

NONEQUILIBRIUM RADIATION OF A STRONG SHOCK WAVE

A. D. Nadezhin and E. A. Romishevskii

Zhurnal Prikladnoi Mekhaniki i Tekhnicheskoi Fiziki, Vol. 10, No. 1, pp. 27-32, 1969

We examine the nonequilibrium radiation from the first negative band of the molecular nitrogen ion N_2^+ . The various N_2^+ ion excitation mechanisms are discussed. It is shown that for a shock wave velocity in air 8 km/sec the primary excitation mechanism is electronic impact.

It has been established experimentally that behind the strong shock wave front in air under certain conditions there is a peak of the nonequilibrium radiation, which is basically determined by the molecular bands of nitrogen and oxygen [1]. In this case, one of the most important radiators will be the nitrogen ion N_2^+ . In the following we examine the nonequilibrium radiation from the first negative band of N_2^+ .

The upper estimate of the nonequilibrium radiation in the molecular bands can be obtained by assuming that the excited electronic level of the molecule is in equilibrium with the ground level. However, previous estimates based on such assumptions yield results which are significantly higher than the experimental results. Consequently, for the correct calculation of nonequilibrium radiation intensity we need to know not only the distribution of the temperatures, densities, and component concentrations behind the shock wave front but also the elementary mechanisms for excitation of the electronic states of the molecules.

To determine the densities, concentrations, and temperatures we used the calculation of the structure of the normal compression shock in air, analogous to the calculation carried out in [2]. The chemical reaction scheme is that generally used and is the same as that of [2]. We used the values of the chemical reaction constants taken from [2-4]. The vibrational relaxation was accounted for using the mechanism proposed in [5, 6]. The calculations of the normal shock wave structure were made by Vertushkin and Gladkov. Typical results of the calculations for the shock wave velocity of 8 km/sec are shown in Figs. 1 and 2. These figures also show the results of calculation of the concentrations of the excited molecular nitrogen ion N_2^{+*} which were made in the present study.

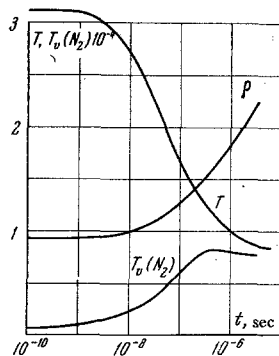


Fig. 1. $T_0 = 288^\circ \text{K}$, $p_0 = 1 \text{ mm Hg}$ are the temperature and pressure ahead of the shock wave front; T and T_v are the translational and vibrational temperatures ($^\circ\text{K}$); ρ is density (10^{-5} g/cm^3); $t = x/v(x)$ is physical time (x is distance from the viscous wave front, $v(x)$ is the gas velocity behind the wave).

Excitation mechanisms. Excitation by electronic impact must be separated from the elementary mechanisms for excitation of the electronic states of the molecules, since inelastic collisions of molecules with atoms and molecules have considerably smaller cross section and very high excitation threshold.

However, one elementary mechanism should be mentioned which was proposed in [6], where it is assumed that excitation of the electronic states of the molecular nitrogen ion N_2^+ takes place upon collision with the vibrationally

excited molecule N_2^V . It is believed that the cross section of this process has a large value ($\sigma \sim 5 \cdot 10^{-15} \text{ cm}^2$). This assumption is not without foundation, since there are experimental and theoretical data on the quenching of sodium radiation [7, 8], where the conversion of vibrational energy into electronic energy is accomplished comparatively easily. However there are neither experimental nor theoretical results indicating complete analogy between these two processes.

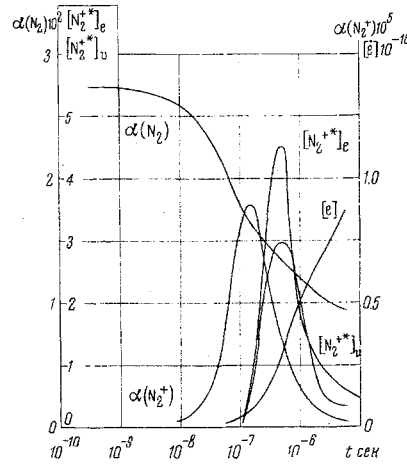


Fig. 2. [i] is the concentration of the i-th component of air (cm^{-3}); $\alpha_i = N_0 \rho [i]$; N_0 is Avogadro's number; $[N_2^{+*}]_e$ (10^{11} cm^{-3}) is the excitation by electronic impact; $[N_2^{+*}]_v$ (10^{10} cm^{-3}) is the excitation by N_2^V .

