Nonequilibrium Radiation of Shock-Heated CH₄-N₂ Gas Mixture

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Abstract- The computational model of nonequilibrium radiation of shock-heated gases is presented in this paper. In the model the flow in the relaxation zone behind the shock front is considered. The hydrodynamic description of the relaxation zone is performed in the framework of Euler system of equations. In the model equations of chemical kinetics and vibrational relaxation are solved. Also the energy balance equation for the temperature of electron gas calculation is included in the model. For the determination of the population of excited states of molecules the approach that we refer to as "hybrid collisional-radiative" is used. The "just-overlapping" line model is used for the calculation of radiative characteristics of shock-heated gases. The model is validated against the results of measurements of radiation in shock tube experiments performed on X2 facility.

Keywords- Nonequilibrium Radiation; Shock-Heated Gas Mixtures; Chemical Kinetics; Vibrational Relaxation

I. INTRODUCTION

Over the past decade a number of papers dedicated to the experimental registration of nonequilibrium radiation of shockheated gases emerged [1-6]. These studies share the common feature: the results presented there are in absolute units. It was possible to perform such measurements due to the appearance of high-resolution and high-speed optical instruments. These devices were not available when the investigation of nonequilibrium processes behind the shock waves in shock tubes began, i.e. in the second half of XX century.

With the appearance of high amount of new experimental data it became possible to check the validity of various models (such as models of nonequilibrium dissociation, chemical kinetics models, models for the calculation of constant rates for electron impact excitation of electronic states of molecule, etc.). Combining an experience accumulated in our group in the field of calculation of radiative properties of high-temperature gases (also in absolute units) [7] with the knowledge of the state of the problem a decision was made to perform an extensive comparison of the results of shock tube experiments on the measurements of nonequilibrium radiation with the numerical results obtained using the theoretical approach developed earlier in our group [3, 8-10].

This paper presents our attempt to perform an analysis of the experimental data presented in [2] as a part of the comprehensive validation of our theoretical approach. In [2] the experimental investigation of nonequilibrium radiation of a shock-heated CH_4 -N₂ gas mixture has been performed in a wide range of pre-shock pressures and shock velocities. In the presented paper the main attention was paid to the analysis of spatial distributions of the radiation emitted by a shock-heated gas mixture and integrated over a specific wavelength region.

The content of the paper is as follows: in Section II the description of the model of nonequilibrium radiation of shockheated CH_4 -N₂ gas mixtures is presented; the comparison of the results of numerical simulations and experimental measurements and the corresponding discussion are given in Section III.

II. THE DESCRIPTION OF THE MODEL [3, 8-10]

The algorithm presented below is based on the marching method. All the equations are solved along x-axis. The shock front is situated at the point x=0. The initial conditions for the problem are formulated in the following way. The pressure, density, velocity and the translational temperature of heavy particles at point x = 0 are determined based on their values in the unperturbed gas and the equations that relate the flow variables at the surface of the discontinuity [11]. The vibrational temperatures, the temperature of gas of electrons and concentrations of chemical components at point x = 0 assume their values in the unperturbed gas.

A. The Calculation of the Gasdynamic Parameters

The parameters of the flow in the relaxation zone are determined in the framework of Euler system of equations. The equation of energy is modified in order to take into account the fact that the considered gas mixture is multicomponent and chemically reacting.

$$\frac{d}{dx}(\rho u) = 0, \ \frac{d}{dx}(p + \rho u^2) = 0, \ \frac{d}{dx}(h + \frac{u^2}{2}) = 0$$
(1)

$$p = \frac{\rho R_0 T}{M_{\Sigma}}; M_{\Sigma} = \sum_{i=1}^{N_*} \eta_i x_i; \eta_i = m_i N_A$$
$$h = \left[(T - T^0) \left(\frac{5}{2} + \sum_{i=1}^{N_M} x_i \right) + \sum_{i=1}^{N_M} x_i \sum_{j=1}^{N_{V,i}} g_{i,j} \frac{\theta_{i,j}}{\exp(\theta_{i,j} / T_{V,i,j}) - 1} + \sum_{i=1}^{N_*} \Delta_f H_i^0 x_i \right] \frac{R_0}{M_{\Sigma}}$$
(2)

Here p, ρ , u, T - pressure, density, velocity and translational temperature; x_i , m_i - molar fraction and mass of *i*-th chemical component (atom or molecule); $T_{V,i,j}$, $\theta_{i,j}$, $g_{i,j}$ - vibrational temperature, characteristic vibrational temperature and degeneracy of *j*-th vibrational mode of *i*-th molecule, N_s - number of chemically reacting components; N_M - number of diatomic and three atomic molecules; $N_{V,i}$ - number of vibrational modes of *i*-th molecule.

