Ionization of atoms in radiative collisions

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Resonance processes occurring in collisions between atoms in a monochromatic external field are considered. The transfer of excitation from atom to atom accompanied by the simultaneous absorption of quanta (radiative collisions[1,2]) is analyzed for the case when the quantum energy is sufficient for the photoionization of an excited atom (Fig. 2). Expressions are obtained for the radiative collision cross section in the following cases: a) the transfer of excitation from atom to atom; b) the transfer of excitation followed by the ionization of an atom. The efficiencies of these reactions are compared with the efficiency of the direct photoionization of an excited atom. Experimental results[7,8] are discussed in relation to these processes.

1. Gudzenko and the present author[1] considered the transfer of excitation from atom to atom accompanied by the simultaneous absorption (emission) of a photon of energy close to the difference between the energies of transitions in these atoms during a collision. This reaction (Fig. 1),

$$X(1) + Y(2) + \hbar\omega \rightleftharpoons X(2) + Y(1), \quad \omega \approx \omega_0, \tag{I}$$

was called in [1,2] the radiative collision.

We shall now explain briefly the nature of a radiative collision. As is known, the cross section for the transfer of energy from atom to atom in the case of large energy defects ($\hbar\omega_0 \sim 1$ eV) and thermal velocities ($v \approx 10^4$–10^5 cm/sec) is usually (i.e., in the absence of term crossing) exponentially small. The field of light of frequency $\omega \approx \omega_0$ seems to lift the energy forbiddenness.

It is interesting to consider radiative collisions because the related effects make it possible to: a) influence selectively the kinetics of the processes occurring in a gas (or plasma); b) obtain experimental data on the characteristics of the interaction between atoms.

The earlier assumption that ω_0 does not coincide with the frequencies of atomic transitions made it possible to consider only a two-level system. The situation becomes more complex if the excitation energy of the state 2 of an atom X is higher than the ionization energy of an atom Y (Fig. 2). In this case, apart from the radiative collision reaction (I), we must also consider the transitions corresponding to the ionization of the atom Y by the excitation of the atom X:

$$X(2) + Y(1) \to X(1) + Y^+ + e \tag{II}$$

and the photoionization of the excited atom Y(2) by a photon of frequency ω:

$$Y(2) + \hbar\omega \to X(1) + Y^+ + e, \quad Y^+ + e = Y(\nu) \tag{III}$$

(ν represents the indices of states in a continuous spectrum). Clearly, we must now consider not only the two states of the quantum system comprising the atom X, the atom Y, and the electromagnetic field:

$$1 \equiv \{X(2),\ Y(1),\ \bar{n}_\omega\},\ 2 \equiv \{X(1),\ Y(2),\ \bar{n}_\omega + 1\},$$

which have been discussed in the earlier communications, but also the states in the continuous spectrum ν of the atom Y

$$\nu \equiv \{X(1),\ Y(\nu),\ \bar{n}_\omega\}.$$

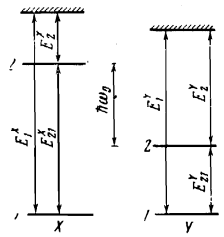

FIG. 1. Atomic Terms. Reaction (I).

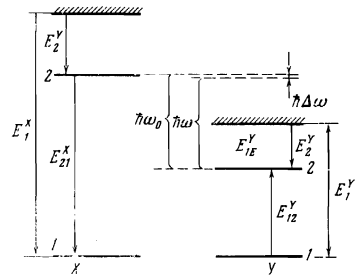

FIG. 2. Atomic terms. Reactions (I)-(III).

We must also allow for the interference between the various states, which will be discussed on the following basis.

