Energy balance in sulfur contained, radiative MW discharge

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Abstract: Optical and chemical properties of MW discharge contained Sulphur were calculated. 3D CFD model of MW discharge was elaborated and coupled with radiation transfer phenomena. Optical, thermophysical properties of plasma were calculated based on first principal-based data about electronic structure of the molecules and interaction potentials. It was shown that presence of molecular Sulphur leads to essential input of radiation in total energy balance of the discharge. Dependence of emission spectra of the plasma on external parameters (pressure, chemical composition) was analysed.

Keywords: MW discharge, S_2, H_2S, spectrum.

1. Introduction

Plasma of MW and other discharges is widely used for treatment of sulphur contained gases like H_2S [1,2]. However, it is well known [3] that MW discharge in atmosphere of S_2 can be effective source of visual radiant energy. Fraction of radiation in energy balance may reach value about 70%. Principal channel of such effective energy conversion is related with S_2 dissociation in hot zone of plasma and subsequent radiation of electronically excited $S_2(B^3\Sigma^-_u)$ state, formed due to recombination of S atoms, in relatively "cold" area. This radiation spectrum is continuous and overlaps the eye sensitivity curve very well. "Fine" structure of the spectrum (j,v transitions) can be used for experimental recovering of the characteristic of the such MW plasma like translational and vibrational temperatures. Mentioned above features of MW discharge in presence of sulphur makes theoretical investigations of his properties practical and needful for possible applications.

2. Properties of H-S plasma

Transport and radiation properties like thermal conductivity, viscosity, electrical conductivity, absorption and radiation coefficients are important characteristics which determines behavior of thermal plasma vs pressure and temperature. Transport coefficients μ, λ, σ (viscosity, thermal and electrical conductivities) are calculated based on the Chapman-Enskog (CE) method [4]. The gas flow is assumed continuous media in the thermal and chemical equilibrium (LTE). The gas and plasma are considered as ideal ones. The exact formulas of the CE method are used to calculated $\mu(\xi)$, $\lambda(\xi)$, $\sigma(\xi)$ with account for higher approximations ξ. The viscosity $\mu(\xi)$ is calculated in the second approximation ξ=2. The effective thermal conductivity is calculated as the sum of translational, internal and "reaction" conductivirties: $\lambda_{eff}(\xi)=\lambda^{tr}(\xi)+\lambda^{int}+\lambda_r$ The $\sigma(\xi)$ $\lambda^{tr}(\xi)$ are calculated in the third approximation (ξ=3). The λ^{int} is calculated by the Mason-Monchick theory provided the necessary parameters (e.g. the collision number for rotational relaxation Z_{rot}) are known for the molecules of the mixture. The λ_r is calculated by the advanced version of Butler-Brokaw approach.

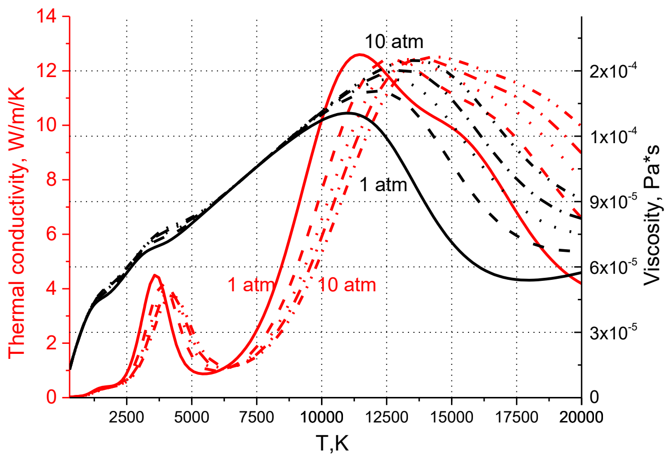

Fig.1 Thermal conductivity (red lines) and viscosity (black lines) of H_2S plasma at pressures 1(solid line), 3(dashed), 5(dotted), 7(dash-dotted) and 10(dash-dot-dotted) atm.