Radiative-gasdynamic interaction (the term taking into account the energy loss by the emission of radiation in the third equation of the system (1)) is not included in the model.

It is worth noticing that a specific heat capacity at constant pressure is calculated using the vibrational temperature that is different from the translational temperature of heavy particles. The calculation is performed according to the equations of the quantum theory of the heat capacity. Its results are similar to the results of the classical theory when the vibrational temperature tends to the higher values. The calculation of the translational and rotational contributions to the specific heat capacity is performed according to the theorem of the equipartition of energy over the degrees of freedom of a molecule and under the assumption that the translational and rotational temperatures are equal.

B. The Calculation of the Chemical Composition

The system of chemical kinetic equations for the determination of the molar fraction of chemical components is written in the following form:

$$\frac{dX_k}{dx} = \sum_{j=1}^{N_r} (b_{kj} - a_{kj}) \left[k_j^f \prod_{i=1}^{N_s} X_i^{a_{ij}} - k_j^r \prod_{i=1}^{N_s} X_i^{b_{ij}} \right], \ k = \overline{1, N_s}$$
(3)

Here X_k - a molar volume concentration, a_{kj} , b_{kj} - stoichiometric coefficients of the *j*-th forward and backward reactions for the *k*-th chemical component, k_j^f , k_j^r - forward and backward rate coefficients of *j*-th reaction. The system of chemical equations is written as follows:

$$\sum_{i=1}^{N_s} a_{ij}[X_i] \underset{k_j}{\overset{k_j}{\Leftrightarrow}} \sum_{i=1}^{N_s} b_{ij}[X_i], j = \overline{1, N_r}$$

$$\tag{4}$$

Here $[X_i]$ - a symbol that corresponds to the *i*-th chemical component, N_r - the total number of reactions. The list of chemical reactions and the corresponding rates for the CH₄-N₂ gas mixture were borrowed from [12] (except for the dissociation reaction of N₂ and the associative ionization of N₂-[13]; the associative ionization of CN – [14]). These data with the corresponding backward reaction rates are presented in Table 1. The coefficients presented in Table 1 are related to the reaction rates using the following formulas:

$$k_{i}^{f} = A_{i}^{f} T^{B_{i}^{f}} e^{-\frac{C_{i}^{f}}{T}}; \ k_{i}^{r} = A_{i}^{r} T^{B_{i}^{r}} e^{-\frac{C_{i}^{r}}{T}}$$
(5)

Here A_i^f , A_i^r - the pre-exponential factors; B_i^f , B_i^r - the dimensionless index of power; C_i^f , C_i^r - the activation energy of forward/backward reactions correspondingly. In Table 1 n and m are the numbers of reacting particles in the forward and backward reactions. The calculation of backward reaction rates is based on the equilibrium constants presented in [15] and on the detailed balance principle:

$$K_i^{eq} = \frac{k_i^f}{k_i^r} \tag{6}$$

As was stated in the abstract, for the determination of population of electronically excited states of molecules the hybrid collisional-radiative approach is used. It means that only those excited electronic states of molecules are considered as separate chemical components that are important from the point of view of radiation. For these states the kinetic mechanism of

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excitation/deactivation is formulated, corresponding chemical kinetic equations are solved. As a result, one can obtain the population of these states that is possible to be used in the calculations of radiative characteristics of shock-heated gases.