If the Hamiltonian $\hat{H} = \hat{H}_0 + \hat{V}(t)$ corresponds to the system of equations

$$i\hbar\dot{a}_n = \sum_{n'} V_{nn'} \exp\{i\omega_{nn'}t\}a_{n'} + \int V_{n\nu} \exp\{i\omega_{n\nu}t\}a_\nu\, d\nu, \tag{1.1a}$$

$$i\hbar\dot{a}_\nu = \sum_{n'} V_{\nu n'} \exp\{i\omega_{\nu n'}t\}a_{n'} \tag{1.1b}$$

for the amplitudes of the probabilities of the discrete $\{n\}$ states resonating against the background of the continuum $\{\nu\}$, we can simplify this system considerably. Integrating the right-hand side of Eq. (1.1b) with respect to time and substituting it into Eq. (1.1a), we simplify our expressions on the assumption that the distance to the nearest boundary of the continuum is short compared with the reciprocal of the perturbation variation time. In this way we obtain a system of equations for a discrete spectrum

$$i\hbar\dot{a}_n = \sum_{n'}\left(V_{nn'} - \frac{i}{2}W_{nn'}\right)\exp\{i\omega_{nn'}t\}a_{n'}, \tag{1.2a}$$

where

$$W_{nn'}(t) = 2\pi\left[\frac{d\nu}{dE}V_{n\nu}(t)V_{\nu n'}(t)\right]_{\nu=\nu_0(E)}.$$

In this case, the probability of a transition to the continuous spectrum

$$\dot{w} = d\left(\int |a_\nu|^2 d\nu\right) \Big/ dt$$

is given by

$$\dot{w} = \frac{1}{\hbar}\sum_{n,n'} W_{nn'}(t)\exp\{i\omega_{nn'}t\}a_n^*(t)a_{n'}(t). \qquad (1.2b)$$

The system (1.2) includes interference effects. Its solution without allowance for the interference (i.e., the substitution $a_n = 1$, $a_{n'} = 0$, $n' \neq n$) results in considerable error (see, for example, the correction of the error in [3] reported by Fano himself;[4] an elegant allowance for the photoionization of atoms was also made by Kompaneets[5]).

2. We shall assume that the motion of the nuclei is classical. In this case, $\hat{V}$ is the interaction operator of the atomic shells with one another and with the external electromagnetic field. It follows from Sec. 1 that a correct allowance for the transitions (I), (II), and (III) requires the solution of the following system of equations:

$$i\dot{a}_1 = \left(V_1 - \frac{i}{2}W_1\right)a_1 + \left(V - \frac{i}{2}W\right)e^{i\Delta\omega t}a_2, \qquad (2.1a)$$

$$i\dot{a}_2 = \left(V_2 - \frac{i}{2}W_2\right)a_2 + \left(V - \frac{i}{2}W^*\right)e^{-i\Delta\omega t}a_1, \qquad (2.1b)$$

which describe the amplitudes of the states of the complex quantum system comprising the atom X, the atom Y, and the electromagnetic field. The following notation is used in these equations:

$$V_n = V_{nn}/\hbar,\ W_n = W_{nn}/\hbar,\ W = W_{12}/\hbar,\ V = V_{12}/\hbar,\ \Delta\omega = \omega_0 - \omega.$$

The probability of a transition (per unit time) to one of the states in the continuum is

$$\dot{w} = W_1|a_1|^2 + 2\mathrm{Re}(We^{i\Delta\omega t}a_1^*a_2) + W_2|a_2|^2. \qquad (2.2)$$

The expressions (2.1) and (2.2) are valid if

$$(|E_{12}^X| - |E_1^Y|)\tau/\hbar \gg 1, \qquad (2.3)$$

where τ is the flight time. The first term in Eq. (2.2) represents the probability of the reaction (II) and the third the probability of the reaction (III); the second term represents the interference between these two reactions (transitions).

