Ionization of highly excited atoms in their own gas

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A model is proposed which makes it possible to obtain analytic expressions for the cross section and for the rate constant of the ionization of highly excited atoms in their own gas. The velocity distribution of the emitted electrons is obtained. Good agreement is observed between theory and experiment.

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1. Collision processes with participation of highly excited atoms have recently become the subject of intensive experimental and theoretical research, since they play an important role in gas-discharge physics and in astrophysics.[1] The ionization of the highly excited states of an atom A^* when it collides with its own atom proceeds via two channels:

$$A^*+A\to\begin{cases}A^++A+e & (1a)\\ A_2^++e & (1b)\end{cases}.$$

The channel (1b) is called associative ionization and predominates in slow collisions. Inasmuch as in the initial state one of the colliding atoms is a state with a large quantum number $n (n\gg 1)$, we can assume that the process (1) takes place at large distances R between the nuclei. This in turn allows us to introduce a number of assumptions that simplify greatly the solution of the problem connected with determining the cross section and the rate constant of the reaction (1).

First, we are justified in using the asymptotic theory[2] to describe the behavior of the terms of the system (1) in the initial and final states. Second, we can introduce two small parameters:

$$1/\gamma^2R\ll 1, \qquad (2)$$

$$R/n^2\ll 1, \qquad (3)$$

where $\gamma^2/2=I$, I is the binding energy of the electron in the atom A in the ground state, and R is the distance between the colliding partners. In addition, the states of an electron in a highly excited atom will be regarded as hydrogenlike states of an electron with the principal quantum number n and orbital angular momentum l, moving in the Coulomb field of an effective charge $Z_{\rm eff}\sim 1$. Here and below we use the atomic system of units: $e=m=\hbar=1$.

The calculation of the cross section of the process (1) is a rather complicated quantum-mechanical problem, and the previously obtained results were mainly estimates and did not always describe correctly the behavior of the rate constant of the reaction (1) as a function of the various observable parameters when comparison was made with experiment.[3-5] In the present paper, on the basis of the assumptions made above, we have succeeded in finding, within the framework of perturbation theory, an analytic expression for the ionization cross section (1) in a wide range of variation of the relative collision rate v, and this has made it possible to determine the rate constant of the process (1) and to obtain limiting expressions for the dependence of the rate constant on n. A comparison of our calculations with the experimental data[3,6] has shown sufficiently good agreement between theory and experiment.

When the condition (3) is satisfied, the highly excited electron has practically no influence on the energy of the interaction between the atoms. Therefore, first, we are justified in using perturbation theory to solve our problem (since $R/n^4\ll 1/n^2$) and, second, we exclude this electron from consideration when determining the behavior of the curves of the potential energy of the interaction of the atoms in the initial state. Then the course of the potential curves describing the initial and final states of the system is determined by the behavior of the potential curves of the molecular ion A_2^+.

We confine ourselves for simplicity to the case when the atom in the ground state has only one valent s electron. Then the main contribution to the cross section of the process (1) is made by a system initial state whose evoluation is determined by the behavior of the repulsion term ${}^2\Sigma_u^+$ of the molecular ion A_2^+, since the other terms have no intersection points with the term that describes the final state of the system ${}^2\Sigma_g^+$, and transitions from these terms are adiabatically unlikely. Within the framework of the asymptotic theory[2] the potential energies of the terms in the initial and final states can be expressed in the form

$$U_i({}^2\Sigma_u^+)=-\alpha/2R^4+\Delta(R)/2, \qquad (4)$$

$$U_f({}^2\Sigma_g^+)=-\alpha/2R^4-\Delta(R)/2, \qquad (5)$$

where α is the polarizability of the atom in the ground state and

$$\Delta(R)=BR^{2/\gamma-1}e^{-\gamma R}$$

is the energy of the exchange interaction of the ion with its atom.[2]

