A THERMAL EXCITATION MECHANISM OF ELECTRONIC STATES OF DIATOMIC MOLECULES BEHIND A SHOCK FRONT

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On the example of CN and C_2 we consider the mechanism of efficient excitation of electronic states of diatomic molecules behind a strong shock front at temperatures of 4000-8000°K.

We consider processes which can populate excited electronic states of molecules in shock waves. Here belong, first of all, collisions with electrons which have large excitation cross sections. However, in the temperature range considered here, the concentration of electrons in the gas behind the shock front is small, and the excitation of molecules in collisions with electrons can be neglected. Exothermic chemical reactions of the type

$$AC + B \rightleftarrows AB^* + C \tag{1}$$

can directly excite higher electronic states of molecules. However, for a number of reasons the probability of these reactions is small and at the present time, only a very few of such reactions have been established [1]. No reactions of type (1) are known which can lead to the formation of CN^* and C_2^* in the mixtures of gases CO (CO_2) – N_2 which are considered here.

Another process which can populate electronic states is the resonance energy transfer in the collision of molecules with other particles:

$$AB + M^* \rightleftarrows AB^* + M. \tag{2}$$

Molecules AB are formed in the chemical reactions in the electronic ground state; M* is an electronically excited atom or molecule, or a vibrationally excited molecule with a high level of excitation. Reactions of type (2) have a large interaction cross section since, e.g., in the case [2]:

$$\mathrm{CN}(X^2\Sigma,\ v''=0)+\mathrm{CO}(X^1\Sigma,\ v'=13)\rightarrow\mathrm{CN}(B^2\Sigma,\ v'=0)+\mathrm{CO}(X^1\Sigma,\ v''=0). \tag{3}$$

The requirement of exact resonance implies that processes of type (3) are rare and cannot play a significant role in the population of excited states. It was shown in [3] that behind the shock front, reaction (3) gives a small contribution to the excitation and quenching of molecules CN ($B^2\Sigma$).

One of the channels of population of excited electronic states of diatomic molecules is the recombination of atoms in the collision with a third particle:

$$A + B + M \rightleftarrows AB^* + M. \tag{4}$$

Near the shock front, this process does not play a significant role because the concentration of A and B atoms is small. It was shown in [3] that even in the nonsteady-state flow region in the shock wave, reaction (4) gives a small contribution to the population of electronic states CN ($B^2\Sigma$) and $C_2(d^3\Pi_g)$ relative to the process

$$AB + M \rightleftarrows AB^* + M, \tag{5}$$

where the partner M can be an arbitrary particle. Ibragimova [4] considered a concrete example of this process by studying the excitation of electronic states $A^2\Pi_i$ and $B^2\Sigma$ of cyanogen molecules. This is a multistep process and includes the rotational–vibrational excitation of molecules in all electronic states, as well as the nonradiative transitions between excited electronic states in collisions with particles of the surrounding gas.

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It is known that the rates of rotational and vibrational relaxation are much larger than the rates of chemical transformations. Nonradiative impact processes in diatomic molecules are also fast. Their rates are often of the same order of magnitude as the rate of gas-kinetic collisions, and the transition time is of the order of the rotational relaxation time [5-11]. The numerous perturbations of electronic states of molecules and the transitions between them, induced by collisions with other particles, suggest that the mechanism of population of higher excited states of cyanogen which we have proposed in [4] is more universal, and is also suitable for other diatomic molecules. This is confirmed by experiments on the radiationless transitions in the molecules of CO [5, 6, 8, 9, 12], C_2^- and C_2 [13], CS [14], and CS^+ [15].

We consider the following processes as the mechanism of thermal excitation of electronic states of diatomic molecules behind the shock front:

$$AB\,(\text{or}\quad AB^*) + M \rightleftarrows AB_v\,(\text{or}\quad AB_v^*) + M, \tag{6}$$

$$AB_v + M \rightleftarrows AB^*_{v_1} + M, \tag{7}$$

$$AB^*_{v_1} + M \rightleftarrows AB^{**}_{v_2} + M, \tag{8}$$

$$AB^*_{v_1} \rightarrow AB + h\nu_1 \tag{9}$$

$$AB^{**}_{v_2} \rightarrow AB + h\nu_2. \tag{10}$$

Here the AB molecules are either formed in chemical reactions in the electronic ground state, or are present in the initial state of the gas mixture.

Reaction (6) denotes the vibrational relaxation in the ground and excited electronic states. Reactions (7) and (8) are nonradiative impact transitions between the ground and excited states, or between two excited states. Reactions (9) and (10) correspond to spontaneous emission. It is seen that in the mechanism of processes (6)-(8), a significant role is played by the collision partner M, both in the vibrational relaxation, as well as in the impact transitions. Due to the reversibility of reactions (7) and (8) [6], this mechanism does not in general exclude the participation of processes (1)-(4) in the formation of AB^* and AB^{**}. This is because in mechanism (6)-(10) it does not matter if the population of electronic states of molecules takes place from above or from below. We also note that reactions (7) and (8) do not require an exact resonance between excited levels [5, 6]. The combination of the fast rate of the rotational–vibrational relaxation and of the large cross sections of processes (7) and (8) makes this mechanism the most probable and most efficient in comparison with (1)-(4).