As before,[1] we shall select the perturbation operator in the form

$$\hat{V}(t) = \frac{\gamma_{ij}}{R^3(t)}d_i^X d_j^Y + (d_i^X + d_i^Y)\mathscr{E}_i(t).$$

Here, d_i^X and d_j^Y are the vectors of the dipole moment operators of the atoms X and Y; $\gamma_{ij} = \delta_{ij} - 3e_ie_j$; δ_{ij} is the Kronecker delta; $e_i = R_i/R$ is a unit vector directed along the line joining the two nuclei; R_i is the vector representing the distance between the nuclei; $\mathscr{E}_i(t)$ is the electric field intensity. [The spatial indices, which are i and j in Eq. (2.1), always imply the usual summation in tensor algebra]. The justification for regarding the atomic interaction as of the dipole-dipole type at $\omega \approx \omega_0$ is given in [1]. We shall assume that the reactions in question are significant when the distance between the atoms is much less than the wavelength of the field $c/2\pi\omega$ and we shall take the field intensity to be

$$\mathscr{E}_i(t) = \mathscr{E}_{0i}\cos\omega t.$$

In calculating the matrix elements we shall limit ourselves to the first nonvanishing term. Then, V_1, V_2, and V become

$$V_1 = C_1/R^6,\ V_2 = C_2/R^6,\ V = B_3\mathscr{E}_0/R^3 \qquad (2.4a)$$

(the values of the constants C_1, C_2, and B_3 are given in [1]), whereas W_1, W_2, and W become

$$W_1 = C_3^2/R^6,\ W_2 = D^2\mathscr{E}_0^2,\ W = C_3D\mathscr{E}_0/R^3, \qquad (2.4b)$$

where

$$C_3 = \sqrt{\frac{2\pi}{\hbar}\frac{d\nu}{dE}}\gamma_{ij}\langle 2|d_i^X|1\rangle\langle 1|d_i^X|\nu\rangle,$$
$$D = \frac{1}{2}\sqrt{\frac{2\pi}{\hbar}\frac{d\nu}{dE}}\langle\nu|d_i^X|2\rangle\mathscr{E}_{0i}/\mathscr{E}_0. \qquad (2.5)$$

The quantities in Eq. (2.5) are calculated using the wave function of an electron in the field of the atomic core Y^+ ignoring the effects associated with the scattering of this core by the atom X. This approximation is permissible if the exchange interaction is unimportant. In fact, the wave function of an electron is distorted significantly only near the atom X. On the other hand, the assumption that the exchange interaction is negligible implies, in particular, that the wave functions of the states 1 and 2 are small near the atom X. Consequently, in this case, the scattering of an electron by the atom X does not alter significantly the quantities in Eq. (2.5).

We shall now consider the deactivation of the atom Y, which is in the state 2 before the collision. Therefore, the initial conditions are

$$a_2(-\infty) = 1,\quad a_1(-\infty) = 0. \qquad (2.6)$$

We shall ignore the probability of direct photoionization in flight and, therefore, we shall omit W_2 from the right-hand side of Eq. (2.1b). We shall justify this later.

The efficiency of the transfer of excitation and ionization in radiative collisions can be represented conveniently by the cross sections of these processes:

$$\sigma_e = 2\pi\int_0^\infty d\rho\,\rho|a_1(\infty)|^2, \qquad (2.7a)$$

$$\sigma_i = 2\pi\int_0^\infty d\rho\,\rho\int_{-\infty}^\infty dt'\{W_1(t')|a_1(t')|^2 + 2\,\mathrm{Re}[W(t')e^{i\Delta\omega t'}a_1^*(t_1')a_2(t')]\}. \qquad (2.7b)$$

To avoid misunderstanding we must point out that the radiative collision cross sections introduced above differ considerably, in the physical sense, from the usual photoabsorption and photoionization cross sections of a quasimolecule formed by the colliding atoms. The usual photo-process cross sections are defined relative to the flux of incident photons whereas the radiative collision cross sections represent atomic collisions (in a specified external magnetic field). We shall assume that $R = \sqrt{\rho^2 + v^2t^2}$, where v is the relative velocity of the atoms and ρ is the impact parameter.

