau_e) d\tau_e \qquad (7)$$

is the electronic transition moment. The variation of R_e with internuclear distance r is slow and R_e may be replaced by an average value $\overline{R}_e$. With this assumption we obtain

$$\overline{R}_e^2 \left|\int \psi_{v''} \psi_E dr\right|^2 \qquad (8)$$

The overlap integral

$$q_{v''E} = \int \psi_{v''} \psi_E dr \qquad (9)$$

is the Franck-Condon density. It has a maximum value when the broad maximum of the repulsive function lies approximately above the maximum of the vibrational wave function of the lower state.

In first approximation, very simple form of repulsive wave function can be used[4]: it is replaced by a *d*-function, which is different from zero only at the classical turning point r_n (see Fig. 2) .

Then the overlap integral for a given energy of the repulsive state is simply equal to the value $|\psi_{v''}(r_v)|^2$, where $\psi_{v'}$ is to be taken for the r value that corresponds to the frequency n considered. Supposing $\psi_{v''}(r)$ are harmonic oscillator wave functions

$$|\psi_{v''}(r)|^2 = \sqrt{\frac{\alpha}{\pi}} \frac{\exp(-\alpha x^2)}{2^{v''} v''!} \left[H_{v''}(\sqrt{\alpha} x)\right]^2 \qquad (10)$$

where $x = r - r_e$, $\alpha = \frac{4\pi^2 \mu \nu_{osc}}{h}$, $\nu_{osc} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$, $H_v(\sqrt{\alpha} x)$ are Hermitean polynoms.

The continuous spectrum corresponding to transition from the lower vibrational state $v'' = 0$ has one maximum, transitions from the vibrational state $v'' = 1$ show two intensity maxima, since the probability density distribution curve has two maxima. Similarly, three maxima are to be expected for transitions from $v'' = 2$, etc. In absorption at high temperatures the continua corresponding to $v'' = 0,1,2,...$ are superimposed, and in general only a single maximum arrives which is broader and less high than at low

temperature.

Absorption coefficients for dissociative transition from a bound vibrational level v'' of a lower state to the vibrational continuum of an upper state is given by

$$\kappa^{v'} = N_{v''}\sigma_{v''} \tag{11}$$

where $N_{v''}$ is the number density of molecules in the lower vibrational state v'', and the cross section according Herzberg[4]

$$\sigma_{v''} = \frac{16\pi^3\nu}{3hc}\sqrt{2\mu}\,\overline{R}_e^2\left|\psi_{v''}(r_v)\right|^2 \tag{12}$$

The classical turning point r_n is the solution of equation

$$h\nu = V(r) - hc\omega_{v''} \tag{13}$$

Here $V(r)$ is the potential energy curve of upper molecular state, $hc\omega_{v''}$ is the energy of the lower vibrational term.
Total spectral absorption coefficient is given by

$$\kappa_\nu = \sum_{v''}\kappa^{v'} = \frac{N}{Q(T)}\frac{\sigma_{v,0}}{\nu_0}\sqrt{\frac{\pi}{\alpha}}\,\nu\sum_{v''=0}^{6}\exp\left(-\frac{hc\omega_{v''}}{kT}\right)\left|\psi_{v''}(r_v)\right|^2 \tag{14}$$

Only first 7 vibrational levels of the lower electronic state were taken into account. N is the total number density of absorbing molecules, $Q(T)$ denotes the partition function

$$Q(T) = \sum_{v''=0}^{\infty}\exp\left(-\frac{hc\omega_e''v''}{kT}\right) = \frac{1}{1-\exp\left(-\frac{hc\omega_e''}{kT}\right)} \tag{15}$$

$\sigma_{v,0}$ and ν_0 are empirical data – photodissociation cross section at low temperature and corresponding radiation frequency of absorbed photon.

3.1. Photodissociation of O_2

The most important photodissociation transition of O_2 molecule is the convergence limit of $X^3\Sigma_g^- \rightarrow B^3\Sigma_u^-$ (Schumann-Runge continuum). It corresponds to dissociation $O_2 \rightarrow O(^3P) + O(^1D)$ (Fig. 1).

The potential curve of the upper state was approximated by Morse potential

$$V(r) = T_e + D_e\left(1 - e^{-\beta(r-r_e)}\right)^2 \tag{16}$$

where $\beta = \sqrt{\frac{2\pi^2 c\mu}{D_e h}}\,\omega_e$, T_e is the electronic term energy, D_e denotes dissociation energy from the ground vibrational state $v = 0$, r_e is the equilibrium internuclear distance, ω_e is the vibrational constant, and μ the reduced mass. Values of molecular parameters are given in Tab. I.