Knowing the behavior of the terms of the molecules A_2^+ and A^*_2 we can draw the conclusion that at collision energies $E<U_i(R_{\rm int})$, where $R_{\rm int}$ is the term intersection point, the probability of the reaction (1) is determined by the penetrability of a potential barrier of height $U_i(R_{\rm int})$, and is exponentially small, so that the contribution of energies $E<U_i(R_{\rm int})$ to the reaction (1) can be neglected. If $U_i(R_{\rm int})<E<1/2n_{\rm eff}^2$, then the quasimolecule A^*_2 decays via the channel (1*b*)–associative ionization. At $E>1/2n_{\rm eff}^2$, besides the associative ionization process, the other channel (1a) is opened–ionization of the excited atom with production of an atomary ion. Here $1/2n_{\rm eff}^2=E_n$, where E_n is the

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binding energy of the highly excited electron.

2. In first-order perturbation theory, the probability of the decay of the quasimolecule A^*_2 per unit time with transition of the electron into the continuous spectrum is determined by the expression[7]

$$dw_{if}=2\pi|\langle\Psi_i|\hat{V}|\Psi_f\rangle|^2\delta(E_i-E_f)\rho_\varepsilon d\varepsilon, \tag{6}$$

where $\Psi_{i,f}$ and $E_{i,f}$ are the wave functions and energies of the initial and final states, ρ_ε is the density of the final states of the electron in the continuous spectrum, and $\hat{V}$ is the perturbation operator.

Within the framework of the Born-Oppenheimer approximation, the motions of the nuclei and of the electrons separate, so that the wave functions of the system in the initial and final states are determined by the product of the nuclear (χ) and electronic (φ) wave functions:

$$\Psi_{i,f}=\varphi^{\mathrm{el}}_{i,f}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})\chi^{\mathrm{nuc}}_{i,f}(\mathbf{R}). \tag{7}$$

Here $\mathbf{r}_1$ and $\mathbf{r}_2$ are the coordinates of the electrons of the atoms relative to their atomic residues, and $\mathbf{R}$ is the vector that determines the positions of the nuclei of the colliding partners relative to one another.

In the initial state, the nuclear wave function $\chi^{\mathrm{nuc}}_i(R)$ is a distorted plane wave[7] normalized to a unit flux density:

$$\chi^{\mathrm{nuc}}_i(\mathbf{R})=\frac{1}{2\mu v^{1/2}}\sum_{j_1=0}^{\infty}(2j_1+1)\Psi_{Ej_1}(R)P_{j_1}(\cos\theta_{\mathbf{vR}}), \tag{8}$$

where j_1 is the angular momentum of the motion of the nuclei, $P_{j1}(\cos\theta_{\mathbf{vR}})$ is a Legendre polynomial corresponding to this momentum; $\theta_{\mathbf{vR}}$ is the angle between the $\mathbf{R}$ axis joining the nuclei and the relative velocity $\mathbf{v}$; $\Psi_{Ej1}(R)$ is the radial wave function, which is a solution of the Schrödinger equation for the nuclear motion in a central potential

$$U^i_{\mathrm{eff}}=U_i(R)+j_1(j_1+1)/2\mu R^2 \tag{9}$$

and is normalized to a delta-function of $(2\mu E)^{1/2}/2\pi$; μ is the reduced mass of the colliding atoms, $E=\mu v^2/2$; $U_i(R)$ is defined in (4).

In the final state there are two channels of the reaction (1), which differ in the total nuclear-motion energies. The reaction of the associative ionization is described by a discrete energy spectrum $\varepsilon_f=\varepsilon_v$, wherein ε_v, which is reckoned from the end point of the continuous spectrum, is less than zero, $\varepsilon_v<0$, and in accordance with the energy conservation law the channel (1b) is open at collision energies

$$E<1/2n^2_{\mathrm{eff}}+k^2/2, \tag{10}$$

where $k^2/2$ is the energy of the emitted electron.

