High resolution technique for studying the energy exchange near the shock wave front

V S Ziborov¹, V P Efremov¹, M M Kuznetsov², V E Fortov¹, T A Rostilov¹, V V Shumova¹
¹ Joint Institute for High Temperatures of the Russian Academy of Sciences, Izhorskaya 13 Bldg 2, Moscow, 125412, Russia
² Moscow Region State University, Radio st. 10A, Moscow, 105005, Russia
E-mail: ziborov.vsa@yandex.ru

Abstract. The structure and properties of the shock wave front propagating in binary gas was investigated by multi-channel emission spectroscopy and electrostatic probe located in a flow core. The experimental conditions allowed to consider the energy exchange processes in the front like interaction of isolated cold heavy molecules \( \text{Mo(CO)}_6 \) with shock wave front of light noble gas (He, Ar). Measurements were carried out in a weak incident shock waves (Mach number \( M = (2.5 \div 3.6) \)) in the high vacuum shock tube at equilibrium temperature of 850–1400 K and pressure of 0.1–1.1 bar, \( \text{Mo(CO)}_6 \) concentration \( 5 \times 10^{13} \div 3 \times 10^{14} \text{ cm}^{-3} \). An influence of heavy molecules on thermodynamics was negligible and free paths of “heavy” molecules between collisions “heavy–heavy” were longer then 1 mm. Nearby shock wave front the conductivity and the electron precursor zones caused by ionization and charge separation were detected and measured. The dependence of probe current on the energy of pair collisions was found. The length of charge separation in SW front was measured and free electrons concentration was estimated.

1. Introduction
The border between a hot moving gas and cold immovable one, called shock wave front, is a subject of continues interest. The propagation of shock waves in binary mixtures of noble and heavy gases causes the over-equilibrium radiation and even ionization nearby density gradient of shock wave, the zone called shock wave front. These effects usually have time duration comparable with the time of translational relaxation behind shock wave, or depend on life times of emitting excited states of atoms or molecules. The possible applications of such short-living over-equilibrium states of gas behind shock waves are the subject of discussion for a long time. An idea to use these processes for initiation of chain reactions behind shock wave with the shorter induction time belongs to [1, 2]. However, up to now there are not enough experimental observations to point out the real source of nonequilibrium radiation and to choose quantitatively mechanism of these phenomena.

For the first time, the peaks of nonequilibrium radiation were observed in front of weak shock waves in binary gas mixtures [3], where the heavy gas was a small admixture in a light carrier gas. The radiation quantum \( h\nu \) was of the order \( 2 \div 3 \text{ eV} \), while the average energy of pair collision was of about factor 20 less. In that case the nonequilibrium radiation was interpreted as result of high energy collisions with the average energy of about several eV. The frequency
of such collisions was supposed to be high enough in the hot tail of nonequilibrium partition function of pair collisions. Later, the similar peaks were observed in spectral lines of shock heated Ar which was a small admixture in hydrogen [4]. Strong peaks of the nonequilibrium radiation behind a front of shock waves propagating in noble gases with admixture of iron carbonyl were studied in [5]. In this work the role of very fast decay of heavy molecules with further recombination of iron atoms along with the hypothesis of high energy collisions was supposed to be the reason for that radiation. These authors made more strongly pronounced conclusion that the radiating and ionizing species were iron clusters excited in exothermic reactions of condensation of supersaturated iron vapor forming after the instant decomposition of parent molecules after the shock wave arrival.

The hypothesis of influence of high energy collisions in shock wave front on ignition and detonation was used to explain decreasing ignition delay times in O₂/H₂ mixtures when heavy carrier gas argon was replaced by light helium [6, 7]. Detonation threshold shift upon adding small amount of xenon in He—O₂—H₂ mixtures was experimentally observed in [8] and confirmed by Monte-Carlo simulations in [9]. The detonation acceleration was associated with in the shock wave front.

Most of the available data have several imperfections and do not allow extracting quantitative information of the phenomenon. The absence of clear approach and suitable experimental technique for reliable registration of fast energy-exchange processes nearby the front of shock wave seems to be the main reason for the ambiguous interpretation of mechanism of over-equilibrium front emission. One of difficulties in data interpretations is an overlap of numerous energy exchange processes within the zone of shock wave front. The second problem is connected with high difference between the thickness of shock wave front and commonly available space resolution of shock tube emission-absorption and probe measurements.

