Letters to the Editor

SUPERELASTIC COLLISIONS AND THE ELECTRON DISTRIBUTION FUNCTION IN THE POSITIVE COLUMN OF NITROGEN DISCHARGE*

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СВЕРХУПРУГИЕ СТОЛКНОВЕНИЯ И ФУНКЦИЯ РАСПРЕДЕЛЕНИЯ ЭЛЕКТРОНОВ В ПОЛОЖИТЕЛЬНОМ СТОЛБЕ РАЗРЯДА, ПРОИСХОДЯЩЕГО В АЗОТЕ

A numerical solution of the Boltzmann equation for the electron gas in the positive column of the DC discharge in molecular nitrogen is presented. Besides the electronic states also the vibrational states (6 levels in the electronic ground state) take part in forming the distribution with the deexcitation by the second kind collisions included. The vibrational level population is fixed by the vibrational temperature and an assumed overpopulation of the zero vibrational level. For the processes whose thresholds lie higher than a certain energy limit the influence of the second kind collisions is reduced to a mere proportionality.

The glow discharge in nitrogen constitutes a useful tool of plasma chemistry. The plasma of its positive column contains a number of activized particle species, which, according to varying opinions of several authors participate to a different extent in chemical reactions, such as nitridation. All the excited particle species originate primarily from collisions between the electrons and the neutral gas. The electron gas acts as an intermediary, which draws energy from the external electric field and only then this energy is transferred to the heavy particle species.

The external electric field is, however, not the only energy source as regards the electron gas. A certain part of energy previously lost by the electrons in collisions with the neutrals may be returned to them. This is due to a reversed collisional process, often called superelastic, or second kind collision.

In a noble gas discharge the energy levels of metastable states lie too high and their population is too tiny to be of any practical significance in the electron energy balance; in a molecular gas, however, the vibrational levels of the electronic ground state are only by a fraction of eV distant from the zero vibrational level and are thus easily populated by the electronic collisions. The second kind collisions may therefore be quite effective in increasing the number of fast electrons and hence influencing the rates of various production processes in the plasma.

To gain a quantitative picture of the influence of the second kind collisions we undertook the task of solving the electron Boltzmann equation numerically with the second kind collisions included. Their

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efficiency depends on the vibrational level populations. For a self-consistent solution it would be necessary to incorporate also a set of vibrational level balance equations, as only then the interdependence between the level populations and the electron distribution would be correctly accounted for. This would, however, be a formidable task from the point of view of the computer time. We therefore preferred, to regard the vibrational level populations as given and solved the Boltzmann equation alone in the following form:

$$E_z \frac{d}{dU}(Uf_1) - n_g \frac{6m_e}{M_g}\frac{d}{dU}(U^2 Q_d f_0) + \sum_{i,f} 3n_i\,[UQ_{if}(U) f_0(U) -$$

$$-(U + U_f - U_i) Q_{if}(U + U_f - U_i) f_0(U + U_f - U_i)] = 0\,,$$

$$E_z \frac{df_0}{dU} - (n_g Q_d + \sum_{i,f} n_i Q_{if}) f_1 = 0;$$

f_0 is the symmetric and f_1 the azimuthal component of the distribution function. The difference terms express the backscattering due to the inelastic $U_f > U_i$ and superelastic $U_f < U_i$ collisions, U_f and U_i being the energies of the final and initial state. E_z is the longitudinal field, n_i are densities of different excited particles (including the ground state), n_g is the total density of the heavy particles, Q_d is the transport cross-section for the elastic scattering on the molecules in the ground state (elastic scattering crosssections on the excited species are also set equal to Q_d), Q_{if} is the integral cross-section for the transition from the state i to f, including the direct ionization, U is the voltequivalent of the kinetic energy, m_e/M_g is the mass ratio.

In the calculations only the molecular nitrogen was considered. Apart from the ground state we took into account seven electronically excited states of the nitrogen molecule and the direct ionization Fig. 1. The first six excited vibrational levels in the electronic ground state were included with all the 42 possible transitions between them. Their populations were chosen as governed by a Boltzmann distribution with the vibrational temperature T_v. We also allowed for a certain deviation from the strict Boltzmann distribution by admitting an overpopultation of the ground level in a given ratio γ Fig. 2. The electron distribution was calculated from several values of T_v, γ and E_z/n_g.