For the reaction (1a) we have $\varepsilon_f>0$, i.e.,

$$E>1/2n^2_{\mathrm{eff}}+k^2/2. \tag{11}$$

In this case the nuclear wave function in the final state can be written in the form

$$\chi^{\mathrm{nuc}}_f(\mathbf{R})=\Psi_{\varepsilon_f}(R)Y_{jM_j}(\mathbf{R}/R), \tag{12}$$

where $Y_{jM_j}(\mathbf{R}/R)$ is a spherical wave function corresponding to the angular momentum j and its projection M_j. The radial wave function $\Psi_{\varepsilon f}(R)$ is a solution of the Schrödinger equation in the field of the effective potential

$$U^f_{\mathrm{eff}}=U_f(R)+j(j+1)/2\mu R^2, \tag{13}$$

where U_f is defined in (5). At $\varepsilon_f>0$ the function $\Psi_{\varepsilon f}(R)$ is normalized to a delta function of the energy and corresponds to channel (1a). At $\varepsilon_f<0$, the function $\Psi_{\varepsilon f}=\Psi_{\varepsilon v}$ is normalized to unity and corresponds to the channel (1b).

At collision energies $E>U^i_{\mathrm{eff}}$, the radial wave functions $\Psi_{Ej1}(R)$ and $\Psi_{\varepsilon fj}(R)$ in (8) and (10) can be written within the framework of the quasiclassical approximation[7]:

$$\Psi_{Ej_1}(R)=\frac{2}{R}\left(\frac{\mu v}{p_{j_1}}\right)^{1/2}\cos\left(\int^R p_{j_1}dR-\frac{\pi}{4}\right), \tag{14}$$

$$\Psi_{\varepsilon_v j}(R)=\frac{1}{R}\left(\frac{2\mu}{\pi p_j}\frac{d\varepsilon_v}{dv}\right)^{1/2}\cos\left(\int^R p_j dR-\frac{\pi}{4}\right),\quad \varepsilon_v<0 \tag{15a}$$

$$\Psi_{\varepsilon_f j}(R)=\frac{1}{R}\left(\frac{2\mu}{\pi p_j}\right)^{1/2}\cos\left(\int^R p_j dR-\frac{\pi}{4}\right),\quad \varepsilon_f>0, \tag{15b}$$

where

$$p_{j_1}=[2\mu(E-U^i_{\mathrm{eff}}(R))]^{1/2},\quad p_j=[2\mu(\varepsilon_f-U^f_{\mathrm{eff}}(R))]^{1/2}.$$

To determine the electronic wave functions we use the following model. We assume that the excited electron in the initial bound state and in the final continuous-spectrum state with energy $k^2/2$ moves in the Coulomb field of the atomic residue with charge $Z_{\mathrm{eff}}\approx 1$. The second electron is strongly bound to its atom and determines the electronic terms of the molecular ion of the initial and final states—${}^2\Sigma_u^+$ and ${}^2\Sigma_g^+$, respectively.

Since $n\gg 1/\gamma$, the electronic wave function $\Psi^{\mathrm{el}}_{if}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})$ can be represented as a product of the wave functions of the first and second electrons:

$$\Psi^{\mathrm{el}}_{i,f}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})=\Psi^{\mathrm{el}}_{i,f}(\mathbf{r}_1,\mathbf{R})\Psi^{\mathrm{el}}_{i,f}(\mathbf{r}_2,\mathbf{R}). \tag{16}$$

Here $\Psi^{\mathrm{el}}_{i,f}(\mathbf{r}_2,\mathbf{R})$ is the Coulomb wave function; in the initial state it is normalized to unity, and in the final state this wave function can be written in the Sommerfeld representation,[7], i.e., it can be expanded in the Coulomb functions of the continuous spectrum, and $\Psi^{\mathrm{el}}_{i,f}(\mathbf{r}_2,\mathbf{R})$ are the molecular wave functions of the strongly bound electron and correspond to molecular-ion states of various parities.