Absorption coefficient was calculated based on the general expression for Einstein coefficients of the quantum transition between states $\alpha \to \beta$ in the diatomic molecular spectra in the Born-Oppenheimer approximation:

$$A_{i,v,J;j,v',J'} = \frac{4}{3g_i}\cdot\left(\frac{e^2}{\hbar c}\right)^3\cdot\omega^3_{i,v,J;i,v',J'} \cdot |\langle v(i)|D_{ij}(R)|v'(j)\rangle|^2\cdot S_{JJ'},$$

$$S_{JJ'} = \sum_{M,M'} |<J\Omega\Sigma|\vec{n}|J'\Omega'\Sigma'>|^2$$

α,β designate the sets of the electron, vibrational and rotational energy levels of diatomic molecules

$$\langle\alpha| \to |\beta\rangle \equiv \langle i,v,J| \to |j,v',J'\rangle$$

,where R is the internuclear distance between the atoms of diatomic molecule, $D_{ij}(R)$ is the reduced matrix element of the electronic dipole operator due to the transition between the electron states of the upper $\langle i|$ and lower $|j\rangle$ terms. Vibrational quantum numbers{v(i), v'(j)} are related to the initial and final electronic potential terms $U_i(R), U_j(R)$ with the total angular momenta J, J' and their projections on the OZ axis of the lab reference frame $\{M, M'\}$.$\{\vec{S}, \vec{S}'\}$ *is* the total spin and its projection on the internuclear axis is $\{\Sigma, \Sigma'\}$. $\{\vec{L}, \vec{L}'\}$ is the electronic angular momentum and its projection of on the internuclear axis is $\{\Lambda, \Lambda'\}$. The sum of spin and electronic angular momentum projections on the internuclear axis Ω, $\{\Omega=\Lambda+\Sigma,\ \Omega'=\Lambda'+\Sigma'\}$. $<S_{JJ'}>$ is the Hönl-London factor. Vibrational wave functions were calculated in uniform quasiclassical approximation.

Absorption coefficient $k=k_\omega$ and transport coefficients were tabulated as a function, temperature, pressure and wavelength (in case of k_{abs}) for pre-calculated plasma composition. These tables were used then in the modeling of MW discharge.

Figure 1 shows dependence of thermal conductivity and viscosity of H_2S plasma for different temperatures and pressures. These dependences are not monotonic because of dissociating of molecules at low temperatures and ionisation of atoms at high temperatures.

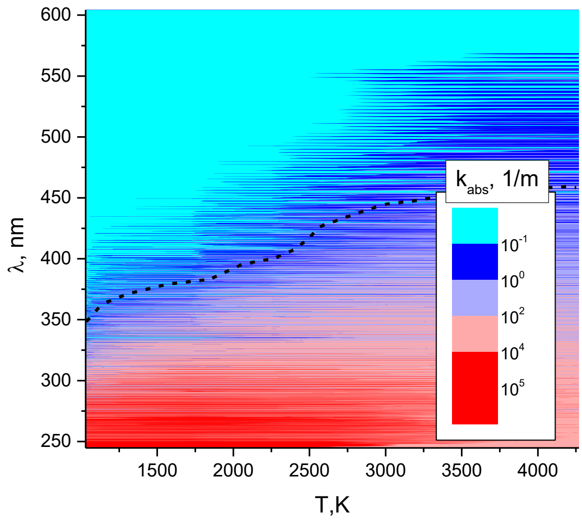

Fig.2 Absorption coefficient of S_2 as a function of wavelength λ and temperature T. Dashed line corresponds to conditions where optical thickness of plasma is about 1.

Figure 2 demonstrates contour profile of absorption coefficient of sulphur as a function of wavelength at different temperatures. Dashed line indicates area where optical thickness of plasma $\theta=k_{abs}*L$ is about 1, where L is characteristic size of investigated system. The complex structure of k_{abs} is related with electronic-vibrational-rotational nature of absorption of S_2 molecule. Because of both the upper and lower states are $^3\Sigma$ states, only transitions with changing of rotational level by ΔJ= 1,0, -1 are possible. Taking into account that Hönl -London factor for ΔJ=0 (Q branch) is $S_J^J=0$, only branches R and P with changing of rotational level by ΔJ= 1 and -1 give input in radiation spectrum. They form very dense, quazi continuum structure (see Fig.3). Mentioned above peculiarities behaviour of transport and radiation coefficient provides plasma specific steady-state conditions where absorbed MW power is balanced by radiation and convection losses.

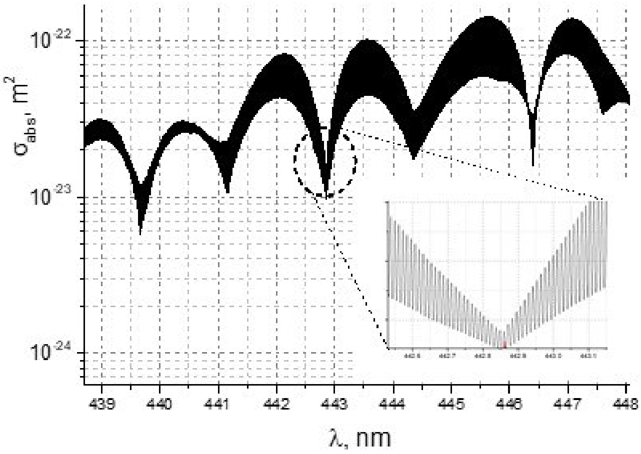

Fig.3 Rotational-vibrational structure of absorption cross section of S_2 around 439-448 nm. Insertion – high resolution of J-J' transition for R and P branches.