The value of empirical data was determined from Baulch at all[6]

$$\frac{\sigma_{v,0}}{\nu_0} = 6.55\times10^{-33}\,\mathrm{cm}^2.\mathrm{s}$$

Table I
Molecular parameters of O_2 (α is parameter in wave function of lower state) from Herzberg at all[5]

State	T_e [cm^{-1}]	ω_e [cm^{-1}]	r_e [10^{-10}m]	
$B^3\Sigma_u^-$	49793	709.3	1.604	D_e = 0.95 [eV]
$X^3\Sigma_g^-$	0	1580.2	1.207	α = 7.5e18 (cm^{-2})

Photodissociation cross section of Schumann-Runge continua for different temperatures is shown in Fig. 3. Comparison is made with the calculations of Mnacakanjan[7], good agreement was achieved.

3.2. Photodissociation of H_2^+

The transition $X^2\Sigma_g^+ \rightarrow A^2\Sigma_u^+$ of H_2^+ ion provides the clearest example of direct photodissociation (Fig. 2). The upper potential curve was approximated by exponential decay

$$V(r) = V_0 + A\exp\left(-\frac{r}{t}\right) \tag{17}$$

where V_0, A, and t are fit parameters. Their values are given in Tab. II, together with molecular parameters for the lower state. The value of empirical data was determined from Van Dishoeck[8]

$$\frac{\sigma_{v,0}}{\nu_0} = 2.795\times10^{-33}\,\mathrm{cm}^2.\mathrm{s}$$

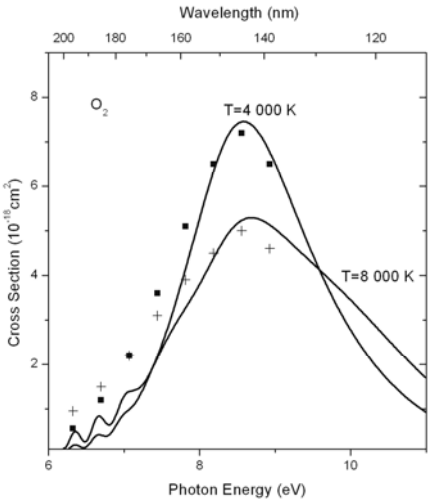

Fig. 3. **The photodissociation cross sections for Schumann-Runge continuum of molecule O_2 at different temperatures.** Solid lines: present work; squares and crosses: calculations from Mnacakanjan[7] for 4000 K and 8000 K, resp.

Table II
Molecular parameters of H_2^+ and OH from Herzbergat all[5]

Molecule	State	ω_e [cm^{-1}]	r_e [10^{-10}m]	α[cm^{-2}]
H_2^+	$X^2\Sigma_g^+$	2321.7	1.052	3.345e17
OH	$X^2\Pi$	3737.8	0.969	1.027e18
Molecule	State	V_0 [eV]	A [eV]	t [10^{-10}m]
H_2^+	$A^2\Sigma_u^+$	0.546	66.261	0.546
OH	$1^2\Sigma^-$	4.353	27.57	0.492
OH	$1^2\Delta$	6.883	138.42	0.253
OH	$B^2\Sigma^+$	8.497	82.123	0.283

The photodissociation cross sections are presented in Fig. 4. Calculation was performed for first 7 vibrational levels (solid curve) and for transition from the vibrational level $v'' = 0$ only (dashed curve). Comparison with Dunn[3] (dotted curve) and Van Dishoeck[8] (dash-dot curve) shows good agreement.

3.3. Photodissociation of OH

Direct photodissociation from the ground $X^2\Pi$ state may take place by absorption into three higher states, the $1^2\Sigma^-$, $1^2\Delta$, and $B^2\Sigma^+$ state. The three states are repulsive in the Franck-Condon region of the ground state (Fig. 5). Data for repulsive potential curves were taken over from paper of Van Dishoeck at all[9]; curves can be approximated by exponential