Let us consider the shock wave propagation in a binary mixture of heavy and light gases as a joint motion of atoms or molecules with essentially different masses. As a result of complete relaxation within the translational relaxation zone called shock wave front, the “cold” velocity distributions of both components transform into “hot” ones with their inherent relaxation rates. This transformation results from a large number of pair collisions between particles. At the same time the common gas temperature settles between heavy and light gas fractions with the rate roughly proportional to the ratio of heavy to light gas mole masses multiplied by the frequency of pair molecular collisions. It is the slowest relaxation process that determines the length of shock wave front and possible effects of over equilibrium radiation etc.

Generally, in shock tube studies, the length of translational relaxation zone is less than the space resolution of spectroscopic techniques by the factor of 10² ÷ 10⁴ and cant be resolved. If time resolution is high enough, the recorded shock wave emission signal represents the emission integrated over the tube cross section and gives information about the energy exchange in the trek of translational relaxation. A goal of the present work was to find the experimental conditions when the shock wave front becomes long enough and its structure may be resolved with acceptable accuracy using high-resolution probe and emission registering technique.

2. Experimental approach
For the present study the high vacuum shock tube of 108 mm internal diameter and conventional sizes was used. A residual bath gas pressures was about ~ 8 × 10⁻⁷ mbar, whereas a rate of desorption and leakage was ~ 2 × 10⁻⁶ mbar/min. These leakage parameters permitted to attain the concentration of impurities below 10⁻⁶% and neglect their influence on the kinetics of processes.

The multi-channel emission spectroscopy was used in a number of cross sections along shock tube (figure 1). The emission signals were measured in narrow spectral range using monochromator ACTON 502 with interference light filter with λ = 313.3±3 nm. Emission space
resolution was \( \sim 0.4 \) mm. The bending deflection of shock wave front estimated in accordance with [10] was less than space resolution in all regimes investigated. Time resolution of electric circuit was better than \( \sim 100 \) ns [11]. A multi-needles electrostatic probe was installed in the dielectric end of shock tube in a flow core with the aim to avoid he boundary influence. The distance between the cross section of spectroscopic measurements and the probe position was 10 cm. Probe needles were parallel to the flow axis and their ends were disposed in one plate. The probe space and time resolutions were better than 0.2 mm and 100 ns respectively. The distance between spectroscopic measurements cross section and probe was 10 cm.

The shock wave velocity was measured by four piezoelectric pressure gages located along the shock tube end. The distance from the probe cross section and nearest to it gage cross section was less than 0.1 of the base of the measurement of shock wave velocity. A special series of the measurements of the arrival time of the density gradient by Schlieren method and emission in the shock front in one cross section of the shock tube in the perpendicular channels was carried out. It is found that the beginning of the sharp increase of radiation at \( \lambda = 313.3 \pm 3 \) nm coincides with the schlieren signal. The error in the measurements of the shock wave velocity and the dynamical characteristics of the pressure gage determine the maximum error in measurement of the instant of density gradient arrival at the probe cross section of about 0.3 \( \mu \)s.

The search of possible ways to stretch the zone of translational relaxation was the first step of present study.

One possible way is to increase the mass ratio of light and heavy gas. From this point, the mixture \( \text{Mo(CO)}_6 + \text{He} \) with mole mass ratio 264/4 was chosen. The translation relaxation zone of \( \text{Mo(CO)}_6 \) increases up to 0.1 mm in comparison with the length of the relaxation zone in the absence of heavy molecules at the same temperatures and pressures. This value is comparable with the space resolution of measurements 0.4 mm. Next, one may reduce the concentration of heavy gas. Concentrations of heavy molecules \( \sim 10^{-2}\% \) do not noticeably affect on the thermodynamics of shock wave as far as a mass fraction of them does not exceed 1% in mixtures. As relative concentrations of \( \text{Mo(CO)}_6 \) become smaller, the free paths of molecules between “heavy-with-heavy” collisions increase up to \( (1 \div 4) \) mm. The influence of such collisions on kinetic processes can be neglected within the characteristic lengths of shock wave front in He. Third, one have to use weak SW (Mach numbers \( \sim 3 \)), which allows to increase time of translation relaxation and to reduce effect of thermalization processes on the processes.
under consideration. This experimental approach gives opportunity to consider the shock wave propagation as an interaction of heavy “cold” molecules with shock wave front of light noble gas.