TABLE 1 THE CHEMICAL KINETIC SCHEME FOR THE CH_4 - N_2 GAS MI	XTURE
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Equation of the reaction	A ^f , (cm ³ /mol) ⁿ⁻¹ /s	B ^f	C ^f , K	A ^r , (cm ³ /mol) ^{m-1} /s	B ^r	C ^r , K
$N_2+A \rightarrow N+N+A^1$	2.320E+18	-0.5	113200	1.232E+17	-0.5	0.0
N_2 +Mol \rightarrow N+N+Mol ²	5.800E+17	-0.5	113200	3.080E+16	-0.5	0.0
$N_2+E \rightarrow N+N+E$	3.000E+24	-1.6	113200	4.350E+21	-1.2	0.0
$CH_4+M\rightarrow CH_3+H+M^3$	4.700E+47	-8.2	59200	7.200E+32	-4.75	0.0
$CH_3+M\rightarrow CH_2+H+M^3$	1.020E+16	0.0	45600	1.560E+19	-0.93	0.0
$CH_3+M \rightarrow CH+H_2+M^3$	5.000E+15	0.0	42800	1.570E+20	-1.31	0.0
$CH_2+M \rightarrow CH+H+M^3$	4.000E+15	0.0	41800	7.430E+20	-1.42	0.0
$CH_2+M\rightarrow C+H_2+M^3$	1.300E+14	0.0	29700	2.930E+19	-1.26	0.0
$CH+M\rightarrow C+H+M^3$	1.900E+14	0.0	33700	9.840E+16	-0.53	0.0
$C_2+M\rightarrow C+C+M^3$	1.500E+16	0.0	71600	5.240E+12	0.73	0.0
$H_2+M \rightarrow H+H+M^3$	2.230E+14	0.0	48350	4.440E+15	-0.31	6642
$CN+M\rightarrow C+N+M^3$	2.530E+14	0.0	71000	3.120E+16	-0.5	0.0
$NH+M \rightarrow N+H+M^3$	1.800E+14	0.0	37600	2.270E+16	-0.4	0.0
$HCN+M\rightarrow CN+H+M^3$	3.570E+26	-2.6	62845	3.010E+23	-2.02	0.0
$CH_3 \!\!+\!\! N \!\!\rightarrow\!\! HCN \!\!+\!\! H \!\!+\!\! H$	7.000E+13	0.0	0.0	9.380E+13	0.0	7150
$CH_3+H\rightarrow CH_2+H_2$	6.030E+13	0.0	7600	9.160E+10	0.61	4232
$CH_2+N_2 \rightarrow HCN+NH$	4.820E+12	0.0	18000	1.430E+16	-0.98	9830
$CH_2+N \rightarrow HCN+H$	5.000E+13	0.0	0.0	1.230E+15	-0.11	59834
$CH_2\!\!+\!\!H\!\!\rightarrow\!\!CH\!\!+\!\!H_2$	6.030E+12	0.0	-900	2.460E+12	0.04	456
$CH+N_2 \rightarrow HCN+N$	4.400E+12	0.0	11060	6.270E+17	-1.15	13118
$CH+C\rightarrow C_2+H$	2.000E+14	0.0	0.0	1.710E+22	-1.64	43437
$C_2+N_2\rightarrow CN+CN$	1.500E+13	0.0	21000	1.610E+13	-0.18	12618
$CN+H_2 \rightarrow HCN+H$	2.950E+05	0.0	1130	3.460E+07	-0.45	770
$CN+C\rightarrow C_2+N$	5.000E+13	0.0	13000	1.580E+16	-0.59	0.0
$N+H_2 \rightarrow NH+H$	1.600E+14	0.0	12650	1.560E+11	0.56	0.0
$C+N_2 \rightarrow CN+N$	5.240E+13	0.0	22600	2.160E+15	-0.56	0.0
$C+H_2 \rightarrow CH+H$	4.000E+14	0.0	11700	8.380E+12	0.26	0.0
$H+N_2 \rightarrow NH+N$	3.000E+12	0.5	71400	9.510E+08	0.95	0.0
$H+CH_4 \rightarrow CH_3+H_2$	1.320E+04	3.0	4045	7.100E-05	4.92	1146
$N+N \rightarrow N_2^++e$	4.440E+10	0.7	67500	1.500E+22	-1.50	0.0
$N+e \rightarrow N^++e+e$	2.500E+34	-3.82	168600	1.970E+41	-5.08	0.0
$C+e \rightarrow C^++e+e$	3.700E+31	-3.00	130720	2.330E+40	-4.60	0.0
$H+e \rightarrow H^++e+e$	2.200E+30	-2.80	157800	3.970E+39	-4.50	0.0
$Ar+e \rightarrow Ar^++e+e$	2.500E+34	-3.82	181700	5.920E+42	-5.56	0.0
$CN^++N \rightarrow CN^++N^+$	9.800E+12	0.0	40700	3.480E+13	-0.11	36895
$C^+ + N_2 \rightarrow N_2^+ + C$	1.110E+14	-0.11	50000	5.360E+14	-0.53	0.0
$C+N\rightarrow CN^++e$	2.940E+10	0.92	75000	4.700E+18	-0.55	0.0