The perturbation operator $\hat{V}$ in (6) is the operator of the interaction of the valence electrons of the colliding atoms:

$$\hat{V}=1/|\mathbf{r}_1-\mathbf{r}_2|. \tag{17}$$

Integrating in (6) with respect to the coordinates of the second electron and using the fact that the internuclear distance is much larger than the dimensions of the unexcited atom [condition (2)], and the fact that the average distance at which the highly excited electron is located is much larger than R [condition (3)], we can write Eq. (6) in the single-electron approximation:

$$dw=2\pi|\langle\chi^i_{\mathrm{nuc}}|\hat{V}|\chi^f_{\mathrm{nuc}}\rangle|\delta(E_i-E_f)\rho_\varepsilon d\varepsilon, \tag{18}$$

where V is defined as

$$V=\frac{1}{2}\left\langle \Psi_{\mathrm{el}}{}^{i}(\mathbf{r}_1)\left|\frac{\mathbf{r}_1\mathbf{R}}{r_1{}^3}\right|\Psi_{\mathrm{el}}{}^{f}(\mathbf{r}_1)\right\rangle. \tag{19}$$

Under the normalization conditions chosen by us, Eq. (18) determines the differential cross section of the reaction.

Integrating (8) with respect to the internuclear distance R with the quasiclassical wave functions (14) and (15),1) and replacing the summation over the vibrational and rotational quantum numbers of the molecular ion by integration, we obtain the following expression for the cross section of the reaction (1):

$$\sigma=\frac{\pi}{3(2l+1)\gamma v}\frac{g_f}{g_A g_{A^*}}\int dk R_p{}^4[\Delta(R_r)]^3\left[1-\frac{U_i(R_r)}{E}\right]^{1/2}$$
$$\times[l|M_{n,l}^{k,l-1}|^2+(l+1)|M_{n,l}^{k,l+1}|^2]. \tag{20}$$

Here R_r is the resonance point defined by the condition

$$E-\varepsilon_f=U_i(R_r)-U_f(R_r); \tag{21}$$

g_A and g_A^* are the statistical weights of the colliding atoms A and A^*, g_f is the statistical weight of the final electronic state,

$$M_{n,l}^{k,l\pm1}=\int_0^\infty R_{k,l\pm1}R_{n,l}r^3\,dr,$$

and R_{nl} is the radial wave function of the electron.

The resonance condition (21) can be rewritten in the following form:

$$\Delta(R_r)=k^2/2+1/2n_{\mathrm{eff}}^2. \tag{22}$$

The cross section for the associative ionization channel (1b) is obtained from Eqs. (20)–(22) with account taken of satisfaction of the condition (10), while for channel (1a) it is obtained with account taken of satisfaction of the condition (11).

3. We determine now the rate constant of the reaction (1)

$$K=\langle\sigma(v)v\rangle, \tag{23}$$

where σ is defined by Eq. (20), and the angle brackets denote averaging over the velocity distribution function. Assuming the distribution function to be Maxwellian, we obtain a general formula for the rate constant of the reaction (1):

$$K(n)=\frac{g_f c}{2\gamma g_A g_{A^*}}\int R_r{}^4\left(\frac{k^2}{2}+\frac{1}{2n_{\mathrm{eff}}^2}\right)^2\exp\left[-\frac{U_i(R_p)}{T}\right]\sigma_{\mathrm{ph}}(k)\,k\,dk. \tag{24}$$

Here T is the temperature of the gas, $c=137$ is the velocity of light in atomic units, $\sigma_{\mathrm{ph}}(k)$ is the cross section for the photoionization of the excited atom A^*, which is connected with the matrix elements $M_{n,l}^{k,l\pm1}$ in the following manner[8]:

$$\sigma_{\mathrm{ph}}(k)=\frac{2\pi}{3(2l+1)kc}\left(\frac{k^2}{2}+\frac{1}{2n_{\mathrm{eff}}^2}\right)[l|M_{n,l}^{k,l-1}|^2+(l+1)|M_{n,l}^{k,l+1}|^2]. \tag{25}$$