We shall solve the system (2.1) for weak fields (see also[1]). Interchanging the variables

$$a_1(t) = b_1(t)\exp\left\{-i\int_{-\infty}^t\left[V_1(t') - \frac{i}{2}W_1(t')\right]dt'\right\},$$
$$a_2(t) = b_2(t)\exp\left[-i\int_{-\infty}^t V_2(t')dt'\right], \qquad (2.8)$$

we shall assume approximately that $b_2(t) = 1$ and then we shall find a_1 and a_2. The substitution of a_1 and a_2 into Eq. (2.7) yields the following expression for the excitation cross section:

$$\sigma_e = 2\pi\mathscr{E}_0^{2/5}v^{-6/5}B_3^{2/5}C_{12}^{-2/5}\left(1 + \frac{C_3^2D^2}{4B_3^2}\right)\chi\left(\frac{\Delta\omega C_{12}^{1/5}}{v^{6/5}}, \frac{C_3^2}{C_{12}}\right), \qquad (2.9a)$$

where $C_{12} = C_1 - C_2$

$$\chi(\alpha,\beta) = 4\int_0^\infty\frac{dy}{y^3}\left|\int_0^\infty\frac{dx}{(1+x^2)^{3/2}}\exp\left\{i\left[\alpha yx + \left(\frac{i}{2}\beta \pm 1\right)\frac{f(x)}{y^5}\right]\right\}\right|^2,$$

$$f(x)=\frac{x}{4(1+x^2)^2}+\frac{3x}{8(1+x^2)}+\frac{3}{8}\operatorname{arctg} x. \qquad (2.10a)$$

The ionization cross section of radiative collisions can be represented by

$$\sigma_i=2\pi\mathscr{E}_0 v^{-5/5}B_3^2C_{12}^{-2/5}\left\{\frac{C_3^2}{C_{12}}\left(1+\frac{C_3^2D^2}{4B_3^2}\right)\zeta\left(\frac{\Delta\omega C_{12}^{1/5}}{v^{6/5}},\frac{C_3^2}{C_{12}}\right)+\frac{C_3D}{B_3}\chi\left(\frac{\Delta\omega C_{12}^{1/5}}{v^{6/5}},\frac{C_3^2}{C_{12}}\right)\right\}, \qquad (2.9b)$$

where

$$\zeta(\alpha,\beta)=4\int_0^\infty\frac{dy}{y^3}\int_{-\infty}^{\infty}\frac{dx}{(1+x^2)^3}\left|\int_0^x\frac{dz}{(1+z^2)^{3/2}}\times\exp\left\{i\left[\alpha yz+\left(\frac{i}{2}\beta\pm1\right)\frac{f(z)}{y^5}\right]\right\}\right|^2. \qquad (2.10b)$$

The plus sign in the arguments of the exponential functions in Eq. (2.10) corresponds to $C_1 - C_2 > 0$ and the minus to $C_1 - C_2 < 0$.

The target parameters ρ_0 which make the greatest contribution to the cross section are those for which the modulus of the exponential functions in the expressions for the amplitudes a_1 and a_2 is unity. This gives

$$\rho_0\approx\left(\frac{1}{v}\left|C_{12}-\frac{i}{2}C_3^2\right|\right)^{1/5}. \qquad (2.11)$$

In the derivation of Eq. (2.9) the diagonal matrix elements (2.1) are included in full, whereas the nondiagonal matrix element is assumed to be small. Comparing the quantities $|V-(1/2)iW|$ and $|V_1-V_2+(1/2)iW|$ for $R\sim\rho_0$, we obtain the following weak-field condition:

$$\mathscr{E}_0\ll\mathscr{E}_{cr}\left(1+\frac{C_3^4}{4C_{12}}\right)^{1/5}\left(1+\frac{C_3^2D^2}{B_3^2}\right)^{1/4}, \qquad (2.12a)$$

where $\mathscr{E}_{cr}\equiv v^{3/2}C_{12}^{2/5}/B_3$ (see[1]). We shall now obtain the condition for ignoring the probability of direct photoionization in flight. Comparing the coefficient which has been ignored, $(1/2)iW_2$, with the smallest of those which has been included, $V-(1/2)iW$, we find that

$$\mathscr{E}_0\ll\mathscr{E}_{cr}\frac{2B_3^2}{C_{12}D^2}\left(1+\frac{C_3^2D^2}{4B_3^2}\right). \qquad (2.12b)$$

