Comment on "Shock-wave-induced enhancement of optical emission in nitrogen afterglow plasma"

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Sieffert *et al.* [Phys. Rev. E **72**, 066402 (2005)] have recently presented experimental results on optical emission enhancement at the front of shockwaves propagating in nitrogen afterglow. They claim that their results point to local heating of electrons at the shock front. In this Comment it is shown that the observed emission enhancement can be explained on the basis of a commonly accepted model of nitrogen discharge and afterglow, so that the use of unfounded assumption of local electron heating is not required.

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Sieffert, Ganguly, and Bletzinger [1] have recently presented experimental results on optical emission enhancement at the front of weak shockwaves propagating in the afterglow of nitrogen discharge. Analyzing these results, the authors of [1] come to the conclusion that the observed emission enhancement is an indirect evidence for local heating of electrons at the shock front, due to formation of a shockwave-induced strong double layer. However, as it is noted in [1], there is no known theoretical foundation for such layer formation at a weak collisional shock front. The aim of this Comment is to show that emission enhancement observed in [1] can be described on the basis of available information on kinetic processes and parameters of nitrogen discharge and its afterglow, without using unfounded assumption of local electron heating.

In experiments [1] propagation of shockwaves with Mach number M from 1.5 to 3.8 in the afterglow of nitrogen discharge in a glass tube with radius $R=1.5$ cm at pressure $p=0.75$ Torr and discharge current $I=20$ mA was studied. Emission of the first ($B\,^3\Pi_g \rightarrow A\,^3\Sigma_u^+$) and second ($C\,^3\Pi_u \rightarrow B\,^3\Pi_g$) positive systems has been measured in the discharge and in the afterglow, both before and after arrival of the shock front. In this Comment, emission of the second positive system is analyzed in detail (some remarks concerning emission of the first positive system are given in the end of the Comment).

Observed pattern of the time dependence of the emission intensity S of the band $C\,^3\Pi_u(v=0) \rightarrow B\,^3\Pi_g(v=0)$ is as follows (Fig. 5 of [1]): there is a steep decrease, about six times, just after switching off the discharge, a slow decrease in the afterglow, and a steep increase, up to sixteen times (depending on the Mach number), at the arrival of the shock front. To model the behavior of S at these three stages (discharge, afterglow, and shock front arrival), one should consider the processes of production and loss of radiating molecules $N_2(C\,^3\Pi_u, v=0)$. According to kinetic models of nitrogen discharges and post-discharges at low pressures (see, e.g., a review paper [2] and references therein), the major processes of production of $N_2(C\,^3\Pi_u, v=0)$ are the excitation of nitrogen molecules by electron impact

$$N_2(X^1\Sigma_g^+) + e \rightarrow N_2(C\,^3\Pi_u, v=0) + e \qquad (1)$$

and the pooling reaction

$$N_2(A\,^3\Sigma_u^+, v=0,1) + N_2(A\,^3\Sigma_u^+, v=0,1) \rightarrow N_2(C\,^3\Pi_u, v=0) + N_2(X^1\Sigma_g^+). \qquad (2)$$

The major loss process is radiation to $B\,^3\Pi_g$ state. Note that the radiative lifetime of $N_2(C\,^3\Pi_u, v=0)$, $\tau_r \approx 0.04$ μs [2], is much smaller than typical times of other relevant processes. Hence, the density of $C\,^3\Pi_u$ state may be evaluated in quasistationary approximation, even at description of jumps related with shutting off the discharge and with arrival of shock front.

The number density n_C of $N_2(C\,^3\Pi_u, v=0)$ in the discharge is given by the relation

$$n_C = \tau_r(k_e n_m n_e + k_{AC} n_A^2), \qquad (3)$$

where k_e and k_{AC} are the rate constants of reactions (1) and (2), n_m and n_A are the number densities of molecules in states $X^1\Sigma_g^+$ and $A\,^3\Sigma_u^+(v=0,1)$, respectively, and n_e is the number density of electrons. After switching off the discharge the first term in the right-hand side in (3) decreases quickly, with a typical time less than 1 μs [2], due to the reduction of the number of fast electrons, capable to excite $C\,^3\Pi_u$ state. The density of $N_2(A\,^3\Sigma_u^+)$ changes at a much larger time scale (see below), and its value just after shutting off the discharge is nearly equal to that in the discharge. Therefore, the ratio ξ of n_C value just after shutting off the discharge to that in the discharge (and, hence, the ratio of the emission intensity S just after shutting off the discharge to that in the discharge) is