The rate constant defined by (24) is the sum of the rate constants of the reactions (1a) and (1b), i.e.,

$$K(n)=K^{(1b)}(n)+K^{(1a)}(n).$$

The rate constant of the associative ionization $K_{\mathrm{ai}}=K^{(1b)}(n)$ is then obtained by simply multiplying the integrand of (24) by the function

$$f=\mathrm{erf}\left(\left(\frac{|U_f|}{T}\right)^{1/2}\right)-\frac{2}{\pi^{1/2}}\exp\left[-\frac{|U_f|}{T}\right]\left(\frac{|U_f|}{T}\right)^{1/2}, \tag{26}$$

where

$$\mathrm{erf}(x)=\frac{2}{\pi^{1/2}}\int_0^x e^{-t^2}\,dt$$

is the error integral.

As seen from (24) and (25), our problem was reduced to finding the photoionization cross section σ_{ph} of a highly excited atom. Since we are not considering here the Rydberg states of an electron with $n\gg1$, we are justified in using the quasiclassical approximation[9] for an estimate of the dependence of the photoionization cross section on n. Within the framework of this approximation (see the Appendix) we have obtained the limiting n-dependences of the rate constant of reaction (1) and of the function f of (26). At $n\gg1/2T^{1/2}$ we have

$$K(n)=\frac{2\pi^2 g_f}{3\gamma g_A g_{A^*}}\frac{R_{\mathrm{int}}^4(2T)^{4/3}}{n^3}\frac{\Gamma(2/3)}{\Gamma^2(4/3)}\left(\frac{2}{9}\right)^{2/3}\exp\left(\frac{\alpha}{2R_{\mathrm{int}}^4T}\right),$$
$$f\approx\frac{1}{3n^3T}\left(\frac{2}{\pi T}\right)^{1/2}, \tag{27}$$

and at $n\ll1/2T^{1/2}$

$$K(n)=\frac{4\pi^2 g_f}{3\gamma g_A g_{A^*}}\frac{R_{\mathrm{int}}^4(2n^2)^{1/3}(2/9)^{4/3}}{n^3\Gamma^2(4/3)}T\exp\left(\frac{\alpha}{2R_{\mathrm{int}}^4T}-\frac{1}{4n^2T}\right), \tag{28}$$
$$f\approx1,$$

where R_{int} is the point of intersection of the terms of the initial and final states, and depends weakly (logarithmically) on n.

It is seen from (27) and (28) that at sufficiently small $n(n\ll1/2T^{1/2})$ the rate constant $K(n)$ increases exponentially with increasing n and the disintegration of the excited atoms proceeds mainly via the associative ionization channel, while at large n $(n\gg1/2T^{1/2})$ we have $K(n)\sim1/n^3$ and the associative ionization can be neglected. The rate constant of the ionization (1) assumes a maximum value in the region $n_{\max}\approx1/2T^{1/2}$. For numerical calculations of the ionization rate constants it is advisable to use for the photoionization cross section (25) the more accurate expressions obtained by Burgess and Seaton[10] on the basis of the quantum-defect method.

The table lists the results of the numerical calculation of the rate constant of the ionization process in collisions of excited cesium with its own atom in the ground state:

$$\mathrm{Cs}^*(np)+\mathrm{Cs}(6s)\to\begin{cases}\mathrm{Cs}_2^+(^2\Sigma_g^+)+e\\ \mathrm{Cs}^++\mathrm{Cs}+e\end{cases},$$

at a gas temperature $T=500$ K. The results of the calculations are compared with experiment.[4,6]

TABLE I.