All discussed above transport and radiation properties of H-S plasma were calculated using Fluid Work Bench software [5].

3. Model of MW discharge

Model includes 3D equations of heat and mass balance coupled with radiation transport. Temperature of heavy particle is equal to temperature of electron. Set of equation includes Maxwell equations for electric field. The boundary conditions are: total power absorbed in the discharge, temperature on the wall and zero derivatives of the electric field, temperature and concentrations in the center of discharge. Thus, the simulation of the MW is provided by solution of steady-state equations of set of multicomponent hydrodynamic together with Maxwell equations.

Total MW power absorbed in the volume is calculated by:

$$W = \int \sigma \frac{E_1^2 + E_2^2}{2} dV$$

To fulfill conditions concerning total absorbed power $W=W_0$, the value of the B_{ind} (value of field on the boundary) was fitted for every iteration:

$$B_{ind}^{*}=B_{ind}\sqrt{\frac{W_0}{W}}$$

Diffusion fluxes are calculated from Stefan-Maxwell equations.

In the radiation transport task, a special module calculates the power density source term due to radiation processes Q_{rad} [W m^{-3}]. This source term is used then in solution of the steady-state heat conduction equation $-\mathrm{div}(\lambda_c \nabla T) \sim ..+Q_{rad}$,where T - is temperature, λ_c - is heat conductivity. In the steady-state case the density of radiative energy is constant and $Q_{rad} = -\mathrm{div}\Phi^{\varepsilon}$ is the divergence of total spectrum-integrated radiation power flux. The radiation flux Φ^{ε} is calculated in each computational cell as a difference of fluxes - outgoing from the cell and ingoing to the cell. Corresponding values are calculated while solving absorption equation along a finite set of rays emitted from each cell of the grid and representing the radiation emitted in the whole solid angle:

$$J = \int d\omega \int \varepsilon_{\omega}(\vec{r})\, exp\left(-\int_{\vec{r}(\Omega)}^{r} k_{\omega} dl\right) d\Omega$$

where $\varepsilon_{\omega} = k_{\omega}\frac{c}{4\pi U_{\omega P}}$, $U_{\omega P}$ is the Planck function. The radiation transfer code module uses as an input the absorption coefficient tables, where the absorption coefficient $k=k_{\omega}$ is tabulated as a function of wavelength and temperature for pre-calculated plasma composition

4. MW S_2 discharge properties

Modelling of MW discharge was carried out for different pressure of sulphur vapor 1-10 atm. The gas mixture was pumped through tube with the size 4 cm. Incoming MW 2.45 GHz power was 1100 W. Figure 4 shows temperature (left side of picture) and atomic sulphur distribution (right side) in the cross section of the tube channel.

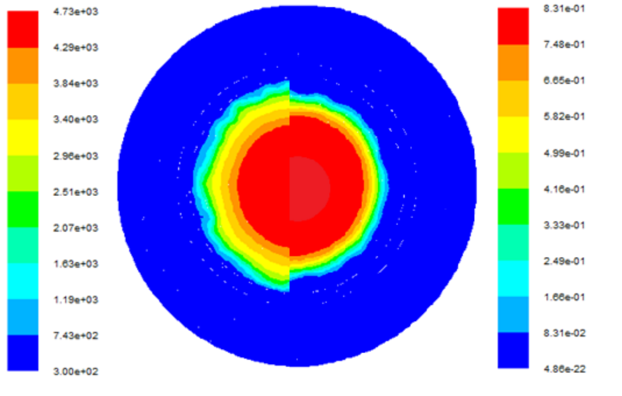

Fig.4 Temperature (left side) and atomic S (right side) distribution in S_2 discharge in cross section of cylindrical channel.

Figure 5 shows radiation spectrum of S_2 plasma at different pressure of S_2 vapor. Analysis of simulation results indicates that the absorbed MW power heats the gas that is the reason of subsequent dissociation of S_2. Dissociation degree can reach value about 80%. Transport (including diffusion, convection and radiative transport) of the atomic sulphur to relatively "cold" zone leads to formation of molecular sulphur in the electronically excited states and, as a sequence, radiation of these states:

$S(^3P)+S(^3P,\ ^1D) \Rightarrow S_2(B''^3\Pi_u, B^3\Sigma^-_u) \Rightarrow S_2(X\ ^3\Sigma^-_g)+\hbar\omega$

Radiation spectrum has continuum type form. Actually, spectrum consists of many vibrational, rotational (J,v) transitions between electronically excited states.