Figs. 3 and 4 show some examples of the calculated distribution in the logarithmic scale. It is seen that apart from the normalization the distribution functions calculated for the same E_z/n_g but different T_v or γ coalesce above a certain energy limit. This particular behaviour is a consequence of the form of the considered vibrational cross-sections [1], whose non-zero values are confined to a comparatively narrow energy interval. This means that above the upper limit of this interval (plus the energy difference exchanged in the superelastic collision) the second kind collisions can no longer influence the shape of the distribution. The implications are clear: all the rates of the inelastic processes with the thresholds above this limit change with the varying T_v or γ in the same ratio (due to the normalization constant), i.e., their values might be derived from their values known under the conditions when the second kind collisions play no significant role and from the changes of just a single of them.

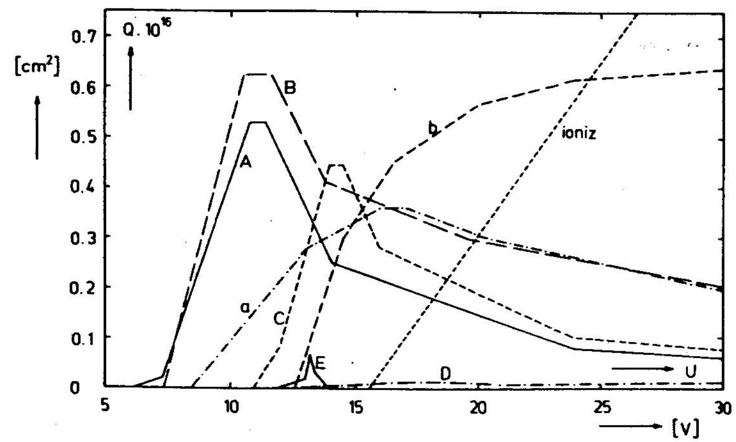

Fig. 1. Effective cross-sections for excitation of the electronic states of the N_2 molecule.

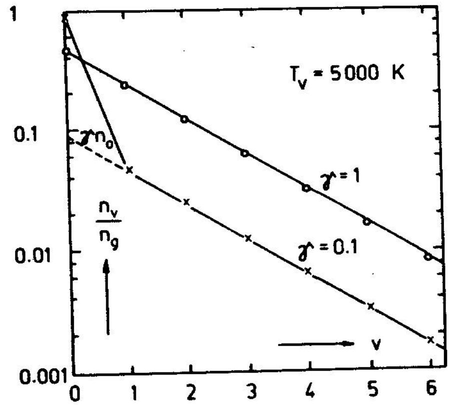

Fig. 2. Population of the vibrational levels.

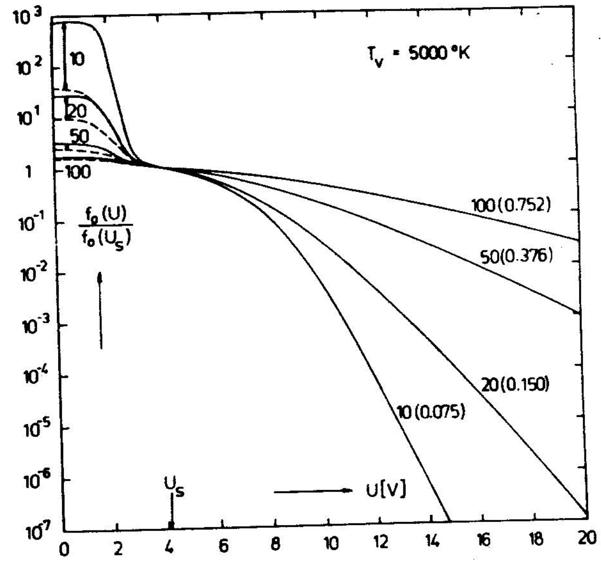

Fig. 3. Electron distribution in nitrogen for T_v fixed. Parametrization by E/P_0 in V/cm Torr (V/cm Pa in brackets). The verticle arrows show the spread of the distribution under the limiting energy U_s due to change of γ from 0 to 1.

On the other hand, the kinetic coefficients and other integral quantities which reach below the above mentioned energy limit vary in a quite general way. This i expressed in Figs. 5—7. Figs. 8 and 9 show some details of the energy balance. It is seen that there is always a net energy loss on the vibrational levels, though the power supplied by the second kind collisions may in extreme conditions exceed the power coming from the electric field.