Disregarding the simplicity of the model of electronic states of AB molecules. The mechanism (6)-(10) makes it possible to qualitatively interpret the results of our experiments presented in [3]. We found that in the steady-state region behind the shock front in the mixture of gases $CO-N_2-Ar$, one observes an equilibrium population of the $B^2\Sigma$ state of cyanogen. This result for cyanogen is valid for any dilution of the gas mixture by argon (up to 99% of Ar). In the emission in Swan bands of C_2, the observed population of the state $d^3\Pi_g$ was below the equilibrium value when the gases CO and N_2 were diluted by argon up to 96-98% (for the identical temperature in the steady-state region T = 6890°K). As the part of molecules CO and N_2 in the mixture increases, the population of the state $d^3\Pi_g$ of C_2 also reaches the equilibrium value.

Suppose that in the scheme (6)-(10) the states $CN(B^2\Sigma)$ and $C_2(d^3\Pi_g)$ correspond to AB^{**}. By writing the kinetic equation for AB^* and AB^{**} and putting $(d/dt)[AB^*] = (d/dt)[AB^{**}] = 0$, we then obtain for the steady-state region

$$[AB^{**}]_{\text{st}} = \frac{K\,[AB]_{\text{eq}}}{1 + \dfrac{k_{10}}{k_{-8}\,[M]}\left(1 + \dfrac{k_8}{k_{-7}}\right) + \dfrac{k_9}{k_{-7}\,[M]}\left(1 + \dfrac{k_{10}}{k_{-8}[M]}\right)}, \tag{11}$$

where k_j and k_{-j} are the rate constants of the forward and reverse reactions (j = 6, ..., 10); $K = K_6K_7K_8(K_8^*)^{-1}$, where K_6, K_7, and K_8 are the equilibrium constants of the reactions (6), (7), and (8), respectively; K_8^*, equilibrium constant for the excitation of vibrations in the state AB^{**}; $[AB]_{\text{eq}}$, equilibrium concentration of molecules AB in the steady-state region; and $[AB^{**}]_{\text{st}}$, concentration of molecules in the emitting electronic state in the steady-state region.

Taking into account that the vibrational degrees of freedom are in equilibrium in the steady-state region we obtain that K is the Boltzmann factor for the corresponding energy level of the excited electronic state AB^{**}.

Then in (11), $K[AB]_{eq} = [AB^{**}]_{eq}$. We assume that $K_7 \approx K_8 \approx 1$ [5, 6]. We shall estimate $[AB^{**}]_{st}$ for the cyanogen molecule. We put $k_{-8} \approx k_8 \approx k_{-7} = 3 \cdot 10^{-10}$ $cm^3 \cdot sec^{-1}$ [6] and by determining the values of $k_9 = (\tau_1)^{-1}$ and $k_{10} = (\tau_2)^{-1}$ from the known values of lifetimes τ_1 and τ_2 for the states $A^2\Pi_i$ and $B^2\Sigma$ [16] we obtain† that the third term in the denominator of the fraction in (11) can be neglected, and the second term is much smaller than unity. In this case $[AB^{**}]_{st} = [AB^{**}]_{eq}$ which agrees with experiment. This conclusion depends to a significant degree on the assumption that $k_8 \approx k_{-7}$. For cyanogen this is justified since the multiplicity of all three states is identical.

We shall apply scheme (6)-(10) to the excitation of a molecule of C_2. According to the mechanism (6)-(10), one of the processes (7) and (8) is a nonradiative transition between states with different multiplicities, and the other is a transition between states with the same multiplicity since between the singlet ground state $C_2(X^1\Sigma_g^+)$ and the excited triplet $d^3\Pi_g$ there are several triplet and singlet electronic states [17]. Therefore, in the case of C_2 we have $k_8 \neq k_{-7}$, and the difference of these values can be large. The existence of a large number of intermediate states makes it impossible to specify the state AB^* for C_2 and consequently, to determine τ_1. The radiative lifetime of the state $d^3\Pi_g$ is $\tau_2 = 1.22 \cdot 10^{-7}$ sec [16]. We shall estimate the denominator of the fraction in (11) by considering various values of k_{-7}, k_8, and τ_1. For $\tau_1 \to \infty$, independently of which case is realized for k_{-7} and k_8 ($k_{-7} > k_8$ or $k_8 > k_{-7}$), the denominator of the fraction in (11) is larger than unity, i.e., the population of $[AB^{**}]_{st}$ is lower than at equilibrium. Since the rate constants of the nonradiative impact transitions in C_2 are unknown we shall assume, by analogy with other molecules, that for a nonradiative transition with spin conservation the rate constants are $k_j \sim 10^{-10}$ $cm^3 \cdot sec^{-1}$, and with a spin reorientation, $k_j \sim 10^{-12}$ $cm^3 \cdot sec^{-1}$. Then $[AB^{**}]_{st}/[AB^{**}]_{eq} \sim 1/6$ which is close to the observed population of the state $d^3\Pi_g$ for a large dilution of CO and N_2 by argon [3]. If $\tau_1 \sim \tau_2$, for $k_{-7} > k_8$ the population of $[AB^{**}]_{st}$ differs even more from the equilibrium value, and for $k_8 > k_{-7}$, we have $[AB^{**}]_{st}/[AB^{**}]_{eq} \sim 1/6$. Independently of the value of τ_1, a smaller difference in the values of k_{-7} and k_8 increases the population of $[AB^{**}]_{st}$, and gives a smaller difference from its equilibrium value at a given temperature. The disappearance of the "underpopulation" effect as the initial concentration of CO and N_2 in the gas mixture increases can be explained by the equalization of the values of k_{-7} and k_8 with the presence of a large quantity of atoms of N, C, and O. Due to their high chemical activity, their collisions with the C_2 molecules leads to a stronger interaction between perturbed states [18], a forbidden transition (e.g., with respect to spin) may become allowed, and the smaller rate constant of the nonradiative transition may increase.

