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ENERGY EXCHANGE BETWEEN ELECTRON AND MOLECULAR GASES

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SUMMARY

The energy exchange between electrons and heavy particles is one of the main problems involved in investigating nonequilibrium plasma. The authors consider the energy exchange between an electron gas and a molecular gas, and show that the exchange mechanism is essentially dependent on the composition of the latter. For a gas consisting of molecules capable of forming an unstable negative ion (N_2, CO, etc.) this process is decisive. Calculations are made of the rate of energy exchange between an electron gas and nitrogen at different temperatures of the two gases. It is shown that the rate of exchange, which is governed by this mechanism, exceeds by several orders of magnitude the corresponding value, linked with other processes, usually taken into account.

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The rate of energy exchange between electrons and heavy particles is one of the essential factors determining the properties of a nonequilibrium plasma. In atomic gases, when temperatures are not too high, the rate of energy exchange is determined by elastic collisions of electrons with atoms and ions. In a plasma, containing molecules, possible also are the collisions attended by variation of the rotational and oscillatory states of molecules. At present these processes are investigated in experiments with monoenergetic electrons (see, for example, [1]); their cross-sections for certain molecules are reliably determined from the analysis of energy losses by electrons in cold gases (for example, [2, 3]; there are also a series of theoretical works. These data may be utilized for the estimate of the rate of energy exchange in a plasma (we shall limit ourselves to the consideration of collisions of electrons with diatomic molecules).

Postulating that the distribution of electrons by velocities is Maxwellian with temperature T_e, and that of molecules by discrete levels is Boltzmann's with temperature T, we shall have for the rate of energy exchange in a unit of volume, conditioned by inelastic processes:

$$dE/dt = N_e \sum_{n=0}^{\infty} N_n \sum_{m=0}^{\infty} (E_n - E_m) P_{nm}(T_e) \qquad (1)$$

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$$P_{nm}(T_e) = \left(\frac{8kT_e}{\pi m_e}\right)^{\frac{1}{2}} \frac{1}{(kT_e)^2} \int_0^\infty \varepsilon e^{-\frac{\varepsilon}{kT_e}} \sigma_{nm}(\varepsilon)\, d\varepsilon, \qquad (2)$$

where N_e is the concentration of electrons, $N_n e^{-\frac{E_n}{kT}}$ is the number of molecules at the discrete level n with energy E_n; σ_{nm} is the inelastic collision cross-section with the electron, transefring the molecule from level n to level m.

Let us consider the collisions of electrons with a neutral homonuclear molecule, accompanying the variation of the rotational state of the latter. It was shown in [2, 3] that the cross-sections computed according to the work by Gerjuoy and Stein [4] agree well with the experiment. The averaging of these cross-sections in correspondence with (2) and the summation according to (1), performed in the work by Mentzone and Row [5], lead to the simple formula

$$(dE/dt)_{rot} = 4BN_e N_{mol} \left(\frac{8kT_e}{\pi m_e}\right)^{\frac{1}{2}} \frac{8\pi}{15} q a_0^2 \frac{T - T_e}{T_e}, \qquad (3)$$

where B is a rotational constant, q is the quadrupole moment of the molecule in atomic units (ea_0^2), for q = 1 at.un. [3].

A direct excitation of oscillation levels of diatomic molecules during collisions with electrons is difficult on account of the sharp difference in masses of colliding particles and a comparatively high value of transmitted energy. However, in certain cases another mechanism of oscillation variation in the state of molecules is possible; for this mechanism the mass ratio of electrons to molecules has no direct significance. Thus, for nitrogen and carbon dioxide molecules a peculiar resonance process is observed, which consists in the trapping of the electron by the molecule with formation of an unstable negative ions [1, 6]. After its "decay" the molecule may find itself in another rotational state, whereupon the energy of the electron changes to a very significant value.

The requirement of accounting for the indicated process for the case of electron collisions with the N_2 molecule was noted in the Hurle work [7]. However, the estimates brought up in [7] are unsatisfactory, for the author utilized the Landau-Teller scheme [8]. This scheme assumes that the transitions take place only between neighboring levels. This is valid at molecule collision with heavy particles, but is not materialized in the considered process. It may be shown that the utilization of the Lansau-Teller scheme results in errors in order of magnitude and also in an incorrect temperature dependence.

This is why we attempted to make more precise the calculation of energy exchange by way of taking into account multiquantum transitions according to (1) and (2). For the case of N_2 we took advantage of the set of effective cross-sections computed in [6] by a method close to that applied in the theory

of resonance nuclear reactions. Unfortunaly, this set is not sufficiently complete (given are the cross-settions for the transitions between the levels $n \to m$, whereupon $n = 0-4$ & $m = 0-9$). Note also that in the region of low electron energies the brought up values of cross-sections are little reliable. However, in the region of energies 1.5 - 3 ev, the cross-sections $\sigma_{0m}(m = 1-8)$ agree satisfactorily with the experimental data of [1] and the values brought out in [3]. It seems to us, however, that the computation presented below eliminates to a known degree these shortcomings.