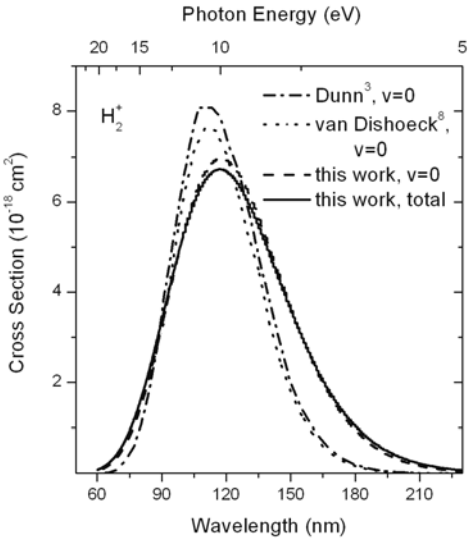

Fig. 4. **The photodissociation cross section for transition $X^2\Sigma_g^+ \rightarrow A^2\Sigma_u^+$ of molecule H_2^+.** Solid line: present work for first 7 vibration levels of lower state; dashed line: present work for transition from only basic vibration lower state $v = 0$; dotted and dash-dot line: data from Van Dishoeck[8] and Dunn[3], resp.

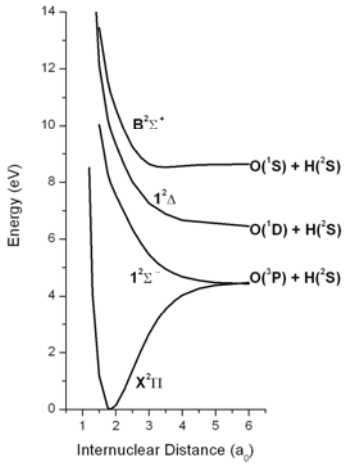

Fig. 5. **Relevant potential energy curves for direct photodisociation of OH from Van Dishoeck at all[9]**

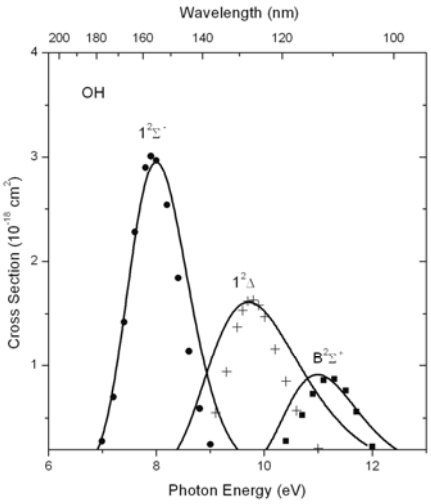

Fig. 6. **The calculated photodissociation cross sections as functions of incident photon energy for the $1^2\Sigma^-$, $1^2\Delta$, and $B^2\Sigma^+$ states starting from the $X^2\Pi$.** Solid line: present work; circles, crosses, squares: calculations from Van Dishoeckat all[9]

decay (*17*). Values of molecular and fit parameters are given in Tab. II.

The photodissociation cross sections for absorption into the $1^2\Sigma^-$, $1^2\Delta$, and $B^2\Sigma^+$ states are presented in Fig. 6. Comparison is made with the calculations of Van Dishoeck at all[9] where configuration-interaction method was used for obtaining approximate electronic wave functions. Very good agreement shows that the simple calculations presented in this work give reliable results.

4. Photoionization

For atoms, a continuous range joins onto each series of discrete electronic states and corresponds to the removal of an electron (ionization) with more or less relative kinetic energy or, conversely, to the capture of an electron by the ion (recombination). Such continuous ranges of energy levels, corresponding to ionization, are possible also for molecules. Ionization potentials of most diatomic molecules are greater than 10 eV and therefore the ionization continua lie in the far ultraviolet.

The processes of interest here are one-photon, single ionization events; they can be written for a prototype molecule AB in the form

$$\mathrm{AB} + h\nu \rightarrow \left[\mathrm{AB}^{+}\right]^{j} + e^{-} \qquad (18)$$

where $h\nu$ is the incident photon energy, AB is the target molecule in the ground electronic state, $[AB^+]^j$ is the molecular ion in the electronic excited state j, and e^- is the ejected electron carrying off kinetic energy.

In the Born-Oppenheimer and Franck-Condon approximation the photoionization cross section of the process (18) can be expressed in the form

$$\sigma(\nu, T) = \sum_{v''v'} w_{v''}(T)\,\sigma_{v''v'}(\nu) \qquad (19)$$

where $w_{v''}$ is the Boltzmann probability of occupation of the vibration level v'' of the ground electronic state of the neutral molecule and the partial cross section $\sigma_{v'v'}$ is from Mnacakanjan[7]

$$\sigma_{v''v'}(\nu) = \frac{\pi r_0}{3R_\infty^2}\frac{\nu}{c}\, q_{v''v'}\, Re^2\, \varphi(\nu - \nu_{v''v'}) \qquad (20)$$