	$K\cdot10^{-10}$, cm^3/sec						
	$n=9$	10	11	12	13	14	15
K^{Theor}	3.2	6.8	9.5	12.0	11.4	11.4	11.1
K^{Expt}	4.8±0.8	6.8±1.2	6.8±1.2	7.2±1.6	6.4±1.2	4.4±1.2	3.6±1.2
$K_{\mathrm{ai}}^{\mathrm{Theor}}$	3.2	6.2	9.0	10.5	10.6	10.4	9.7
$K_{\mathrm{ai}}^{\mathrm{Expt}}$	4.8	6.8	6.8	6.0	4.4	2.8	2.0

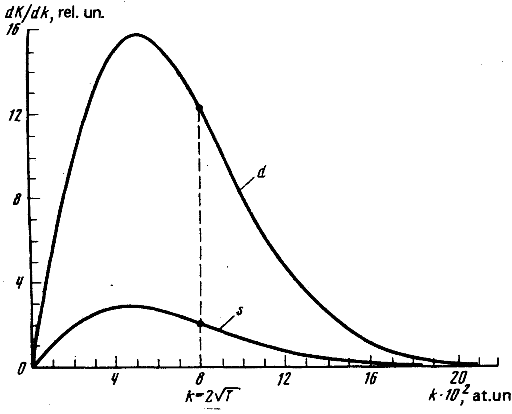

FIG. 1. Spectrum of emitted electrons ($s-s$-electrons, $d-d$-electrons) at $n=15$ and $T=500$ K; k is the electron velocity.

The figure shows the value of $dK_{(n)}/dk$ at $n=15$ for emitted s and d electrons, calculated on the basis of (24). As seen from the figure, the main contribution to the ionization rate constant is made, as expected, by the d electrons and by those values of the emitted-electron momenta which lie in the region $k_{\max}\sim 1/n_{\max}$.

4. Calculations have shown that the main contribution to the ionization cross section is made by the internuclear distances near the intersection point of the potential curves of the initial and final states, with

$$2\gamma^{-1}\ln n \ll R \ll n^2. \qquad (29)$$

Thus, at large values of n the condition for satisfaction of the inequalities (29) makes it possible, on the one hand, to use perturbation theory, and on the other hand to use the asymptotic theory for the description of the behavior of terms of the system (1). In addition, the large values of n justify the hydrogenlike approximation for the description of the states of the electron before and after the collision. This model makes it possible to express the rate constant of the ionization process in terms of observable parameters that characterize the behavior of the system: the gas temperature, the principal quantum number n, the orbital angular momentum l of the highly excited electron, the polarizability α of the atom in the ground state, and the binding energy of the electron in the atom.

Concrete results were obtained here for the case when the colliding atoms have one valence electron each. Within the framework of the given model, the problem can be easily generalized to include the multielectron case. The multielectron character of the system influences here only the behavior of the terms of the system (1) in the initial and final states.

In the case when $1/2n_{\text{eff}}^2>D$, where D is the dissociation energy of the molecular ion A_2^+, there may be no intersection points of the potential curve U_x and U_i. This means that at

$$n_{\text{eff}}<1/(2D)^{1/2}$$

the probability of the process (1) is adiabatically small. This is confirmed by the experimental data.[3,6,11-15]

When solving this problem we neglected the influence of the Coulomb-condensation levels with principal quantum number $n'>n$ on the probability of the ionization. Estimates show that allowance for the Coulomb condensation makes a small contribution ($\sim 1/n^4$) to the ionization rate constant of a highly-excited atom with $n\gg 1$.

In conclusion, the authors thank B. N. Smirnov for suggesting the problem and for a discussion of the results.

APPENDIX

In the quasiclassical approximation, which is valid at $n\gg 1, k\ll 1$, the photoionization cross section σ_{ph}, obtained by Bureeva,[9] is of the form

$$\sigma_{\text{ph}}(n,l,k)=\frac{4\pi^2}{3c}\frac{(\Delta n)^2}{\omega^3 n^5}\left\{(J_{\Delta n}'(\Delta n\nu))^2+\frac{1-\nu^2}{\nu^2}J_{\Delta n}^2(\Delta n\nu)\right\}, \qquad (\text{A}.1)$$

where

$$\Delta n=n^3\omega, \quad \omega=k^2/2+1/2n^2, \quad \nu=[1-(l+{}^1/_2)^2/n^2]^{1/2}$$

and $J_{\Delta n}(\Delta n\nu)$ is a Bessel function. For large values of n, the Bessel function $J_{\Delta n}(\Delta n\nu)$ can be represented in the form of an asymptotic expansion in powers of $\Delta n\nu$:

$$J_{\Delta n}(\Delta n\nu)=\frac{1}{\pi^{1/2}}\left(\frac{2}{\Delta n\nu}\right)^{1/3}\Phi(t). \qquad (\text{A}.2)$$