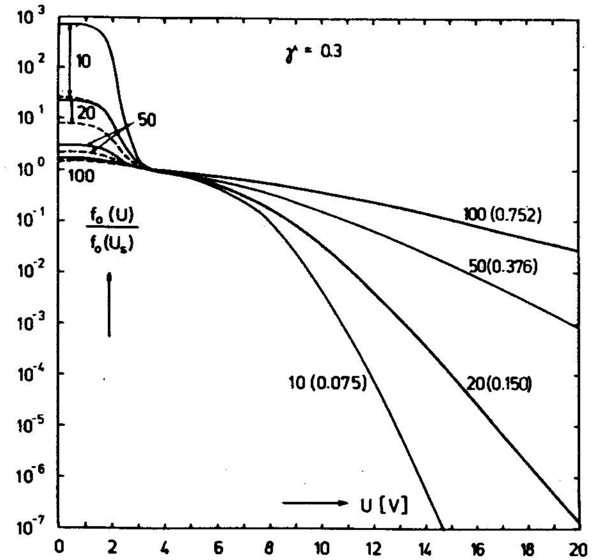

Fig. 4. Electron distribution in nitrogen for a fixed γ. The dependence on T_v (0—10^4 K) shown by the arrows below U_s.

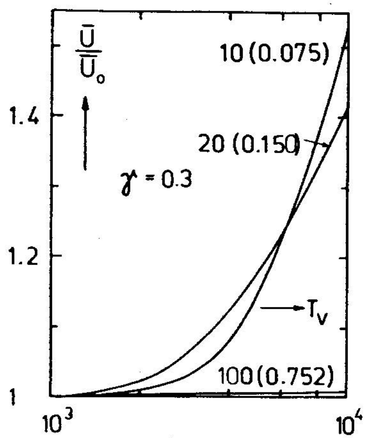

Fig. 5. Relative value of the electron mean energy as a function of T_v.

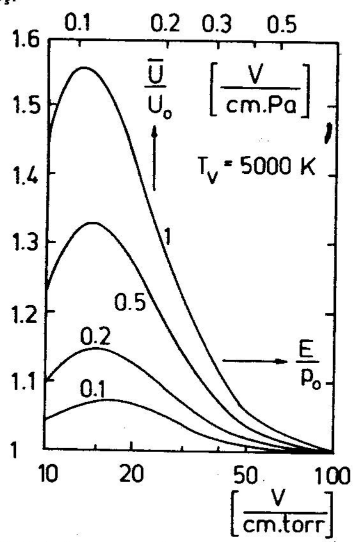

Fig. 6. Relative value of the electron mean energy as a function of E/p_0, parametrization by γ.

In conclusion it should be mentioned that the reliability of our model is somewhat impaired by the fact that we considered just six excited vibrational levels only, which for higher vibrational temperatures is clearly insufficient. Furthermore, the omission of the Coulomb interaction restricts the validity of our results to the low current case.

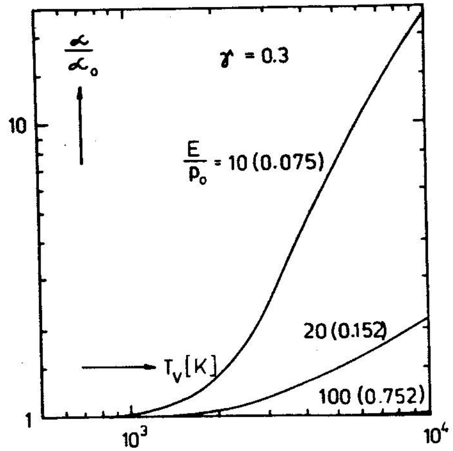

Fig. 7. Relative value of the Townsend coefficient as a function of T_v.

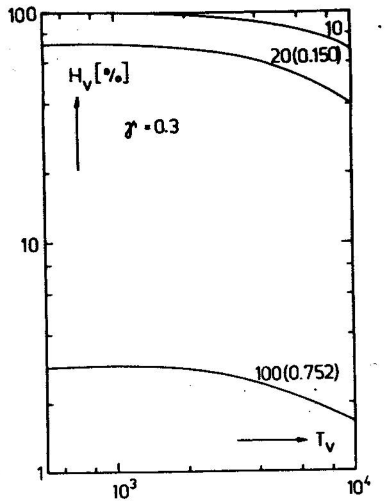

Fig. 8. The net power lost by collisions with vibrationally excited molecules as a function of T_v.

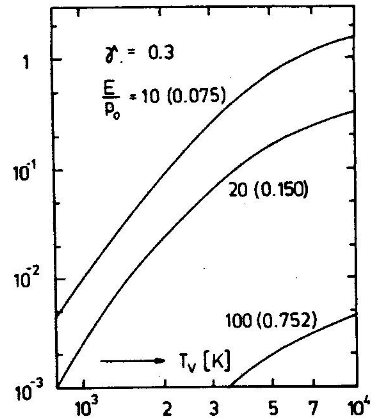

Fig. 9. Energy gain from the vibrational levels relative to the field power input as a function of T_v.

REFERENCES

[1] Chen, J.: J. Chem. Phys., *40* (1964), 3513.

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