¹A=C, N, H, ²Mol= C₂,N₂,H₂,CN,CH,NH,CH₂,CH₃,CH₄,HCN, ³M= C, N, H, C₂,N₂,H₂,CN,CH,NH,CH₂,CH₃,CH₄,HCN

In the study [2] the data on radiation of violet system of CN have been presented. That is why for the analysis of the data of [2] only two electronic states of CN ($A^2\Pi$ and $B^2\Sigma$) have been taken into account. For these states the kinetic mechanism of population is presented in Table 2. It is worth noticing that one can calculate the lifetimes of the excited levels with regard to the spontaneous transitions using the ab-initio Einstein coefficients that are also used for the calculations of spectral profiles [16].

TABLE 2 KINETIC MECHANISM OF POPULATION OF EXCITED ELECTRONIC STATES OF CN MOLECULE

Name of the tansition	A ^f , (cm ³ /mol) ⁿ⁻¹ /s	B ^f	C ^f , K	A ^r , (cm ³ /mol) ^{m-1} /s	B ^r	С ^г , К	Source
$CN(X^{2}\Sigma^{+})+e \rightarrow CN(A^{2}\Pi)+e$	1.065E+15	0.303	13300	5.327E+14	0.303	0.0	ab-initio σ [26]
$CN(X^{2}\Sigma^{+})+e \rightarrow CN(B^{2}\Sigma^{+})+e$	1.965E+13	0.690	37000	1.965E+13	0.690	0.0	ab-initio σ [26]
$CN(A^2\Pi) \rightarrow CN(X^2\Sigma^+) + hv$	1.440E+05	0.0	0.0	0.0	0.0	0.0	calc. in this study
$CN(B^{2}\Sigma^{+}) \rightarrow CN(X^{2}\Sigma^{+}) + hv$	1.200E+07	0.0	0.0	0.0	0.0	0.0	calc. in this study
$CN(B^{2}\Sigma^{+}) \rightarrow CN(A^{2}\Pi) + hv$	1.880E+05	0.0	0.0	0.0	0.0	0.0	calc. in this study
$CN(A^2\Pi)+At\rightarrow CN(X^2\Sigma^+)+At^1$	2.300E+13	0.0	0.0	2.300E+13	0.0	13300	based on [27]
$CN(A^{2}\Pi)+Mol \rightarrow CN(X^{2}\Sigma^{+})+Mol^{2}$	2.650E+11	0.0	0.0	2.650E+11	0.0	13300	based on [27]
$CN(B^{2}\Sigma^{+})+M\rightarrow CN(A^{2}\Pi)+M^{3}$	4.500E+11	0.0	0.0	4.500E+11	0.0	23700	based on [27]

 ^{1}At – collisions with atoms, ^{2}Mol – collisions with molecules, ^{3}M – collisions with any heavy particle of gas mixture

It has been stated already that the energy balance equation for gas of electrons is included in the model, since it is known that behavior of electrons is different from the behavior of heavy particles [17]. The temperature of the gas of electrons is used for the calculation of the reaction rates in which the electrons participate (e.g. the reactions of ionization or the reactions of excitation of electronic states of molecules by the electron impact).

In this work we have taken into account the influence of vibrational nonequilibrium on the chemical kinetics according to the Kuznecov model [18]. The basic relations of the model are as follows:

$$k(T,T_{\nu}) = Z(T,T_{\nu}) \cdot k^{0}(T)$$

$$Z(T,T_{\nu}) = \frac{1 - \exp(-\theta/T_{\nu})}{1 - \exp(-\theta/T)} \cdot \exp\left[E_{\nu}^{*}\left(\frac{1}{T} - \frac{1}{T_{\nu}}\right)\right]$$
(7)

It is possible to generalize this model for the case of polyatomic molecules. Parameter E_v^* has been considered as a fitting parameter of the model:

$$E_{\nu}^{*} = n \cdot T_{front} \tag{8}$$

Here *n* is an empirical parameter and T_{front} is the temperature at the point x=0 (i.e. the temperature obtained using the equations that relate the flow variables at the surface of the discontinuity [11]).