Here $\Phi(t)$ is an airy function of argument $t=n^2\omega^{2/3}(2/\nu)^{1/3}(1-\nu)$. It is easy to verify that $t\ll 1$ at large n and small k, and therefore $\Phi(t)\approx\Phi(0)$ and $\Phi'(t)\approx\Phi'(0)$.

Substituting the asymptotic expression of the Bessel function in (A.1), we obtain an expression for the photoionization cross section:

$$\sigma_{\text{ph}}(n,l)\approx\frac{4\pi^2}{3c\omega n^3}\left\{\left(\frac{2}{9\omega}\right)^{4/3}\frac{1}{\Gamma^2({}^4/_3)}+\frac{(l+{}^1/_2)^2}{\Gamma^2({}^2/_3)}\left(\frac{2}{9\omega}\right)^{2/3}\right\}. \qquad (\text{A}.3)$$

From this, in accordance with (24), the rate constant of the ionization takes in the quasiclassical approximation the form

$$K(n)=\frac{2\pi^2}{3\gamma n^3}\frac{g_f}{g_A g_A^*}\left\{\frac{(l+{}^1/_2)^2}{\Gamma^2({}^2/_3)}\left(\frac{2}{9}\right)^{2/3}\int\limits_{1/2n^2}^{\infty}R_r^4[\Delta(R_r)]^{1/3}\exp\left(\frac{\alpha}{2R_r^4T}\right.\right.$$
$$\left.-\frac{\Delta(R_r)}{2T}\right)d\Delta(R_r)+\frac{({}^2/_9)^{4/3}}{\Gamma^2({}^4/\ )}\int\limits_{1/2n^2}^{\infty}\frac{R_r^4}{[\Delta(R_r)]^{1/3}}\exp\left(\frac{\alpha}{2R\ {}^4T}-\frac{\Delta(R_r)}{2T}\right)d\Delta(R_r\}. \qquad (\text{A}.4)$$

At $1/4n^2T\ll 1$ the integrals in (A.4) can be represented in the form

$$\int\limits_{1/2n^2}^{\infty}R_r^4[\Delta(R_r)]^{1/3}\exp\left(\frac{\alpha}{2R_r^4T}-\frac{\Delta(R_r)}{2T}\right)d\Delta(R_r)$$
$$\approx R_{\text{int}}^4\exp\left(\frac{\alpha}{2R^4T}\right)\Gamma\left(\frac{4}{3}\right)(2T)^{4/3}, \qquad (\text{A}.5)$$

$$\int\limits_{1/2n^2}^{\infty}\frac{R_r^4}{[\Delta(R_r)]^{1/3}}\text{exn}\left(\frac{\alpha}{2R_r^4T}-\frac{\Delta(R_r)}{2T}\right)d\Delta(R_r)$$
$$\approx R_{\text{int}}^4\exp\left(\frac{\alpha}{2R_{\text{int}}^4T}\right)\Gamma\left(\frac{2}{3}\right)(2T)^{2/3}, \qquad (\text{A}.6)$$

where R_{int} is the point of intersection of the terms of the initial and final states.

