RADIATIVE PROCESSES AHEAD OF A SHOCK-WAVE FRONT

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The distribution of excited atoms or molecules ahead of a shock wave front is considered. The excitation is produced by radiation coming from the shock front. The process of nonstationary diffusion of the radiation is taken into account. It is shown that concentrations of excited atoms or molecules corresponding to excitation temperatures close to the temperature of the shock wave are formed in the cold gas ahead of the wave front.

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THERE are a number of papers in the literature (see, for instance, reference 1) devoted to the influence of radiation from a shock wave on the state of the gas ahead of it. These papers discuss the photoelectric absorption of radiation from the shock wave by atoms or molecules which are in the lowest energy state. Thus, only the shortwave region of the absorption spectrum is taken into account; for radiations whose wavelength is greater than the red limit for the photoeffect from the ground state, the gas is considered to be transparent.

In the present communication we treat the absorption of radiation that causes excitation of the atoms or molecules. The treatment takes into account the subsequent process of nonstationary diffusion of the radiation. We show that there is a wave of atomic or molecular excitation ahead of the shock wave front.

1. THE BASIC EQUATIONS AND THEIR APPROX-IMATE SOLUTION

Assume a plane shock wave whose temperature is T, propagating with velocity v in the direction of the x axis. We set up the equations describing the distribution of excited atoms in space and time.* We are interested here only in the concentration of atoms excited to resonance levels. We take into account the possibility of extinction as the result of kinetic processes. The time of flight of the photons will be neglected in comparison with the mean lifetime τ of the excited state of the atom. Using the previously developed theory of the diffusion of resonance radiation,² we find that the concentration of excited atoms $n_a(x, t)$ ahead of the shock wave front is given by the following equation:

$$\frac{\partial n_a(x,t)}{\partial t} = v \frac{\partial n_a(x,t)}{\partial x} + \frac{1}{\tau} \int_0^\infty n_a(\xi,t) K(|x-\xi|) d\xi$$
$$- n_a(x,t) \Big[\frac{1}{\tau} + \sigma(x) \Big] + B(x).$$
(1)

Here

$$K(|x-\xi|) = \frac{1}{2} \int_{1}^{\infty} \int_{0}^{\infty} \varepsilon_{y} k_{y} \exp\{-k_{y} | x-\xi | u\} dy \frac{du}{u}, \quad (2)$$

where the x coordinate is measured from the front of the shock wave. The functions ϵ_{ν} and k_{ν} characterize the shapes of the emission and absorption lines, respectively; $\sigma(x)$ is the probability of extinction per unit time, calculated for a single excited atom; B(x) is the number of excitation events per unit volume per second caused by the absorption of radiation coming directly from the shock wave. The shock-wave radiation, at least in the portions of the spectrum adjacent to the resonance lines, can be considered as black-body radiation. It is then easy to show that

$$B(x) = \int_{0}^{\infty} \frac{E_{v}(T)}{2hv} \int_{1}^{\infty} k_{v} e^{-k_{v} x u} \frac{du}{u^{2}} dv.$$
 (3)

The Planck function $E_{\nu}(T)$ changes slowly with frequency, compared with k_{ν} . Making use of this fact, we obtain

$$B(x) = \frac{n^{0}(T)}{\tau} \Big[1 - \int_{0}^{\infty} K(|x - \xi|) d\xi \Big], \qquad (4)$$

where $n^0(T)$ is the Boltzmann concentration corresponding to the temperature T. This expression is valid for not too large values of x, i.e., when a

^{*}The assumptions used in Secs. 1 and 2 can be used to obtain results for either an atomic or a molecular gas. However, for simplicity we use arbitrarily the terms "atomic" and "spectral line" in these sections.

linear approximation of the function $E_{\nu}/h\nu$ is possible over the frequency interval corresponding to the absorption line of a layer of gas of thickness x.