$$\xi = \frac{k_{AC} n_A^2}{k_e n_m n_e + k_{AC} n_A^2}. \qquad (4)$$

The terms in (4) may be evaluated as follows. The use of experimental data [3] on the vibrational distribution of $N_2(A\,^3\Sigma_u^+)$, obtained in conditions close to those in [1], gives $n_A \approx 2.5\times 10^{12}$ cm^{-3}. Corresponding estimate for the pooling term is $k_{AC} n_A^2 \approx 2\times 10^{14}$ cm^{-3} s^{-1} (the rate constant $k_{AC}=3\times 10^{-11}$ cm^3 s^{-1} is taken from [4]). The excitation rate constant k_e, evaluated at the reduced electric field $E/n_m=100$ Td [1] by multiplying the total rate constant of excitation of $C\,^3\Pi_u$ state from [5] and the Frank-Condon factor for transition to $C\,^3\Pi_u(v=0)$ from [6], is $k_e \approx 3\times 10^{-11}$ cm^3 s^{-1}. The product of k_e and of the number densities of molecules and electrons $n_m=2\times 10^{16}$ cm^{-3}, $n_e=1.7\times 10^9$ cm^{-3} [1]

gives the value of the excitation term $k_e n_m n_e \approx 1 \times 10^{15}$ cm^{-3} s^{-1}. Substituting these estimates of the terms in (4), one arrives at the value $\xi \approx 0.17$, in good agreement with the ratio of the emission intensity S just after switching off the discharge to that in the discharge observed in [1].

The number density n_C at the post-discharge stage is

$$n_C = \tau_r k_{AC} n_A^2. \tag{5}$$

The metastable state $N_2(A\ ^3\Sigma_u^+)$ in the early afterglow is depopulated mainly due to diffusion to the tube walls, quenching in collisions with nitrogen atoms, and pooling reactions leading to production of $N_2(B\ ^3\Pi_g)$ and $N_2(C\ ^3\Pi_u)$ [2]. The number density n_A is governed by the equation

$$\frac{dn_A}{dt} = -\frac{n_A}{\tau_D} - k_N n_N n_A - k_p n_A^2, \tag{6}$$

where τ_D is the diffusion time, n_N is the number density of atoms, k_N and k_p are the rate constants of quenching of $N_2(A\ ^3\Sigma_u^+)$ in collisions with atoms and of the pooling process. The solution of Eq. (6) is

$$n_A(t) = \frac{n_{A0} e^{-t/\tau}}{1 + k_p n_{A0} \tau (1 - e^{-t/\tau})}, \tag{7}$$

where n_{A0} is the number density of $N_2(A\ ^3\Sigma_u^+, v=0,1)$ in the beginning of afterglow stage, equal to the value of n_A in the discharge (time t is counted from the moment of shutting off the discharge), $\tau^{-1} = \tau_D^{-1} + k_N n_N$. Using Eqs. (4), (5), and (7), one arrives at the ratio of the number density $n_C(t)$ in the afterglow to that in the discharge n_{Cd}, and, hence, the ratio of the emission intensity $S(t)$ to that in the discharge S_d

$$\frac{S(t)}{S_d} = \frac{n_C(t)}{n_{Cd}} = \frac{\xi n_A^2}{n_{A0}^2} = \frac{\xi e^{-2t/\tau}}{[1 + k_p n_{A0} \tau (1 - e^{-t/\tau})]^2}. \tag{8}$$

Evaluation of the parameters in (7), (8), using the number density of atoms measured in [7] in conditions close to those in [1], $n_N \approx 6 \times 10^{13}$ cm^{-3}, the rate constants $k_p = 4 \times 10^{-10}$ cm^3 s^{-1} [4] and $k_N = 4 \times 10^{-11}$ cm^3 s^{-1} [8], and the diffusion rate $\tau_D^{-1} = 7 \times 10^2$ s^{-1} (the diffusion coefficient was taken from [2]) gives $\tau \approx 300$ μs and $k_p n_{A0} \tau \approx 0.3$.

At the shock front arrival the number density of $N_2(A\ ^3\Sigma_u^+)$ jumps, similarly to that of the gas density, the jump φ being specified by the Rankine-Hugoniot relationship

$$\varphi = \frac{(\gamma + 1) M^2}{(\gamma - 1) M^2 + 2}, \tag{9}$$

where γ is the specific heat ratio (for nitrogen $\gamma = 1.4$). As the relaxation time of the state $C\ ^3\Pi_u(v=0)$, about 0.04 μs, is much smaller than the time resolution at measurement of the emission intensity in [1], about 1 μs, the jump of n_C may be considered in quasi-stationary approximation. The use of Eq. (5) gives the jump of n_C and, hence, of S at the shock front

$$\frac{S_b}{S(\tau_{\text{decay}})} = \frac{n_{Cb}}{n_C(\tau_{\text{decay}})} = \varphi^2 \frac{k_{AC}(T_b)}{k_{AC}(T_a)}. \tag{10}$$

Here index "b" corresponds to the values behind the shock front, T_b and T_a are the gas temperatures behind and in front of the shock, τ_{decay} is the time passed from the shutting off the discharge to arrival of the shockwave. Using Eqs. (8) and (10), one arrives at the resulting expression for the emission enhancement, defined in [1] as the ratio of the emission intensity behind the shockwave front to that in the discharge:

$$\frac{S_b}{S_d} = \frac{\varphi^2 \xi e^{-2\tau_{\text{decay}}/\tau}}{[1 + k_p n_{A0} \tau (1 - e^{-\tau_{\text{decay}}/\tau})]^2} \frac{k_{AC}(T_b)}{k_{AC}(T_a)}. \tag{11}$$

Available information on the temperature dependence of k_{AC} is rather scarce. According to [9], the values of the pooling rate constant at temperatures 98 K and 300 K are nearly equal. In our calculations it is assumed, by analogy with standard models (e.g., [2]), that k_{AC} is independent of T.