C. The Calculation of the Vibrational Temperatures

In order to determine the distribution of the temperature of an individual vibrational mode behind the shock front the relaxation equation is solved. For the CH_4 - N_2 mixture we have taken into account only the vibrational mode of N_2 . The choice was made due to the high initial concentration of N_2 (98%, so the strongest influence on the distribution of the translational temperature has to be due to the relaxation of this vibrational mode). The application of the modal approximation for the problem under consideration is based on the assumption that at least the lowest vibrational levels of the molecules are populated according to the Boltzmann distribution with a temperature that is not equal to the translational temperature of heavy particles. This behavior of the distribution function of molecules on the vibrational levels was discussed in [19, 20].

The relaxation equation has been considered in the following form:

$$\frac{de_m}{dt} = Q_{VT}^m + Q_{CV}^m \tag{9}$$

Here e_m - the number of vibrational quanta, Q_{VT}^m - the term responsible for the change in the vibrational energy of molecules due to the interaction with the translational degrees of freedom of other particles, Q_{CV}^m - the term taking into account the gain and loss of vibrational energy due to the chemical reactions:

$$Q_{VT}^{m} = \frac{e_{m}^{0} - e_{m}}{\tau_{m}}; \ \tau_{m} = \left(\sum_{i=1}^{N_{VT,m}} \frac{x_{i}}{\tau_{m,i}}\right)^{-1}$$

$$e_{m} = [\exp(\theta_{m} / T_{V,m}) - 1]^{-1}$$
(10)

In the paper the rate of the VT-exchange reaction $N_2(V=1)+M \leftrightarrow N_2(V=0)+M$ was taken from [21] (cm³/s):

$$k = T \cdot \exp(-24.06 - 237.15 \cdot T^{-1/3} + 60.67 \cdot T^{-2/3} - 0.0405 \cdot T^{1/3})$$
(11)

Using this rate constant it is possible to calculate the corresponding relaxation time [18]:

$$\tau = \frac{1}{p} \cdot \frac{k_B T}{k(1 - \exp(\theta_{N_2} / T))}$$
(12)

Here k_B , [erg/K] is the Boltzmann constant; θ_{N_2} =3396 K is the characteristic temperature of N₂ vibrational mode; p, [erg cm⁻³] is the pressure of the gas mixture.

The term Q_{CV}^m was calculated using the Treanor-Marrone model [22].

D. The Calculation of the Temperature of the Gas of Electrons

In order to determine the electron gas temperature one should solve the corresponding energy balance equation:

$$\frac{d}{dx}\left(\frac{3}{2}T_eX_eu\right) + T_eX_e\frac{du}{dx} = Q_{ei} + Q_{ea} + Q_{ai} + Q_{ion} + Q_{ev}$$
(13)

The formulas describing the terms on the right-hand side of (12) are presented below (K mol/(s cm³)):

$$Q_{ei} = 1.21 \times 10^{20} X_e X_i \frac{T - T_e}{T_e^{3/2}} \ln \Lambda$$
(14)

$$Q_{ea} = 3.378 \times 10^{10} X_e X_a \sqrt{T_e} (T - T_e) \left[1 - \left(1 + \frac{T_e}{T_a^*} \right)^{-3} \right]$$
(15)

$$Q_{ai} = T \sum_{q=1}^{N_{ai}} \alpha_q k_q^f X_{a_q} X_{b_q} - T_e \sum_{q=1}^{N_{ai}} \beta_q k_q^r X_e X_{(a_q b_q)^+}$$
(16)

$$Q_{ion} = -\sum_{i=1}^{N_{ion}} \gamma_i E_{ion,i} k_i^f X_{a,i} X_e$$
⁽¹⁷⁾

$$Q_{ev} = 6.022 \times 10^{23} \sum_{m} X_e X_m \theta_m P_{10,m} \cdot \left(q_m(T_{V,m}) - q_m(T_e) \right) \cdot \left(q_m(T_{V,m}) + q_m(T_e) + 1 \right)$$
(18)

$$q_m(T) = \left(\exp(\frac{\theta_m}{T}) - 1\right)^{-1}, \ T = \{T_e, \ T_{V,m}\}$$

$$\ln \Lambda = 7.47 + 1.5 * \log_{10}(T_e) - 0.5 * \log_{10}(n_e)$$

Here X_e is the molar concentration of the electrons; X_i is the molar concentration of the ions; X_a is the molar concentration of the atoms; X_{a_q} , X_{b_q} , $X_{(a_qb_q)^*}$ are the molar concentrations of atoms and the molecular ion participating in the q-th reaction of associative ionization; k_q^f , k_q^r are rates of the q-th reaction of associative ionization and dissociative recombination; N_{ai} is the number of associative ionization/dissociative recombination reactions; $X_{a,i}$ is the molar concentrations of atoms participating in *i*-th ionization reaction; $E_{ion,i}$ is the ionization energy of an atom in *i*-th ionization reaction; N_{ion} is the total number of ionization reactions; X_m is the molar concentration of molecules, corresponding to the *m*-th vibrational mode.