The solution of the integro-differential equation (1) entails great mathematical difficulties, and can hardly be solved at all in the general form. At the same time it has been shown previously³ that, in the case of integral equations with the kernel (2), good results have followed from the use of an approximate method involving the introduction of the concept of an effective lifetime of the excited state of the atom

$$\tau_{eff}(x) = \tau / \Theta(x),$$
 (5)

where $\Theta(x)$ is the total probability that a photon emitted from the point x will reach the boundaries of the space under consideration without being absorbed. In our case,

$$\Theta(x) = 1 - \int_{0}^{\infty} K(|x-\xi|) d\xi.$$
 (6)

Making use of the approximate method, we obtain instead of Eq. (1)

$$\partial n_a(x, t) / \partial t = v \partial n_a(x, t) / \partial x$$

$$-n_a(x, t) \left[\Theta(x) / \tau + \sigma(x)\right].$$
(7)

The solution of Eq. (7), with the initial conditions $n_a(x, t) = 0$ for $t \le 0$, is the function

$$n_{a}(x, t) = \frac{n^{o}(T)}{\tau} \int_{0}^{t} \Theta(x + vt') \exp\left\{-\frac{1}{\tau} \int_{0}^{t} [\Theta(x + vt'') + \sigma(x + vt'')] \partial t''\right\} dt'.$$
(8)

This function can be written in the somewhat different form

$$n_{a}(x,t) = n_{a}(x,\infty) \left\{ 1 - \frac{\varphi(x,t)}{\varphi(x,0)} e^{-j(x,t)} \right\},$$
 (9)

where

$$f(x, t) = \int_{0}^{t} \left[\Theta\left(x + vt'\right)/\tau + \sigma\left(x + vt'\right)\right] dt', \quad (10)$$

$$\varphi(x, t) = n^{0}(T) \Big[1 - e^{f(x, t)} \int_{t}^{\infty} \sigma(x + vt') e^{-f(x, t')} dt' \Big],$$
(11)

with

$$n_a(x,\infty) = \varphi(x,0) = n^0(T) \left[1 - \int_0^\infty \sigma(x+vt') e^{-i(x,t')} dt' \right].$$

2. DISCUSSION OF THE APPROXIMATE SOLUTION

In certain special cases the expression (9) can be written in simpler forms.

a.
$$\sigma = 0$$
, $\mathbf{v} \neq 0$:
 $n_a(x, t) = n^0(T) \left[1 - \exp\left\{ -\frac{1}{\tau} \int_0^t \Theta(x + vt') dt' \right\} \right].$ (12)

Consequently, in the absence of extinction, a wave of excited atoms is gradually formed in the cold gas ahead of the shock wave front, with a concentration equal to the Boltzmann value for the temperature T. This result holds for any value of the velocity v.

The latter fact is explained by noting that the exciting radiation contains a great many photons corresponding to the "tails" of the absorption line. A finite fraction of these photons undergo their first absorption so far from the shock wave front that the excited atoms so formed cannot reach the plane x = 0 within the time τ .

b. v = 0, $\sigma \neq 0$:

$$n_{\alpha}(x, t) = \frac{n^{0}(T)}{1 + \sigma(x) \tau_{eff}(x)} \left\{ 1 - \exp\left\{ - \left[1 + \sigma(x) \tau_{eff}(x) \right] t / \tau_{eff} \right\} \right\}.$$
(13)

As $t \rightarrow \infty$ we have the following distribution:

$$n_{a}(x, \infty) = n^{0}(T) / [1 + \sigma(x) \tau_{eff}(x)].$$
 (14)

The ratio of the extinction probability to $1/\tau_{\rm eff}(x)$, the effective probability of a radiative transition, serves as a parameter in expressions (13) and (14). As a criterion of the time t* required to establish a stationary distribution, we may take the condition that the argument of the exponential function in (13) be equal to unity:

$$t^{*} = \tau_{eff}(x) / [1 + \sigma(x) \tau_{eff}(x)].$$
 (15)

 $\tau_{\rm eff}(x)$ increases with increasing distance from the wave front so that for constant σ at large values of x the quantity t* becomes of the order of $1/\sigma$. When x is so small that $\sigma(x) \tau_{\rm eff}(x) \ll 1$, the rise time is t* ~ $\tau_{\rm eff}(x)$.

c. $\sigma \neq 0$, $v \neq 0$. In this case substantial simplification of expression (9) can be obtained only by choosing a specific form for the functions $\sigma(x)$ and $\Theta(x)$. It is natural to assume that the extinction does not depend on the coordinates ($\sigma = \text{const.}$). Then, bearing in mind that $\Theta(x)$ decreases with increasing x, it is easy to show that $n_a(x, t)$ is less when $v \neq 0$ than when v = 0, i.e., that (13) is the upper limit of (9).