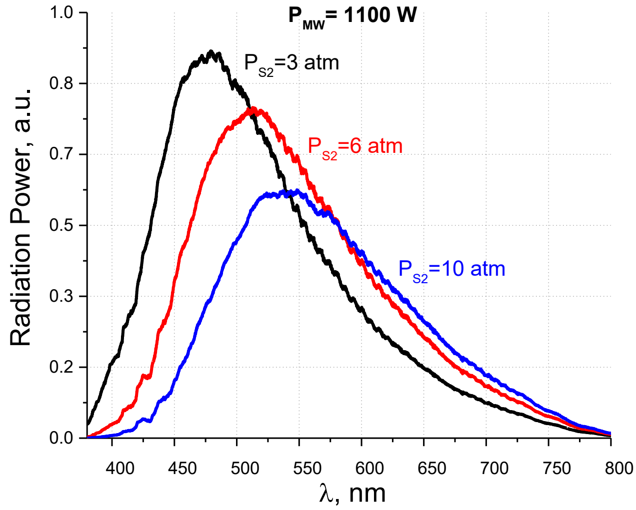

Fig.5 Radiation spectrum of S_2 plasma at power 1100 W, at different pressure of S_2.

Overlapping of these (J,v) transitions leads to formation of the "continuum" type spectra. Input of radiation in total energy balance is 42%, 37% and 32% at pressures 3,6 and 10 atm. The principal input in the radiation is related with formation of state $B^3\Sigma^-_u$ (correlates with $S(^3P)+ S(^1D)$), because transition to X state has large transition dipole moment. Transition from $B''^3\Pi_u$ (correlates with $S(^1D)+ S(^1D)$), is optically forbidden (see Figure 6).

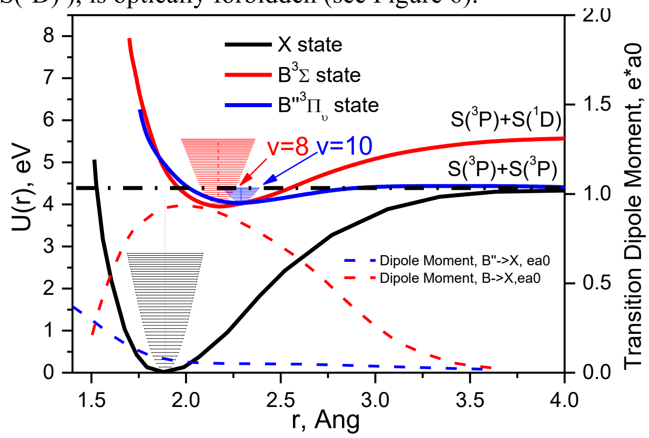

Fig.6. Potential energy curves of principal radiative states of S_2 and transition dipole moments.

However, this state populates $B^3\Sigma^-_u$ state due to kinetic mixing of the B<=>B" states and participates indirectly in the radiation formation. Because of mixing phenomena has a large characteristic time (as well as molecular radiation has frequency about 10^6s), the processes of excited states quenching becomes compatible with radiation at high pressures. Along with radiation trapping phenomena it leads to decreasing of radiation power with increasing of pressure (see Fig.5).

5. Conclusions

Modelling of sulphur contained MW discharge was carried out at different pressures. It was shown that at relatively high pressures (P>2atm.) about 80% dissociation degree of molecular sulphur can be achieved in hot zone of such flowing system. It leads to essential input of radiation in energy balance of the system due to formation of radiated states of S_2. The effective energy transfer of translation energy of plasma to emission of light can be high as 40% and limited by competition of processes of radiative transition $S_2(B''^3\Pi_u,\ B^3\Sigma^-_u) \Rightarrow S_2(X\ ^3\Sigma^-_g)$ with radiation trapping and thermal relaxation of excited states. It permits to determine dependence of radiation spectrum of plasma upon external parameters like Pressure, Temperature and energy input in system.

6. References

[1] A.V.Balebanov, V.K.Jivotov, B.V.Potapkin, V.D.Rusanov et al., Dokl. Akad. Nauk SSSR, 1985, vol. 283, pp. 657 – 660.

[2] J.B. Harkness, ea. "Plasma -chemical waste treatment of acid gases," Argonne National Laboratory Report, 1993.

[3] C W Johnston, J. Phys. D: Appl. Phys. **37** (2004) 211–220

[4] Hirschfelder J.O., Curtiss C.F., Bird R.B. Molecular Theory of Gases and Liquids. Wiley, New York, 1964

[5] Fluid Work Bench, KintechLab, http://www.kintechlab.com/products/fluid-workbench/