In (*20*)*n* is the photon frequency, r_0 is the Bohr radius, R_∞ is the Rydberg constant, c is speed of light, $q_{v'v'}$ are Franck-Condon factors for transitions between vibronic levels of the neutral molecule and the ion, and $Re^2\,\varphi(\nu - \nu_{v'v'})$ represents the electronic part of the transition dipole moment. Both the constant part Re^2 and the frequency variation $\varphi(\nu - \nu_{v'v'})$ can be determined from experimental results in cold gas. Three different types of frequency variation $\varphi(\nu - \nu_{v'v'})$ were used:

$$\varphi_1(\nu - \nu_{v''v'}) = \begin{cases} 0 & \nu < \nu_{v''v'} \\ (\nu_{v''v'}/\nu)^4 & \nu > \nu_{v''v'} \end{cases} \qquad (21)$$

$$\varphi_2(\nu - \nu_{v''v'}) = \begin{cases} 0 & \nu < \nu_{v''v'} \\ (\nu_{v''v'}/\nu)^3 & \nu > \nu_{v''v'} \end{cases}$$

$$\varphi_3(\nu - \nu_{v''v'}) = \begin{cases} 0 & \nu < \nu_{v''v'} \\ (\nu_{v''v'}/\nu)^2 & \nu > \nu_{v''v'} \end{cases}$$

4.1. Examples of Photoionization

Calculations were performed for molecules O_2, N_2, NO, and H_2. The molecules were in their ground electronic states. Following partial photoionization cross sections were computed: for the production of O_2^+ in the states $X^2\Pi_g^+$, $b^4\Sigma_g^-$, and $a^4\Pi_u + A^2\Pi_u$; for the production of N_2^+ in the states $X^2\Sigma_g^+$, $A^2\Pi_u^+$ and $B^2\Sigma_u^+$; for the production of NO^+ in the states $X^1\Sigma^+$ and $A^1\Pi$; and for the production of H_2^+ in the state

Table III
Recommended data for Franck-Condon factors, Re^2, and $\varphi(\nu - \nu_{v''v'})$ for photoionization of O_2, N_2, NO, and H_2

O_2	O_2^+	FC factors	Re^2	$\varphi(\nu - \nu_{v''v'})$
$X^3\Sigma_g^-$	$X^2\Pi_g^+$	Ref [11]	1	φ_2
	$a^4\Pi_u + A^2\Pi_u$	Ref [11]	0.4	φ_2
	$b^4\Sigma_g^-$	Ref [11]	1	φ_1
N_2	N_2^+	FC factors	Re^2	$\varphi(\nu - \nu_{v''v'})$
$X^1\Sigma_g^+$	$X^2\Sigma_u^+$	Ref [12]	3.7	φ_3
	$A^2\Pi_u$	Ref [12]	5	φ_3
	$B^2\Sigma_u^+$	Ref [12]	1	φ_2
NO	NO^+	FC factors	Re^2	$\varphi(\nu - \nu_{v''v'})$
$X^2\Pi$	$X^1\Sigma^+$	Ref [13]	1.25	φ_3
	$A^1\Pi$	Ref [13]	1.25	φ_2
H_2	H_2^-	FC factors	Re^2	$\varphi(\nu - \nu_{v''v'})$
$X^1\Sigma_g^+$	$X^2\Sigma_g^+$	Ref [14]	2	φ_1

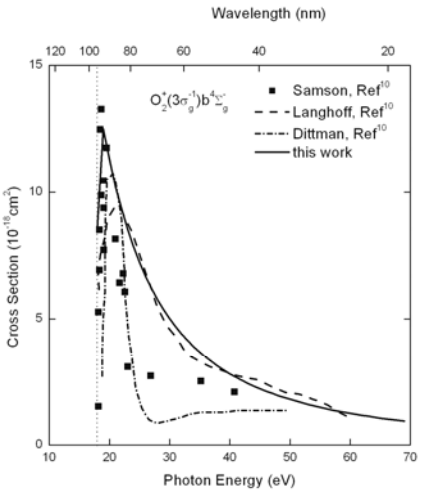

Fig. 7. **Partial photoionization cross section for O_2 ($X^3\Sigma_g^-$) → O_2^+($b^4\Sigma_g^-$) as a function of photon energy.** Comparison is made with data available in Gallagher at all[10]