Excitation as a result of electronic impact was not considered in [6], since a shock wave with velocity $\sim 6 \text{ km/sec}$ was investigated and in this case the electron concentration behind the shock wave front is low.

In the major computational study [9] electronic impact is considered as one of the mechanisms for the excitation of the molecular nitrogen ion N_2^+ . The excitation cross section of N_2^+ was taken from the experimental study [10]. However, in [10] excitation of the molecular ion N_2^+ by electronic impact was not investigated; rather the formation of the excited molecular ion N_2^{+*} during collision of the neutral nitrogen molecule with the impinging electron was studied. The threshold energy of this process is about 20 eV, considerably higher than the threshold for excitation of the N_2^+ ion (3.16 eV) and the value of the cross section is $\sim 10^{-18} \text{ cm}^2$.

Excitation cross section for electronic impact on molecular nitrogen ion. In the following, we consider cross sections averaged with respect to the velocities of the impinging electrons; therefore, it is very important to know the correct magnitude and behavior of the cross section near the threshold. The formula for the excitation cross section of the molecular nitrogen ion N_2^+ by electronic impact is derived in the dipole approximation, which yields good results at the threshold velocities for excitation of atomic ions [11]. Let us examine the process



The complete Hamiltonian of such a system in atomic units is written in the form

$$H = H_{N_2^+} - \frac{z}{|\mathbf{r} - 1/2 \mathbf{R}|} - \frac{z}{|\mathbf{r} + 1/2 \mathbf{R}|} + \sum_{j=1}^{2z-1} \frac{1}{|\mathbf{r} - \mathbf{r}_j|} - \frac{1}{2} \Delta_{\mathbf{r}}. \quad (2)$$

Here $H_{N_2^+}$ is the Hamiltonian of the molecular ion, \mathbf{r} , is the coordinate of the impinging electron relative to the center of gravity of the molecule, \mathbf{R} is the distance between the nuclei, \mathbf{r}_j are the coordinates of the bound electrons. In order to use perturbation theory, we write (2) in the form

$$H = H_0 + W, \quad H_0 = H_{N_2^+} - \frac{z}{r} - \frac{1}{2} \Delta_{\mathbf{r}}, \quad W = \frac{z}{r} - \frac{z}{|\mathbf{r} - 1/2 \mathbf{R}|} - \frac{z}{|\mathbf{r} + 1/2 \mathbf{R}|} + \sum_{j=1}^{2z-1} \frac{1}{|\mathbf{r} - \mathbf{r}_j|}. \quad (3)$$

The solution of the unperturbed wave equation

$$H_0\Psi = E\Psi \quad (4)$$

breaks down into the product of the Coulomb wave function Ψ_c of the impinging electron and the molecular wave function. Consequently, the wave function of the initial state of the entire system Ψ_i and that of the final state Ψ_f can be written in the form

$$\Psi_i = \Psi(N_2^+) \Psi_c(\mathbf{k}_i, \mathbf{r}), \quad \Psi_f = \Psi(N_2^{+*}) \Psi_c(\mathbf{k}_f, \mathbf{r}). \quad (5)$$

Here $\Psi(N_2^+)$ and $\Psi(N_2^{+*})$ are, respectively, the wave functions of the ground and excited states of the molecular ion, and $\Psi_c(\mathbf{k}_i, \mathbf{r})$ and $\Psi_c(\mathbf{k}_f, \mathbf{r})$ are the conventional Coulomb wave functions of the electron in a unit positive charge field; \mathbf{k}_i and \mathbf{k}_f are the wave vectors of the impinging and scattered electrons. Using conventional perturbation theory, we obtain the following formula for the total excitation cross section:

$$\sigma_{ij} = \frac{1}{4\pi^2} \frac{k_f}{k_i} \frac{1}{2J+1} \sum_{f'} \int |A_{fi}|^2 d\Omega, \quad (6)$$

$$A_{fi} = \langle \Psi_f | W | \Psi_i \rangle.$$

Here the sum over f' denotes summation over the number of final vibrational and rotational states; J is the total molecular moment. To calculate A_{fi} we expand the last term in the perturbation W into a series for $r \gg r_j$ and limit ourselves to the second term of the

$$\frac{1}{|\mathbf{r} - \mathbf{r}_j|} \approx \frac{1}{r} + \frac{\mathbf{r}\mathbf{r}_j}{r^3} + \dots \quad (7)$$