Thus, we have found that at $n\gg 1/2T^{1/2}$

$$K(n)=\frac{4\pi^2}{3\gamma}\frac{g_f T R_{\text{int}}^4}{g_A g_{A^*} n^3}\left\{\left(l+\frac{1}{2}\right)^2\Gamma^{-2}\left(\frac{2}{3}\right)\left(\frac{2}{9}\right)^{2/3}\Gamma\left(\frac{4}{3}\right)(2T)^{1/3}\right.$$
$$\left.+\Gamma\left(\frac{2}{3}\right)\Gamma^{-2}\left(\frac{4}{3}\right)\left(\frac{2}{9}\right)^{2/3}\frac{1}{(2T)^{1/3}}\right\}\exp\left(\frac{\alpha}{2R_{\text{int}}^4 T}\right). \quad \text{(A. 7)}$$

If $T \ll 1$, then the first term in (A. 7) can be neglected. In the opposite limiting case $n \ll 1/2T^{1/2}$ we have

$$\int_{1/2n^2}^{\infty} R_r^4[\Delta(R_r)]^{1/3}\exp\left(\frac{\alpha}{2R_r^4 T}-\frac{\Delta(R_r)}{2T}\right)d\Delta(R_r)$$
$$\approx 2R_{\text{int}}^4\exp\left(\frac{\alpha}{2R_r^4 T}-\frac{1}{4n^2 T}\right)\frac{T}{(2n^2)^{1/3}}, \quad \text{(A.8)}$$
$$\int_{1/2n^2}^{\infty}\frac{R_r^4}{[\Delta(R_r)]^{1/3}}\exp\left(\frac{\alpha}{2R_r^4 T}-\frac{\Delta(R_r)}{2T}\right)d\Delta(R_r)$$
$$\approx R_{\text{int}}^4\exp\left(\frac{\alpha}{2R_{\text{int}}^4 T}-\frac{1}{4n^2 T}\right)(2T)(2n^2)^{1/3} \quad \text{(A.9)}$$

and accordingly the ionization rate constant is determined at $n \ll 1/2T^{1/2}$ by the expression

$$K(n)=\frac{4\pi^2}{3\gamma}\frac{g_f}{g_A g_{A^*}}\frac{T}{n^3}R_{\text{int}}^4\exp\left(\frac{\alpha}{2R_{\text{int}}^4 T}-\frac{1}{4n^2 T}\right)$$
$$\times\left\{\left(l+\frac{1}{2}\right)^2\Gamma^{-2}\left(\frac{2}{3}\right)\left(\frac{2}{9}\right)^{2/3}(2n^2)^{-1/3}+\left(\frac{2}{9}\right)^{4/3}\Gamma^{-2}\left(\frac{4}{3}\right)(2n^2)^{1/3}\right\}. \quad \text{(A. 10)}$$

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1)The integration is carried out by the stationary-phase method, as was done for the case of collisions of the second kind.[7] In our case $|\Delta F| = |d\Delta/dR|_{R=R_r} \approx \gamma\Delta(R_r)$, ΔF is the difference between the slopes of the curves of the potential energy at the resonance point R_r.

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On vibrational energy exchange between strongly excited polyatomic molecules

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Processes involving the exchange of vibrational energy in collisions between strongly excited polyatomic molecules are studied. Relaxation equations are obtained in the dipole-dipole approximation for the vibrational energy in a nonequilibrium molecular gas and also a kinetic equation for the distribution function of the vibrational states. The relation between the dynamic relaxation characteristics and the spectral properties of the gas is found. A comparison of the *V-V* relaxation time with the experimental data gives satisfactory results in the region of high excitation ($T_{\text{vib}} \geq 600$ K).

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The development of researches on the laser separation of isotopes by the method of photodissociation of polyatomic molecules in a strong infrared (IR) field makes timely the investigation of processes of exchange of vibrational energy in the collisions of strongly excited molecules.

The problem of the rate of collisional exchange of the vibrational energy has been studied in the example of diatomic and weakly excited polyatomic molecules.[1,2] An important feature of the vibrational spectrum in these cases is its discreteness; therefore, the calculation of the transition probabilities reduces to the problems of the excitation of an oscillator, or of transitions in a two-level system or in a system of two weakly interacting oscillators. In polyatomic molecules, the density of the vibrational spectrum increases rapidly with increase in the vibrational energy and can exceed the duration of the collision process at energies lying significantly below the dissociation threshold. It should be

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