Furthermore, with constant σ , the region of integration in (9) is restricted in practice by the exponential term exp $(-\sigma t')$. Hence for sufficiently large values of x the function $\Theta(x+vt')$ is very little different from $\Theta(x)$. In this case Eqs. (9) and (13) lead to identical results, so that

at sufficiently large distances the relative distribution of excited atoms does not depend on the speed of the wave. It can be shown that as t increases, the function $\varphi(\mathbf{x}, t)$ decreases. Thus in the course of time a stationary distribution of excited atoms builds up ahead of the shock-wave front. The build-up time will be shorter than the value determined from the equation

$$f(x, t^*) = 1.$$
 (16)

If σ is constant, then for any x and v the inequality $t^* < 1/\sigma$ holds.

3. PROPAGATION OF A SHOCK WAVE IN AN ATOMIC GAS

In the case of an atomic gas the interaction between radiation and the atoms is characterized by linear absorption, whose form is usually determined by the Doppler effect and shock or resonance interactions, the Doppler effect determining the intensity distribution in the central portion of the absorption line. The appearance of excited atoms at considerable distances ahead of the shock wave front is connected with the long free path of the photons corresponding to the tails of the spectral line. Therefore, assuming that the absorption line is of the pure dispersion type, we obtain a solution which to a good approximation applies to the general case.

For a dispersion line

$$k_{\nu} = \frac{k_0}{1 + [2(\nu - \nu_0) / \Delta \nu]^2},$$

where ν_0 is the frequency corresponding to the center of the line and $\Delta \nu$ is the line width,

$$K(|x|) = \frac{k_0}{2\pi} \int_{-\infty}^{\infty} \int_{1}^{\infty} \frac{\exp\left\{-k_0 |x| u/(1+y^2)\right\}}{(1+y^2)^2} \frac{du}{u} dy. \quad (17)$$

Substituting (17) into (6), we obtain an expression for Θ (x). If $k_0 x \ge 1$, then to a good approximation,

$$\Theta(x) \approx (3\sqrt[4]{\pi k_0 x})^{-1}.$$
(18)

When x = 0, $\Theta(x) = 0.5$. Consequently $\tau_{eff}(0) = 2\tau$. Making use of (18) and assuming σ to be constant, we find

$$n_{a}(x,t) = \frac{n^{0}(T)}{\tau_{eff}(x)} \sqrt{\frac{x}{v\sigma}} \exp\left\{\frac{x\sigma}{v}\left[1 + \frac{\Theta(x)}{\tau\sigma}\right]^{2}\right\}$$
$$\times \left\{\Phi\left[\sqrt{\frac{(x+vt)\sigma}{v}}\left(1 + \frac{\Theta(x+vt)}{\sigma\tau}\right)\right]$$
$$-\Phi\left[\sqrt{\frac{x\sigma}{v}}\left(1 + \frac{\Theta(x)}{\sigma\tau}\right)\right]\right\},$$
(19)

where $\Phi(z)$ is the probability integral. As $t \to \infty$, the first term tends to unity.

We now estimate the distribution of excited atoms in front of a shock wave in argon, starting with the wave parameters derived in the paper by Resler et al.⁴ (wave velocity = 18 M; temperature = 14,000°K behind the wave front and 300°K ahead of it; pressure = 10 mm Hg ahead of the front). The resonance lines 1049 A and 1067 A correspond to transitions from the ground state to the excited states $3p^5 ({}^{2}P_{1/2}^{0}) 4s$ and $3p^5 ({}^{2}P_{3/2}^{0}) 4s$. The oscillator strengths for these transitions are equal to 0.2 and 0.05, respectively.⁵

Under the above conditions, the intensity distribution in the tails of the lines depends upon the resonance broadening, which gives $k_0 \approx 1.5 \times 10^5$ cm⁻¹ in both cases (see reference 6).