Then the perturbation W takes the form

$$W = \frac{2}{r} + \frac{z}{|\mathbf{r} - 1/2 \mathbf{R}|} - \frac{z}{|\mathbf{r} + 1/2 \mathbf{R}|} + \sum_{j=1}^{2z-1} \frac{\mathbf{r}\mathbf{r}_j}{r^3}. \quad (8)$$

Only the last term of (8) makes a nonzero contribution to A_{fi} , since all the other terms do not contain the bound electron coordinates r_j and cancel by virtue of orthogonality of the molecular ion wave functions. We have

$$\begin{aligned} A_{fi} &= \langle \Psi_f | \sum_j \frac{\mathbf{r}\mathbf{r}_j}{r^3} | \Psi_i \rangle = \\ &= \langle \Psi(N_2^{+*}) | \sum_{j=1}^{2z-1} \mathbf{r}_j | \Psi(N_2^+) \rangle \langle \Psi_c(\mathbf{k}_f, \mathbf{r}) | \frac{\mathbf{r}}{r^3} | \Psi_c(\mathbf{k}_i, \mathbf{r}) \rangle. \end{aligned} \quad (9)$$

In accordance with the Ehrenfest theorem the force matrix element $\mathbf{r}/r^3 = \ddot{\mathbf{r}}$ can be expressed in terms of the dipole moment matrix element

$$\begin{aligned} \langle \Psi_c(\mathbf{k}_f, \mathbf{r}) | \frac{\mathbf{r}}{r^3} | \Psi_c(\mathbf{k}_i, \mathbf{r}) \rangle &= \omega_{fi}^2 \langle \Psi_c(\mathbf{k}_f, \mathbf{r}) | \mathbf{r} | \Psi_c(\mathbf{k}_i, \mathbf{r}) \rangle, \\ \omega_{fi} &= 1/2(k_f^2 - k_i^2) = \Delta E. \end{aligned} \quad (10)$$

Here ω_{fi} is the transition energy in the molecular ion N_2^+ . The integral $\mathbf{M} = \langle \Psi_c(\mathbf{k}_f, \mathbf{r}) | \mathbf{r} | \Psi_c(\mathbf{k}_i, \mathbf{r}) \rangle$ is known from bremsstrahlung radiation theory and was calculated in [12]. Now let us transform the integral

$$\left| \langle \Psi(N_2^{+*}) | \sum_j \mathbf{r}_j | \Psi(N_2^+) \rangle \right|^2.$$

Since we are considering transition between the Σ -states, the molecular wave function separates into the product of the electronic, vibrational, and rotational wave functions

$$\Psi(N_2^+) = \Psi(\mathbf{r}_j) \Psi_v \Psi_J.$$

Then

$$\begin{aligned} &\left| \langle \Psi(N_2^{+*}) | \sum_j \mathbf{r}_j | \Psi(N_2^+) \rangle \right|^2 = \\ &= \left| \langle \Psi^*(\mathbf{r}_j) | \sum_j \mathbf{r}_j | \Psi(\mathbf{r}_j) \rangle \right|^2 |\langle \Psi_v^* | \Psi_v \rangle|^2 |\langle \Psi_{J'}^* | \Psi_J \rangle|^2 = R^2 q_{vv'} S_{JJ'}. \end{aligned} \quad (11)$$

Here R^2 is the square of the electronic-dipole-transition matrix element; $q_{vv'}$ is the Franck-Condon factor; $S_{JJ'}$ is the Hanley-London factor. The electronic-transition oscillator force is,

$$f_{if} = 2/3 \omega_{if} \left| \langle \Psi^*(r_j) | \sum_j r_j | \Psi(r_j) \rangle \right|^2, \quad (12)$$

and in summing over the final vibrational and rotational states we obtain

$$\sum_{v'} q_{vv'} = 1, \quad \sum_{J'} S_{JJ'} = 2J + 1. \quad (13)$$

Substituting into A_{fi} the matrix element M from [12] and using (11)–(13), we obtain the formula for the total excitation cross section

$$\sigma_{if} = (2\pi)^2 \frac{1}{k_i^2} \frac{f_{if}}{\Delta E} \frac{\exp(2\pi\eta_i)}{[\exp(2\pi\eta_i) - 1][\exp(2\pi\eta_f) - 1]} x_0 \frac{d}{dx_0} |F(i\eta_i, i\eta_f, 1, x_0)|^2. \quad (14)$$

Here $F(i\eta_i, i\eta_f, 1, x_0)$ is the hypergeometric function

$$x_0 = -\frac{4\eta_i\eta_f}{(\eta_i - \eta_f)^2}, \quad \eta_i = -\frac{1}{k_i}, \quad \eta_f = -\frac{1}{k_f}, \quad k_i^2 = 2E.$$