3. We shall consider first the case of weakly excited atoms X and Y and obtain some numerical estimates. Assuming that the atomic constants (in the system of atomic units $e = m = \hbar = 1$) are quantities of the order of unity and that the atomic velocity is $v\sim10^4$ cm/sec, we find that

$$\mathscr{E}_{cr}\sim5\cdot10^9\frac{V}{cm}\left(\frac{v}{2\cdot10^8\,cm/sec}\right)^{3/5}\sim10^7\frac{V}{cm},$$

where the characteristic resonance width is $\Gamma = C_{12}^{-1/5}v^{6/5}\sim10^{-3}$ eV. If $\mathscr{E}_0\sim0.3\mathscr{E}_{cr}$, $\Delta\omega\lesssim\Gamma$, we obtain $\sigma_e\sim\sigma_i\sim(\mathscr{E}_0/\mathscr{E}_{cr})^2v^{-2/5}\sim10^{-15}$ cm^2.

We shall now compare the number of the Y(2) atoms which experience direct photoionization per unit time,

$$W_2N_2^Y, \qquad (3.1)$$

with the corresponding loss of these atoms as a result of radiative collisions involving excitation

$$\langle\sigma_e v\rangle N_1^XN_2^Y \qquad (3.2a)$$

and ionization

$$\langle\sigma_i v\rangle N_1^XN_2^Y. \qquad (3.2b)$$

Here, N_i^Z is the population of the state i of an atom Z.

We shall consider the case $\Delta\omega = 0$. The quantities in Eq. (3.2) are compared with Eq. (3.1) for

$$\frac{4\pi}{3}N_1^XR_0^3=\frac{2}{3\sqrt{\pi}}\left(\frac{B_3^2}{C_{12}D^2}+\frac{C_3^2}{C_{12}}\right)^{-1}\chi^{-1}\left(0,\frac{C_3^2}{C_{12}}\right), \qquad (3.3a)$$

$$\frac{4\pi}{3}N_1^XR_0^3=\frac{2}{3\sqrt{\pi}}\frac{C_{12}D^2}{B_3^2}\left[\left(1+\frac{C_3^2D^2}{4B_3}\right)\times\frac{C_3^2}{C_{12}}\zeta\left(0,\frac{C_3^2}{C_{12}}\right)+\frac{C_3D}{B_3}\chi\left(0,\frac{C_3}{C_{12}}\right)\right]^{-1}. \qquad (3.3b)$$

Here, $R_0 = (C_{12}/v_r)^{1/5}$ is the Weisskopf radius and $v_T = \sqrt{2T/M}$ is the thermal velocity of the colliding atoms.

We have assumed so far that pair collisions predominate. This is quite justified if the Weisskopf sphere surrounding the atom Y(2) contains no more than one particle:

$$\frac{4\pi}{3}NR_0^3\ll1, \qquad (3.4)$$

where N is the total concentration of atoms. Thus, in pair collisions the left-hand sides of Eqs. (3.3a) and (3.3b) contain a small parameter whereas the right-hand sides are of the order of unity. Consequently, in this case, the radiative collision processes do not govern the population of the Y(2) state.[1)] We recall, however, that the transfer of excitation in radiative collisions results in the population of the X(2) state whereas the photoionization process does not produce this state (at least not directly). From this point of view the reactions in question do not compete at all.

We note that by measuring the contribution of the radiative collisions to the deactivation of the state Y(2) and to the photoabsorption at the frequency $\omega\approx\omega_0$ we can obtain valuable information on the characteristics of quasimolecules.