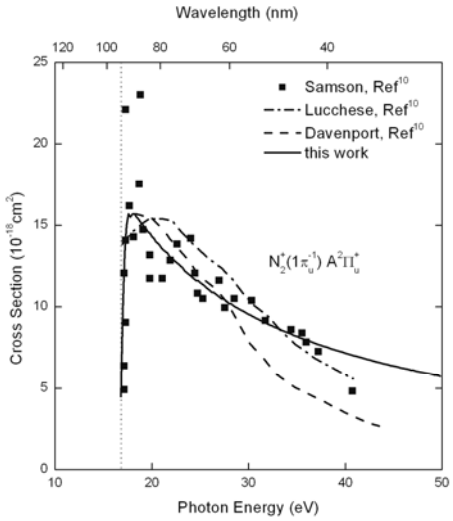

Fig. 8. **Partial photoionization cross section for N_2 ($X^1\Sigma_g^+$) → N_2^+ ($A^2\Pi_u^+$) as a function of photon energy.** Comparison is made with data available in Gallagher at all[10]

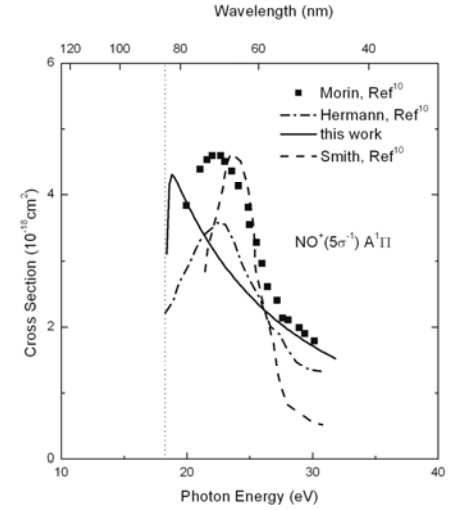

Fig. 9. **Partial photoionization cross section for NO ($X^2\Pi$) → NO^+($A^1\Pi$) as a function of photon energy.** Comparison is made with data available in Gallagher at all[10]

$X^2\Sigma_g^+$. Molecular data for all electronic states under consideration were taken from Herzberg at all[5]. Sources of Franck-Condon factors, and recommended values of Re^2 and the frequency variation $\varphi(\nu - \nu_{v'v''})$ obtained by means of comparison with available experimental data in literature are presented in Tab.3. Results of calculation for transitions O_2 ($X^3\Sigma_g^-$) → O_2^+($b^4\Sigma_g^-$), N_2 ($X^1\Sigma_g^+$) → N_2^+ ($A^2\Pi_u^+$), NO ($X^2\Pi$) → NO^+ ($A^1\Pi$), and H_2($X^1\Sigma_g^+$) → H_2^+($X^2\Sigma_g^+$) are shown in Fig. 7, Fig. 8, Fig. 9, and Fig. 10, respectively.

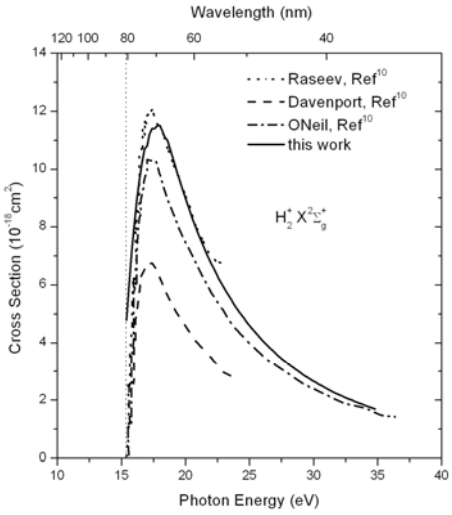

Fig. 10. **Partial photoionization cross section for H_2 ($X^1\Sigma_g^+$) → H_2^+ ($X^2\Sigma_g^+$) as a function of photon energy.** Comparison is made with data available in Gallagher at all[10]

Cross sections are plotted on individual figures as functions of the incident photon energy. Comparison was made with data published in review paper of Gallagher at all.[10] where many experimental and theoretical data are compiled. Cross sections were extracted using standard digitization techniques. The threshold energy for the relevant photoionization process is indicated by a vertical dotted line on each figure.

Discrepancies between measured values and theoretical calculations appear particularly in threshold regions where polarization effects and possible non-Franck-Condon behavior are important.

5. Conclusions

Calculations have been made of the cross sections of direct photodissociation and photoionization of some diatomic molecules. General agreement with other sources of similar data has been reached. The presented simple formulas for cross sections will be used in improved calculation of total spectral absorption coefficients of air and water vapour plasmas. These coefficients are necessary input data for computation of tables of partial characteristics and net emission coefficients of radiation which are widely used for a prediction of the radiation heat transfer in arc plasma.

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