After differentiation we obtain

$$\sigma_{if} = (2\pi)^2 \frac{1}{k_i^2} \frac{f_{if}}{\Delta E} \frac{\exp(2\pi\eta_i)}{[\exp(2\pi\eta_i) - 1][\exp(2\pi\eta_f) - 1]} | [F(-i\eta_i + 1, -i\eta_f, 1, -x_0)]^2 - [F(-i\eta_i, -i\eta_f + 1, 1, x_0)]^2 |. \quad (15)$$

Formula (15) was used to calculate the total electronic excitation cross section σ_{if} of the molecular nitrogen ion N_2^+ by electronic impact. Figure 3 shows the cross section σ_{if} as a function of the impinging-electron energy. The magnitude of the electronic-transition oscillator force f_{if} was taken from [13]. We see from Fig. 3 that the cross section σ_{if} has a finite value at the threshold energy; this agrees with the Wigner rule.

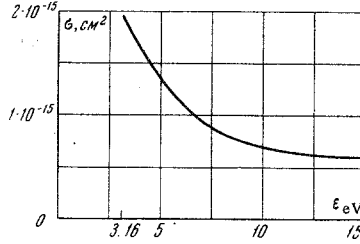


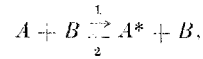
Fig. 3. N_2^+ excitation cross section versus the energy of the impinging electron.

Calculation of nonequilibrium radiation intensity. The radiation intensity in the electronic bands of the molecules is calculated using the formula

$$I_{ij} = \omega_{ij} A_{ij} N_i^*. \quad (16)$$

Here A_{ij} is the Einstein transition coefficient, and N_i^* is the number of excited molecules.

The number of excited molecules for the system, including excitation, deactivation by collisions



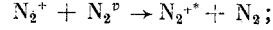
and deactivation by radiation $A^* \rightarrow A + \omega$, is obtained from the equation

$$\frac{d[A^*]}{dt} = k_1[B][A] - k_2[B][A^*] - \frac{[A^*]}{\tau_{ij}}, \quad \left(\tau_{ij} = \frac{1}{A_{ij}} \right), \quad (17)$$

$$k_1 = \langle v\sigma(v) \rangle = 4\pi \left(\frac{M}{2\pi kT} \right)^{3/2} \int_0^\infty \exp\left(-\frac{Mv^2}{2kT}\right) \sigma(v) v^3 dv. \quad (18)$$

Here $[A^*]$, $[A]$, and $[B]$ are the concentrations of the corresponding particles; k_1 is the excitation rate constant, which is the excitation cross section averaged over the Maxwellian velocity distribution; v_0 is the impinging-particle velocity corresponding to excitation threshold; k_2 is the deactivation rate constant, which can be determined from the detailed balance relation (see, for example, [13]); τ_{ij} is the excited state lifetime. Two elementary mechanisms for excitation of the molecular nitrogen ion were examined:

- 1) excitation by the vibrationally excited nitrogen molecule



- 2) excitation by electronic impact (1).

The first mechanism was calculated using the assumptions of [6]

$$k_1 = k_2 = 5 \cdot 10^{-15} \langle v \rangle \text{ cm}^3 \cdot \text{sec}^{-1},$$

$$f = 0.1, \quad [N_2^v] = [N_2] \exp\left(-\frac{3.66 \cdot 10^4}{T_v}\right).$$

Here $\langle v \rangle$ is the average velocity of the molecules; T_v is the vibrational temperature.

The excitation by electronic impact was calculated in the dipole approximation (15). The excited molecular ion concentration was calculated for both excitation mechanisms and for two shock wave velocities ($v = 6$ km/sec and $v = 8$ km/sec). Formula (16) was used to calculate the nonequilibrium radiation peak from the first negative N_2^+ band (Fig. 4).

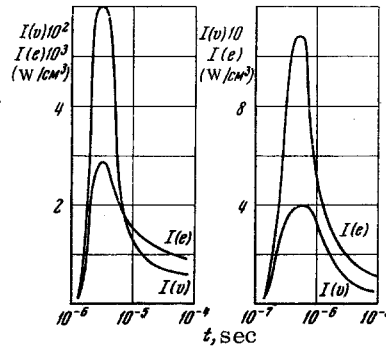


Fig. 4. Radiation intensity from the first negative band of N_2^+ : $I(v)$ is for excitation by the molecule N_2^v , $I(e)$ is for excitation by electronic impact.