The mechanism (6)-(10) is therefore suggested here as the most efficient channel of thermal population of excited states of diatomic molecules. This mechanism explains why the emission of molecules of CN and C_2 observed in the experiments in shock tubes begins immediately behind the front shock. Indeed, in agreement with processes (6)-(10), the equilibrium excitation of electronic states (or the formation of a quasi-steady-state distribution over all electronic states) takes place during time which is comparable with the time of vibrational relaxation of molecules. In comparison with the excitation of the electronic degrees of freedom, the chemical transformations are slower processes. Therefore, at any moment of time there is a quasi-steady-state distribution of molecules over all electronic states behind the shock front. This can be the Boltzmann distribution with the instantaneous temperature, as in the case of cyanogen. At each consecutive moment of time, this distribution varies in response to the changing conditions (for a changing temperature, pressure, and concentration of the particles) in the course of the chemical reactions.

NOTATION

AC and AB, diatomic molecules; A, B, and C, atoms; AB^*, AB^{**}, molecules in excited electronic states; M^*, an electronically excited molecule or atom, or a vibrationally excited molecule with a high level of excitation; M, an arbitrary component of the gas mixture; AB_v, a vibrationally excited molecule in the electronic ground state; AB_v^*, a vibrationally excited molecule in one of the higher electronic states; AB_{v_1}, a vibrationally excited molecule in an intermediate electronic state; $AB_{v_2}^{**}$, a vibrationally excited molecule in the emitting electronic state (these states are $B^2\Sigma$ for CN and $d^3\Pi_g$ for C_2); τ_1, τ_2 are the lifetimes of the electronic states; k_j, k_{-j}, rates of the forward and reverse reactions, respectively ($j = 6, \ldots, 10$); K_j, equilibrium constants of the reactions; e.g., in [AB] the square brackets refer to the concentration of molecules in the corresponding electronic state. The index eq refers to equilibrium conditions, and st refers to the concentration in the steady-state region behind the shock front.

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† $[M] = 1.7 \cdot 10^{18}$ cm^{-3} in [3].

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EXPERIMENTAL STUDY OF THE ACCELERATION OF A LAYER OF LIQUID

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Measurements have been made on the basic dynamic parameters of the process during physical implementation under laboratory conditions.

There has long been an interest in methods of direct conversion of gas thermal energy to liquid kinetic energy in relation to the development or improvement of static devices for liquid transport in various engineering systems [1, 2]. The piston method of liquid acceleration may be used in such devices along with the injection and acceleration of the liquid in a two-phase flow [3-5]. In this method, the liquid is accelerated in individual batches, which are supplied to some channel in turn with the supply of compressed gas or steam, the result being a stratified (piston) flow with regions of liquid (pistons) alternating with regions of gas. In such a flow, the gas or steam can expand by expelling the liquid pistons into a region of lower pressure, where part of the internal energy of the thermodynamic working body is converted to kinetic energy in the liquid.

The basic hydrodynamic effects accompanying the acceleration of liquid pistons are analogous to the phenomena in the rise of large gas bubbles in a liquid [6]. For example [7], the phase interface (initially planar) in the accelerated ejection of a liquid from a channel by gas comes to take the form of a gas cavern entering the liquid with some characteristic velocity v, whose value is related to the other definitive parameters (liquid acceleration a and characteristic transverse dimension d of the channel) by the Froude equation:

$$v/\sqrt{ad} = \mathrm{Fr},$$

where Fr is some constant dependent on the shape of the cross section (Fr = 0.38 for a circular cross section [8]). Because the gas bubble enters the liquid, the part of the liquid around the gas is lost from the acceleration process. The rate of entry of the gas bubble into the liquid in essence defines the rate of disruption of the accelerated liquid layer. One assumes that the energy characteristics of the piston method of liquid acceleration will be largely determined by this effect.

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