We shall now estimate the ratios of the constants on the right-hand sides for the case when the state 2 of the atom Y can be regarded as high-lying and hydrogen-like with a principal quantum number n. Applying the K Kramers formulas,[6] we find that

$$D^2=\frac{1}{\pi\sqrt{3}}\left(\frac{2\,Ry}{\hbar\omega_0}\right)^4\frac{1}{n^3}a_0^2e^2\frac{1}{Ry},$$

The estimates of the other constants yield

$$C_{12}\sim(d^Y)_{nn}^2(d^X)_{11}^2/|E_{12}^X|^2,$$

$$B_3^2\sim(d_{12}^X)^2(d_{1n}^Y)^2(d^Y)_{nn}^2/(\hbar\omega_0)^2.$$

Assuming that $(d_{12}^X)^2\sim(d_{11}^X)^2$, $(d^Y)_{1n}^2\sim a_0^2e^2/n^3$, and $(d^Y)_{nn}^2\sim a_0^2e^2/n^4$, we find that

$$C_{12}D^2/B_3^2\sim(\hbar\omega_0/|E_{12}^X|)^2,$$

$$C_3^2/C_{12}\sim n^{-4},$$

$$C_3D/B_3\sim\frac{|E_{12}^X|}{\hbar\omega_0}n^{-5/2}.$$

Hence, we can see that in the case of highly excited states the cross section for the transfer of excitation in radiative collisions σ_e is much greater than the ionization cross section σ_i.

We shall now estimate the condition for the departure from the pair collision case

$$\frac{4\pi}{3}N_1^Xa_0^3(v_0n^4/v)^{3/5}\sim1$$

for a highly excited state n. If we assume that $n\sim10$, $v\sim10^4$ cm/sec, we find that the collisions are not of the pair type for $N_1^X\sim10^{19}$ cm^{-3}. Thus, even under normal conditions the collisions in highly excited states are not of the pair type.

If the Weisskopf sphere contains, on the average, several particles, the situation becomes much more

complex. This is due to the fact that the broadening of terms is now of the many-body type and also because at distances $(N_1^X)^{-1/3} < R_0 \sim 10^{-7}-10^{-6}$ cm the transfer of excitation from atom to atom is efficient and this reaction must be allowed for simultaneously with those considered above. Moreover, in this case, the exchange interaction is important.

4. It is interesting to consider the experiments ([7] and, particularly,[8]) in which laser-radiation-induced breakdown in a mixture of argon and neon was investigated. The surprising result is that a small ($\sim 1\%$) admixture of neon, whose excitation potential is higher than that of argon, reduces strongly the threshold of breakdown caused by neodymium laser radiation. This effect does not occur if ruby laser radiation is employed.[8]

A self-consistent explanation of this effect may be based on the following hypothesis. An argon atom (in our nomenclature, it is the Y atom) absorbs virtually $(|E_{12}^X|/\hbar\omega - 1) \approx 12$ photons and an additional photon in the course of a radiative collision and the excitation is transferred to neon (atom X). This is followed by the Penning reaction. If under the experimental conditions in [7,8] the radiative collision reaction is more efficient than the direct photoionization, the former reaction reduces the threshold field. The effect is not observed in the experiments with ruby laser radiation because the process is nonresonant for a ruby laser photon (the excitation energy of neon is not equal to an integral number of photons). In the case of neon laser photons, the process can be regarded as resonant if allowance is made for the shift of the excited neon levels.

Unfortunately, the quantitative results obtained above cannot be applied directly to the experimental conditions employed in [7,8] because the condition for pair collisions (3.4) and the weak-field condition (2.12) are both violated. However, our interpretation is the only one that has been proposed. No positive ideas have been put forward in [8]; in the explanation given in [7] (criticized justly in [8]) the description of the formation of excited neon atoms is incorrect.

The efficiency of the mechanism proposed in the present paper can be checked in the experiments with a tunable-frequency laser at lower pressures. The many-photon excitation of neon can be checked by carrying out experiments similar to those in [8] but using xenon instead of argon.

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[1)]We note that at the limit of the range of validity of our discussion [when the left-hand side of Eq. (3.4) becomes of the order of unity but the order of magnitude of the effect can still be estimated] the contribution of the radiative collision reactions to the deactivation of the state Y(2) is comparable with the contribution of the photoionization reactions.

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