For optically thin gas layers the radiative flux can be estimated using the formula

$$q = \int_0^s 2\pi I ds, \tag{19}$$

where s is the thickness of the relaxation zone.

For the shock wave velocity $v = 6$ km/sec the radiational flux from the first N_2^+ band for molecular excitation is $q(v) = 1.24$ W/cm², the radiational flux for electronic impact excitation is $q(e) = 9.87 \cdot 10^{-2}$ W/cm². For $v = 8$ km/sec, $q(v) = 1.95$ W/cm², $q(e) = 8.02$ W/cm², which agrees with the experimental data of [14].

Discussion of results. We see from the curves of Fig. 4 and the calculation of the radiational fluxes that, for a shock wave velocity of 6 km/sec, excitation of the molecular nitrogen ion N_2^+ by the vibrationally excited nitrogen molecule N_2^v is the dominant mechanism in comparison with electronic impact, since in this case the electron concentration is low. For the shock wave velocity 8 km/sec electronic impact is the primary mechanism for excitation of the N_2^+ ion in comparison with excitation by the N_2^v molecule. This is a result of the significant increase of the electron concentration at the 8-km/sec velocity and agrees with the experimental data of [15]. At higher shock wave velocities the electron concentration will increase the effect of the electronic-impact excitation mechanism will increase.

In conclusion the authors wish to thank V. K. Vertushkin and A. A. Gladkov for supplying the calculations on the structure of the normal compression shock and L. I. Ponomarev for helpful discussions.

REFERENCES

1. J. C. Camm, B. Kivel, R. L. Taylor, and J. D. Teare, "Absolute intensity of nonequilibrium radiation in air and stagnation heating at high altitudes," *J. Quant. Spectros. Radiat. Transfer*, vol. 1, no. 1, p. 53, 1961.
2. S. C. Lin and J. D. Teare, "Rate of ionization behind shock-waves in air, vol. II: Theoretical interpretation," *Phys. Fluids*, vol. 6, no. 3, 1963.
3. V. P. Glushko, ed., *Handbook: Thermodynamic Properties of Individual Substances* [in Russian], Izd-vo AN SSSR, Moscow, 1962.
4. J. G. Hall, A. Q. Eschenroeder, and P. V. Marrone, "Blunt-nose inviscid air flows with coupled nonequilibrium processes," *J. Aerospace Sci.*, vol. 29, no. 9, 1962.
5. C. E. Treanor and P. V. Marrone, "Effect of dissociation on the rate of vibrational relaxation," *Phys. Fluids*, vol. 5, no. 9, 1962.
6. P. Hammerling, J. D. Teare, and B. Kivel, "Theory of radiation from luminous shock waves in nitrogen," *Phys. Fluids*, vol. 2, no. 4, 1959.
7. *Atomic and Molecular Processes* [in Russian], Mir, Moscow, 1964.
8. K. J. Laidler, "Mechanism of processes initiated by excited atoms," vol. I: The quenching of excited sodium," *J. Chem. Phys.*, vol. 10, no. 1, p. 34, 1942.
9. A. K. Artamonov, V. N. Arkhipov, and G. E. Starchenko, "Relaxation and radiation behind a normal shock," *Izv. AN SSSR, MZhF [Fluid Dynamics]*, Vol. 1, No. 3, 1966.
10. D. T. Stewart, "Electron excitation functions of the first negative bands of N_2^+ ," *Proc. Phys. Soc.*, vol. A 69, no. 6, p. 438, 1956.
11. M. K. Gailitis, "Calculation of ion excitation by electrons using Coulomb wave functions," *Optika i spektroskopiya*, vol. 14, no. 4, 1963.
12. A. Sommerfeld, *Atombau und Spektrallinien*, Vol. 2 [Russian translation], Gostekhizdat, Moscow, 1956.
13. Ya. B. Zel'dovich and Yu. P. Raizer, *Physics of Shock Waves and High-Temperature Gasdynamic Phenomena* [in Russian], Nauka, Moscow, 1966.
14. R. A. Allen, P. H. Rose, and J. C. Camm, "Nonequilibrium and equilibrium radiation at super-satellite re-entry velocities," *Inst. Aeronaut. Sci.*, papers 63-77, p. 35, 1963.
15. R. A. Allen, "Nonequilibrium shock front; rotational, vibrational, and electronic temperature measurements," *J. Quant. Spectrosc. Radiat. Transfer*, vol. 5, no. 3, p. 511, 1965.

1 July 1968

Zhukovskii