In Figs. 1 and 2 the emission enhancement S_b/S_d is given, both measured in [1] and calculated according to Eq. (11).

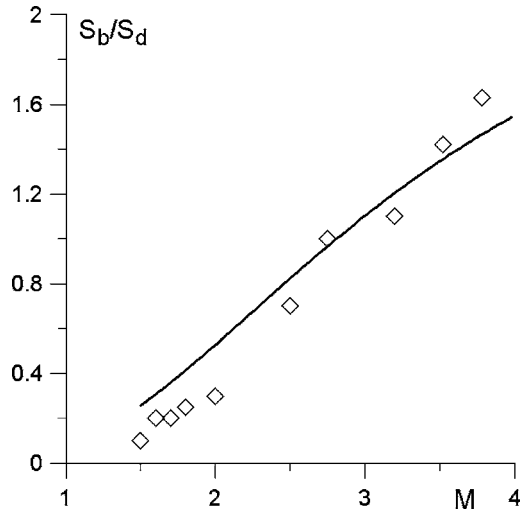

FIG. 1. Dependence of emission enhancement on Mach number for decay time 100 μs. Points—experiment [1], line—calculation according to Eq. (11).

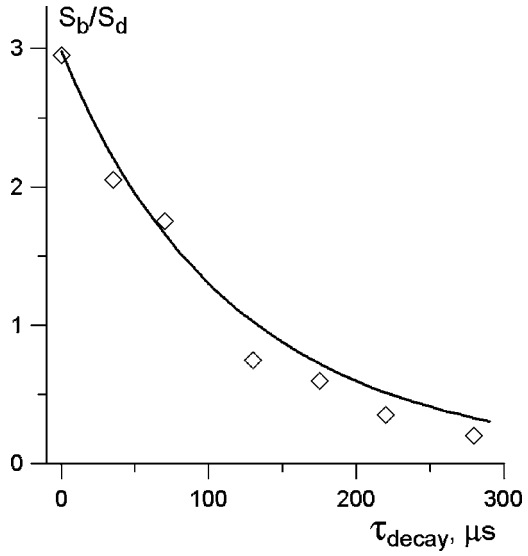

FIG. 2. Dependence of emission enhancement on decay time for Mach number 3.4. Points—experiment [1], line—calculation according to Eq. (11).

The values of parameters used at calculations are those presented above: $\xi=0.17$, $\tau=300$ μs, $k_p n_{A0}\tau=0.3$. [Note that all of these values should be considered as rough estimates, because at evaluation of the parameters in (11) only major processes have been accounted for.] In Fig. 1 the dependence is shown of S_b/S_d on Mach number at fixed τ_{decay}. Figure 2 presents the dependence of S_b/S_d on τ_{decay} at fixed Mach number. It is seen that Eq. (11) describes rather well the dependencies of S_b/S_d on both M and τ_{decay}.

Intensity of $B\,^3\Pi_g \rightarrow A\,^3\Sigma_u^+$ emission also jumps at the shock front [1]. Leading processes of production of $N_2(B\,^3\Pi_g)$ in afterglows are pooling reaction, analogous to (2), and reaction of $N_2(A\,^3\Sigma_u^+)$ with vibrationally excited molecules in $X^1\Sigma_g^+$ state (e.g., [2]). Both production terms increase at the shock front as φ^2. The rate of quenching of $N_2(B\,^3\Pi_g)$ in collisions with $N_2(X^1\Sigma_g^+)$, the major process of loss of $N_2(B\,^3\Pi_g)$ in afterglows [2], increases as φ. It follows that the jump of $B\,^3\Pi_g$ emission intensity at the shock front, evaluated in assumption that the rate constants of relevant processes are independent of the gas temperature, is about φ. [Note that the relaxation time of $N_2(B\,^3\Pi_g)$ is about 1 μs, so the jump of its density may be considered in quasi-stationary approximation.] This estimate, for $M=3.4$, is rather close to observed jump (about five times) of $B\,^3\Pi_g \rightarrow A\,^3\Sigma_u^+$ emission intensity ([1], Fig. 5).

Note that the authors of [1], discussing possible reasons of emission enhancement, considered the pooling processes. However, they ruled out this mechanism, because of erroneous evaluation of the times required to create $B\,^3\Pi_g$ and $C\,^3\Pi_u$ states.

Consideration above shows that optical emission enhancement observed in [1] may be described on the basis of known kinetic models and plasma parameters of nitrogen afterglow. Thus, the conclusion of the authors of [1] concerning a local heating of electrons in a shockwave-induced strong double layer does not follow from their experimental results.

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