Finally, the next experimental conditions were chosen for mixtures of \((6 \times 10^{-3} + 1.2 \times 10^{-2})\)% Mo\((\text{CO})_6\) in helium: incident shock waves with Mach numbers \(M = (2.5 \div 3.6)\), equilibrium temperature \(T_2 = (850 \div 1400)\) K and pressure \(P_2 = (0.1 \div 1.1)\) mbar. Initial pressure range was \(P_1 = (12 \div 110)\) mbar. The bath gas concentration didn’t exceed \(10^{-5}\) mbar or \(0.1\)% of Mo\((\text{CO})_6\) concentration. The noble gases were of high purity (0.99996).

3. Results and discussion

Since electrostatic probe and emission measurements were carried out in different cross sections of shock tube, the exact time of shock wave front arrival measurement was very important point. A special series of experiments in argon diluted by small concentration of Mo\((\text{CO})_6\) was carried out with the aim to determine the real time of arrival of shock wave density gradient and emission start. The typical emission time profile at \(\lambda = 313.3 \pm 3\) nm and laser schlieren signal measured simultaneously in the same cross section are represented in figure 2. The schlieren signal maximum \(b\) coincides in time with the maximum increase of emission signal rate \(b\). It means that the emission signal intensive increase corresponds to the arrival of shock wave front. Nevertheless, one should note that the emission appears earlier, then the schlieren maximum comes in the measurement cross section.

![Figure 2](image-url)

**Figure 2.** Emission at 313.3 ± 3 nm \((a)\) and laser schlieren \((b)\) time profiles measured simultaneously in the same cross section of shock tube in incident shock wave propagating in Ar diluted by Mo\((\text{CO})_6\). DG – time of density gradient arrival. Equilibrium parameters behind the SW: temperature \(T_2 = 980\) K, pressure \(P_2 = 0.36\) bar, Mo\((\text{CO})_6\) concentration – \(1.2 \times 10^{-2}\)%.

The typical time profiles of the probe and photomultiplier signals in He + Mo\((\text{CO})_6\) mixture are represented in figure 3a and in larger scale in figure 3b. Marking point “0” corresponds to a time of density gradient arrival in the measurement cross-section. The emission signal and probe signal come noticeably earlier than the density gradient (figure 3a and figure 3b). The black lines on Fig. 3b are the smoothed lines of figure 3a in larger scale. The interval between “precursor” and the point “0” is known as “precursor time”. The rate of the rise of the signals become higher from point “0”, and both signals reach a maximum during a few hundreds of nanoseconds. The probe signal maximum \(Q_m\) does not change until the conductivity zone leaves the probe needles. The emission signal reaches maximum and decreases to zero in few
Figure 3. Time profiles of the probe signal and emission $313.3 \pm 3$ nm ($T_2 = 1196$ K, $P_2 = 0.74$ bar, $[\text{Mo (CO)}_6] = 3.83 \times 10^{14}$ cm$^{-3}$).

Figures show time profiles with a horizontal axis representing microseconds when the relaxation zone leaves the measurement cross-section. When the concentration of heavy molecules was significantly reduced, the probe signal reduced too but the precursor time of emission essentially increased (figure 4), at that initial pressure ahead shock wave front was less also.

Figure 4. Emission profile $313.3 \pm 3$ nm in SW propagating in mixture He and Mo(CO)$_6$ decreased concentration ($T_2 = 937$ K, $P_2 = 0.53$ bar, $[\text{Mo (CO)}_6] = 5.5 \times 10^{13}$ cm$^{-3}$).
All $Q_m$ data are summarized in quasi-Boltzmann plot on figure 5. X-axis is a unit divided by energy of pair collision of heavy and light particles $E = \frac{\mu u^2}{2}$, $\mu$ - reduced mass, $u$ - mass velocity of shock wave. Y-axis is logarithm of ratio $Q_m$ multiplied by $N^2$ and divided by Mo (CO)$_6$ concentration square. Solid line is the best fit of the data. Its slope shows the existence of a barrier of the process in shock wave ($\sim 0.7$ eV).

The precursor length $L$ is represented in figure 6 versus a square root of $\nu^2/Q_m$. Rhombuses give emission and squares give the probe data. A precursor length was determined by precursor time multiplication by shock wave front velocity $L = t \cdot \nu$. The precursor length increases when the shock wave front velocity increases and the probe current decreases. Both probe and emission data show quit good fit. The probe data absence at higher shock wave velocities was caused by lower initial gas pressure behind the shock wave, which was necessary to obtain the higher shock wave velocities and consequently, by the reduction of absolute concentration of heavy molecules.

Figure 5. Quasi-Boltzmann dependence of maximum probe signal $Q(max)$ divided on Mo (CO)$_6$ concentration square and multiplied on pressure and best fit (straight line).