The extinction depends on the collisions of excited argon atoms with molecules of air which are present as an impurity in the argon. The effective cross sections for extinction of excited argon atoms by N₂ and O₂ molecules are not to be found in the literature. Using data on the extinction of other atoms, and assuming that the concentration of excited atoms does not affect the estimate, we obtain an effective cross section of 10^{-14} cm² for extinction. Thus, for an impurity content of 0.01%, $\sigma \sim 10^4$ sec⁻¹.

The figure shows the concentration of argon atoms in the state $3p^5 ({}^{2}P_{1/2}^{0}) 4s$ as a function of the distance x ahead of the shock front, determined from the above parameters. It will be seen that there is a noticeable concentration of excited atoms (~ 5 × 10¹³ cm⁻³) at a distance of one meter from the shock front. The excitation temperature is equal to 13,500°K, only slightly less than the temperature in the shock wave. The concentration of atoms in the state $3p^5 ({}^{2}P_{3/2}^{0}) 4s$ cannot differ essentially from that shown in the figure, since the lower oscillator strength is to a certain extent compensated by the higher statistical weight.

Because of the relatively small energy difference between the $P_{1/2}$ and $P_{3/2}$ states, direct transitions between them are possible as a result of interactions with unexcited argon atoms. Taking such processes into account should not seriously alter our estimates.



In estimating the concentrations of excited atoms we have used the approximate expression (4). As already mentioned above, the transition from (3) to (4) is valid if a linear approximation to the function $E_{\nu}(T)/h\nu$ is permissible over the frequency interval corresponding to the absorption line for a layer of thickness x. In our example, the limiting value of x is found to be of the order of hundreds of meters.

The distribution shown in the figure was obtained without taking into account the effect of the shock tube walls. At distances less than the radius of the shock tube, this factor can be neglected. At greater distances, two factors must be considered: (1) the reduction in excited atoms due to the absorption of radiation by the walls; (2) an additional weakening of the quantity B(x) as x increases. The latter factor is connected with the decrease in the solid angle through which the primary incident radiation arrives from the shock wave.

Polishing or chrome-plating the interior surface of the shock tube, which is usually done to eliminate contamination, greatly reduces the effect of the above factors. Furthermore, under our conditions the first factor is not serious, since the extinction due to impurities was an order of magnitude larger than the reduction in the number of excited atoms due to radiation absorption by the tube walls.

In constructing the curves it was assumed that the extinction depended on the interaction of excited atoms with impurity molecules, and therefore did not depend on the coordinates. It must however be borne in mind that an appreciable number of free electrons are formed as a result of the photo-ionization of argon atoms by short-wave radiation ahead of the shock front. The concentration of free electrons, taking into account the motion of the wave, will fall off with increase in the x coordinate according to the law e^{-Snx} , where s is the cross section for photo-ionization and n is the concentration of argon atoms in the free state.

An evaluation shows that at distances x < 1 cm extinction by electrons is dominant. Since this

form of extinction increases with proximity to the wave front, there is a possibility of a maximum occurring in the distribution of excited atoms. It is obvious that atoms excited to more highly energetic states would also have a nonmonotonic distribution.

Several reports have been given in the literature of luminosity in the gas ahead of a shock front. In addition, in some cases a maximum has been observed in this luminosity.⁷ Up to the present time, this phenomenon has not had any theoretical explanation. It is possible that this maximum can be explained as a nonmonotonic dependence of the excited atom concentration ahead of the shock wave upon the x coordinate. The absence of sufficiently complete experimental data prevents us from carrying out a quantitative comparison of theory with experiment.

In conclusion it should be mentioned that the presence of considerable numbers of excited atoms or molecules ahead of a shock wave front may lead to the appearance of secondary effects. Thus, for example, the formation of ions at considerable distances from the shock front appears to be the result of photo-ionization of excited atoms or molecules. In certain cases serious energetic effects may arise due to the absorption of radiation from the shock wave by excited atoms.

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