The coefficients α_q and β_q are responsible for the efficiency of energy transformation in the reactions of associative ionization/dissociative recombination. The coefficient γ_i accounts for the step-like mechanism of ionization process, i.e. when ionization occurs from the electronic excited state of an atom and not from the ground state of an atom. These constants are adjustable parameters of the model. The recommended intervals of their variations are 0.05-0.1 and 0.1-1 correspondingly [10]. The values of the parameters affect the results. For all the calculations presented in this work the values of the parameters are $\gamma_i = 1$; $\alpha_q = \beta_q = 1$.

It is assumed that there are no electrons right behind the shock wave front (at point x=0). It means that the first electrons occur as a product of reactions of associative ionization. For the CH₄-N₂ gas mixture these reactions are: C+N→CN⁺+e, N+N→N₂⁺+e. The process of associative ionization is very important for the investigations of the relaxation zone behind the shock front and for the prediction of the emissivity of the heated gases. However, due to complex multistep character of this process, its detailed theoretical and experimental study is difficult.

The term Q_{ev} takes into account the interaction between the electron gas and the vibrational modes of molecules [23]. Index *m* stands for the different vibrational modes. The probability of a single-photon vibrational transition for vibrational mode of N₂ is given by the following formula [23] (cm³/s):

$$P_{10,m} = 4.5 \cdot 10^{-9} \exp\left(-\frac{10000}{T_e}\right).$$
(19)

E. The Calculation of the Spectral Intensity of the Radiation

The "just-overlapping" line model [7] is used in this study in order to calculate the spectral emissivity of the gas heated by the shock wave. This model allows to make the calculation of the spectral intensity of the radiation averaged on the rotational

structure. The corresponding analytical expression of the spectral radiation is given below (W/cm³·sr· μ m):

$$j_{\lambda} = A \frac{N_{eel}}{Q_{VR}\lambda^{6}} \sum_{V} \sum_{V} \frac{S_{VV^{*}}}{|\Delta B_{V}|} \exp\left[-\frac{hc}{kT_{V}} E_{eel}(V')\right] \exp\left[-\frac{hc}{kT_{R}} \frac{B_{V}}{\Delta B_{V}}(\omega - \omega_{VV^{*}} + B_{V})\right]; A = 3.202 \times 10^{-10}$$
(20)

The most important value here is S_{VV} , which is the strength of a vibronic transition. It is connected with the square of the moment of the vibronic transition in accordance with the following relation:

$$S_{V'V^*} = (2 - \delta_{0,\Lambda'+\Lambda^*})(2S+1) \left| R_{V'V^*} \right|^2;$$

$$\left| R_{V'V^*} \right|^2 = \frac{3h}{64\pi^4 a_0^2 e^2} \frac{2 - \delta_{0,\Lambda'}}{2 - \delta_{0,\Lambda'+\Lambda^*}} \frac{1}{\omega_{V'V^*}^3} \cdot A_{V'V^*}$$
(21)

Here $A_{V'V'}$ is the Einstein coefficient of the vibronic transition. One can obtain the $A_{V'V'}$ as a result of the solution of the quantum mechanical problem of the calculation of vibronic wave functions. The values of $A_{V'V'}$ depend only on the initial and final vibronic states of the molecule between which the transition occurs. It means that once the problem is solved for the set of vibronic transitions the values of $A_{V'V'}$ can be tabulated and can be used whenever it is necessary.

It is worth noticing that the spectral emissivity is calculated under the assumption that rotational temperature is equal to the translation. The vibrational temperature is calculated on the kinetic stage of the simulation. The averaging of the rotational structure was used for the deduction of (19) (various averaging models have been studied in [24]). The integration of (19) over wave numbers (wavelengths) with the arbitrary small step is not possible because in this case the error of a physical nature would be introduced to the results (due to the procedure of averaging of rotational structure used for the deduction of (19)).