Figure 6. The precursor length $L$ measured by probe (rhombus) and by emission $313 \pm 3$ nm (squares) versus of square root of particle velocity ($\nu$) square relation to probe current maximum $Q_m$. 
Equilibrium temperature and pressure behind the investigated shock waves look weak enough weak and could not give the chance to observe the visible ionization: $T_2 \sim 900 - 1200$ K, $P_2 \sim 0.5$ bar. There were five experiments carried out at equilibrium temperatures in the range $1200 - 1480$ K only. But it’s important to note that in frame connected with gas flow behind shock wave ordered motion energy of “cold” heavy molecule Mo(CO)$_6$ is about several eV at Mach number $\sim 3$, while ionization threshold of Mo(CO)$_6$ molecule is $\sim (8.2 \pm 8.5)$ eV. One more significant fact is that the energy of several first pair collisions of “cold” heavy molecule and light gas atoms is determined by $u^2$ and is essentially higher than $kT_0 \sim 0.1$ eV. The same reason lays in fact that the frequency of the collisions in shock wave front is higher then in equilibrium behind shock wave front.

Nonequilibrium radiation peaks in wide spectral range ($260 \div 460$ nm) in shock wave front firstly were suggested to be connected with free-free and free-bound transitions in a weakly ionized gas [11]. The emission and probe measurements of present work confirm this suggestion also. Moreover, the dependences of probe current maximum $Q_m$ on $n^2$ and $Q_m$ on a pair collision energy (figure 4) show that factor concentration [Mo(CO)$_6$]$^2$ is very important. Probably this factor means that heavy “cold” gas in front of density gradient “feels” the influence of heavy “hot” gas behind density gradient. The influence becomes apparent particularly in precursor emission and precursor signal on the probe. The precursor lengths $L$ measured by using two independent methods gives very similar dependences in coordinates X-axis $\left(\sqrt{u^2/Q_m}\right)$ (figure 6). Numerator $u^2$ is proportional to ordered motion energy of “cold” heavy molecules relatively to the hot gas behind shock wave front. Coulomb energy is proportional to ions concentration behind shock wave. Denominator $Q_m$ is determined by charged particles concentration. Dependence $L = f \left(\sqrt{u^2/Q_m}\right)$ looks quite reasonable as far as Debye length increases with electron kinetic energy increasing and it decreases with the Coulomb energy increasing. Similar effect was considered for SW propagation in weak ionized plasma by [1]. Its easy to estimate ions concentrations, making the suggestion about temperature of electrons. Concentrations of ions will be $\sim (5 \times 10^3 - 1 \times 10^5)$ cm$^{-3}$ at $T = 1200$ K (if temperature of electrons is equal to equilibrium temperature behind shock wave) if to use data on figure 5. This amount is less than sensitivity threshold of most sensitive probes ($\sim 10^6$ cm$^{-3}$). It is reasonably to assume that the electron temperature in shock wave front is not less then several electron Volts at least, as far as radiation of precursor at 313 nm ($h\nu \sim 3$ eV) was detected. Suggestion of $\sim 10$ eV gives more reasonable concentrations of ions ($5 \times 10^4 - 1 \times 10^6$) cm$^{-3}$.

So the data obtained gave an opportunity to conclude that the nonequilibrium emission in shock wave front is caused by ionization process that appears to be very fast in shock wave front. In addition, the precursor length seems to be quite easy measured and it can be used to study the translation relaxation in shock waves. Cross section of electron capture by a polyatomic molecule is several orders of magnitude larger then for noble gas [1]. Therefore, it can be assumed that heavy molecules of “cold” gas in a certain layer in front of the density gradient are excited by free electrons or, capturing an electron, are transformed into negative ions (the effect of the dissociation electron adhesion). A decay threshold of negative polyatomic ions into charged fragments is low. Apparently, the determined barrier $\sim 0.7$ eV (figure 6) of probe current activation can be caused by similar mechanisms. The obtained probe current dependence on energy of pair collisions allowed to issue that shock wave front role is a cause of observed effects.

4. Conclusion
The experimental technique valid for high time and space resolved study of the structure of shock wave front was elaborated and used for registration of shock wave propagation in the binary gas mixture. The suggested and realized experimental conditions let us to reveal ionization and
charge separation effects near by shock wave front of weak shock waves propagating in binary
gas mixtures where heavy molecules are a small admixture in a light bath gas. Ionization is
accompanied by nonequilibrium emission. The data obtained allowed getting some quantitative
parameters of these effects and gave a key to further investigations of heavy molecules interaction
with shock wave front.

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