Assume that the molecule is a harmonic oscillator ($E_n = nh\omega$) and let us take advantage of the principle of detailed equilibrium ($\theta_e = h\omega/kT_e$)

$$e^{-n\theta_e} P_{nm} = e^{-m\theta_e} P_{mn} \tag{4}$$

Then (1) may be represented in the form

$$(dE/dt)_{vib} = \frac{h\omega}{Q(\theta)} N_e N_{N_2} \sum_k^{\infty} k (e^{-k\theta} - e^{-k\theta_e}) \sum_{n=0}^{\infty} P_{n+k,n}\, e^{-n\theta}$$

$$Q(\theta) = [1 - \exp(-\theta)]^{-1}$$

The computation thus conducted have shown that the values of P_{nm} ($n > m$) practically coincide for all the available n, m. Utilizing these values, we computed $(dE/dt)_{vib}$ according to (5), increasing in sequence the number of levels taken into account, and, accordingly, the number of transmissible oscillation quanta (i.e., k = 1, 2, 3, 4). It was found that for fixed T, T_e, there is convergence to a specific threshold, which is naturally improved at small T.

Taking into account the unreliability of all cross-sections, (besides σ_{10} from [3]) for small energies of electrons and the above indicated coincidence of P_{nm}, we may admit that $P_{n+k,n} \equiv P_{20}$ and is independent of n and k. In this case expression (5) may be written in the closed form

$$(dE/dt)_{vib} = h\omega P_{10}(T_e) N_e N_{N_2} [\epsilon(\theta) Q(\theta) - \epsilon(\theta_e) Q(\theta_e)] \tag{6}$$

$$\epsilon(\theta) = [\exp(\theta) - 1]^{-1}$$

The calculation by formula (6) leads to values not too different from the above mentioned threshold. The value of $P_{10}(T_e)$ in the temperature range $3000°K \leq T_e \leq 15{,}000°K$ is rather accurately approximated by the simple analytical expression

$$P_{10}(T_e) = 4{,}5 \cdot 10^{-9} \exp(-10\,000°K/T_e)\ \text{cm}^3/\text{sec} \tag{7}$$

As may be seen from (7), the value of P_{10} sharply rises with the increase of the temperature of electrons, and then varies very slowly. This circumstance, linked with the resonance character of the process, leads to an additional qualitative peculiarity. If $T_e \to T$, remaining smaller than T, P_{10} rises, while the term in brackets of (6) decreases; the rate of energy exchange may then pass through a maximum.

Note that this process of energy exchange is the most effective and may exceed the rate of energy transfer at elastic collisions and collisions with the variation of rotational energy by one order of magnitude.

T A B L E 1

RATE OF ENERGY EXCHANGE BETWEEN ELECTRONS AND HEAVY PARTICLES IN CONDITIONS OF EXPERIMENT [9]. ($N_{Ar} \simeq 10^{18}$ cm^{-3}; $N_c \simeq 3.5 \cdot 10^{14}$ cm^{-3}; $T_c \simeq 3000$°K)

Component	Ar	Cs^+		N_2	
Process	Elastic scatter	Elastic scatter	Elastic scatter	Exchange with rot	Exchange with rot.
dE/dt, erg/cm sec	$2.3 \cdot 10^7$	$6.6\ 10^7$	$6.8 \cdot 10^8\alpha$	$1.4 \cdot 10^9\alpha$	$2.7 \cdot 10^{10}\alpha$

To the extent known to us, the complex measurements of temperature abruption, carried out in a nonequilibrium molecular plasma, are unavailable. Discharge in argon-caesium plasma with small addition of nitrogen (ratio $\alpha = P_N / P_{Ar}$ varied from 10^{-4} to 10^{-1}) was investigated in [9]. Drop of electron temperature was observed for $\alpha > 10^{-3}$ despite the growth of the field E, sustaining the discharge. Estimates of the rate of energy exchange in those conditions are compiled in Table 1. The concentrations of electrons and the data on argon and caesium were borrowed from the work by Abramova and Tarasova [10]. It may be seen that the rate of energy losses at collisions of electrons with molecules of nitrogen is comparable with the rate of losses on argon atoms as early as at $\alpha = 10^{-3}$, which precisely results in the drop of electron temperature despite the growth of the applied electric field. A more accurate calculation must also take into account the collisions of nitrogen molecules with Ar atoms, leading in the final count to the increase in the progressive temperature of the neutral gas. This was also observed in conditions of experiment [9] at greater α; however, measurements of T and T_e were not conducted.

In conclusion we shall pause at one case, not of little importance in our opinion. The elastic scattering cross-sections of electrons on molecules in a ground oscillatory state are studied fairly well (see, for example [11]). The inelastic processes, and, in particular, the excitation of oscillatory levels, have been much more poorly investigated.

However, as is well known from the quantum theory of scattering, inelastic processes and elastic scattering are not independent. In the presence of a characteristic resonance peak on the curve of elastic cross-section dependence on electron energy, the amplitudes of elastic and inelastic processes are found to be strongly bound, and the decay of the intermediate complex may take place almost with equal probability by any open reaction channel.

The presence of resonance peaks on the curve of elastic scattering of an electron dependence on its energy is evidence that possible also are

inelastic processes leading to the excitation of oscillatory levels. Such are, for example, molecules N_2O, CO_2, HCl, C_2H_2, HCN. This allows us to assume that the inelastic processes of the above-described type, must be realized at collisions of electrons with these molecules. Let us underscore once more that they may be quite essential during estimates of the possibility of materializing electron temperature abruption in a plasma in the presence of molecules.

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