III. RESULTS AND DISCUSSION

The calculations of the radiative characteristics for the parameters of the experiments [2] have been performed according to the model presented in the previous section. The experimental conditions examined in the work are: gas mixture -98% N₂ -2% CH₄, the pressure of an unperturbed gas 133 Pa. The shock wave velocities have been varied in the range 4-7 km/s. In the experiments nonequilibrium radiation of violet system of CN has been studied (the considered spectral region is 310-450 nm).

The results of the spatial distribution of the radiation integrated over the part of the spectrum and the spectral intensity of radiation are going to be presented in the following two subsections. It is worth noticing that the results presented above were obtained using the same set of parameters of the model without any special adjustment.

A. The Spatial Distribution of the Radiation Integrated over a Part of the Spectrum

In Figs. 1a-e the comparison of numerical and experimental results on the spatial distribution of radiation integrated over a wavelength region of 310-450 nm is presented. The numerical results are presented in a dashed line; the experimental results are presented in a solid line. The comparison of the numerical and experimental distributions allows us to make the following conclusions.





Fig. 1 Spatial distribution of radiation integrated over spectral region 310-450 nm, gas mixture 2% CH₄ – 98% N₂, pressure of unperturbed gas 133 Pa, velocities of shock wave a) $V_{sh} = 4.0$ km/s; b) $V_{sh} = 4.4$ km/s; c) $V_{sh} = 5.0$ km/s; d) $V_{sh} = 5.3$ km/s; e) $V_{sh} = 5.7$ km/s; f) $V_{sh} = 6.3$ km/s.

The relative error in the reproduction of the position of the nonequilibrium peak is up to 50%-70% for some of the experimental conditions. The relative error in the reproduction of the peak magnitude is up to 20%-30% for some of the experimental conditions. Considering the uncertainty of, for example, the rates of the excitation of the electronic states of molecules [25] and the fact that not so many efforts were made towards the development of chemical kinetic schemes for CH₄-N₂ gas mixture (as compared with CO₂-N₂ or O₂-N₂ gas mixtures), it is possible to conclude that the agreement between the experimental and numerical results is satisfactory for the current state of the development of the problem.

Also, one can notice that the model reproduces correctly the basic trends of the experimental data presented in [2] and analyzed here, i.e. with an increasing shock wave velocity the level of radiation emitted by the shock-heated gas mixture increases.

B. The Spectral Intensity of the Radiation Results

For some experimental conditions in [2] spectral profiles have been measured at the location of the peak of radiation. In Fig. 2 and Fig. 3 the comparison of numerical and experimental spectral intensities of radiation is shown. The experimental data are presented in a solid line. Numerical results are presented in a dashed line.

If one analyses the magnitude of the peak of radiation integrated over the wavelength region of 310-450 nm (Fig. 1 d and e), then it is easy to see that the maximum value of the experimental and numerical radiation agrees well with each other (it is worth noticing that the spectral profiles in Figs. 2 and 3 correspond to their own positions of the peaks, i.e. the numerical radiation peak located at the position about 2-3 mm behind the shock front, the experimental radiation peak located at the position 6-7 mm behind the shock front). Nevertheless, one can notice that in the spectral region of 400-430 nm the calculated spectral intensity of radiation is about 3-4 times smaller than the experimental values. On the one hand it may indicate that

there may be problems with the ab-initio Einstein coefficients that were used in calculations. On the other hand, this feature may indicate that there is some sort of vibrational (or rotational) nonequilibrium that leads to such spectral profiles. Additional calculations have to be performed in order to be able to give a definite answer to the formulated problem.



Fig. 2 The comparison of the computed and experimental spectral profiles for the experimental conditions: gas mixture 2% CH₄ – 98% N₂, the pressure of unperturbed gas 133 Pa. $V_{sh} = 5.3$ km/s.



Fig. 3 The comparison of the computed and experimental spectral profiles for the experimental conditions: gas mixture 2% CH₄ – 98% N₂, the pressure of unperturbed gas 133 Pa. $V_{sh} = 5.7$ km/s.

IV. CONCLUSIONS

In the present work we have performed calculation of radiative characteristics of the shock-heated CH_4 -N₂ gas mixture for the conditions of the experiments presented in [2]. It was shown that the model presented in the study is capable of reproducing the basic trends of the experimental data presented in [2] and analyzed in the paper. The problem was formulated based on the analysis of the spectral profiles at the peak radiation location. The solution of this problem may be obtained, if one implements a purely collisional-radiative model to the considered conditions.

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