Quenching of electron-excited molecules by electron impact

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A simple semiempirical expression is derived for the electron-impact-quenching rate constant of resonantly excited atomic and molecular states in the case of "direct" quenching in collisions. Another quenching mechanism involving the formation of an electron bound state and an excited molecule with subsequent Penning ionization of this state is considered. It is shown that this mechanism explains the anomalously high values obtained for the quenching-rate constants of excited molecules in measurements on the halides of the inert gases.

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1. The process of formation of the autoionizing state of a negative ion (in those cases when this process is possible) play an important role in the physics of electron-molecule collisions. Thus, the primary, most effective mechanism of excitation of the vibrational states of molecules by electron impact is connected precisely with this process.[1] The indicated process of capture of an electron in the autoionizing state should play a significant role in electron-impact-induced transitions between the electronic states of molecules. In the present paper we show that this mechanism explains the high quenching rate values that have been experimentally obtained[2,3] for the excimeric molecules consisting of an excited inert-gas atom and a halogen atom. To do this, we must separate the mechanism in question from the direct mechanism of quenching, in which a negative ion is not formed in the course of the electron-molecule collision. Therefore, we shall first consider the direct mechanism of quenching of an excited molecule, derive a formula for the quenching rate constant on the basis of the available information, and compare this formula with the known results. This will enable us in each specific case to use the direct mechanism to determine the quenching rate constant with calculable accuracy and to ascertain on the basis of the measured quenching rate values which mechanism determines the rate at which the process proceeds.

2. The direct mechanism of quenching of an excited molecule by electron impact corresponds to the process equation

$$e+\mathrm{AB}^{*}\rightarrow e+\mathrm{AB}+\Delta E. \tag{1}$$

Here we shall limit our analysis to the practically important case of electron energies ε small compares to the characteristic excitation energy ΔE of the atom or molecule. This will allow us to express, using the detailed balancing principle, the energy dependence of the cross section $\sigma_q(\varepsilon)$ for the quenching process under consideration in terms of the threshold dependence of the cross section $\sigma_e(\varepsilon+\Delta E)$ for excitation of an atom or a molecule by electron impact. The indicated relation has, in accordance with the detailed-balancing principle, the form

$$g_0\varepsilon\sigma_g(\varepsilon)=g_eE\sigma_e(E). \tag{2}$$

Here g_0 and g_e are the statistical weights of the particle in the ground and excited states respectively, $E=\varepsilon+\Delta E$, and the cross section values are evaluated at the energies indicated in the parentheses.

As follows from the general quantum-mechanical theory of scattering, the threshold dependence of the cross section for excitation of an atomic particle by electron impact has the square-root form[4]

$$\sigma_e(E)\propto(E-\Delta E)^{1/2}\propto\varepsilon^{1/2}. \tag{3}$$

We conclude on the basis of this relation and the relation (2) that the energy dependence of the cross section for quenching of an excited state of an atomic particle by slow electrons is given by the expression

$$\sigma_g(\varepsilon)=\frac{g_e}{g_0}\frac{\Delta E}{\varepsilon^{1/2}}\frac{d\sigma_e}{d(E-\Delta E)^{1/2}}\bigg|_{E=\Delta E}. \tag{4}$$

The indicated expression has a general character: it is valid

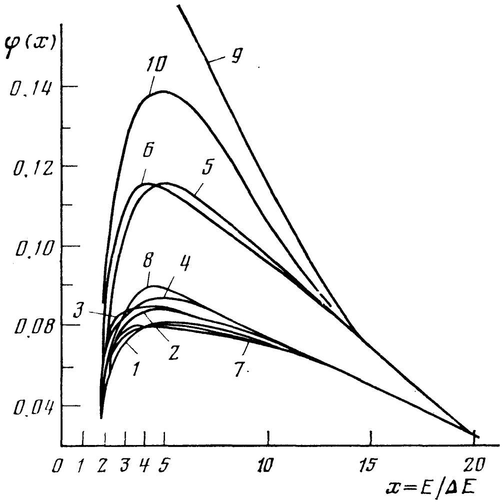

FIG. 1. Values of the function $\varphi(x)$ determined on the basis of the relation (5) from measurements (curves 1–8) and calculations in the first (curve 9) and second (curve 10) Born approximations for the following forms: 1) K (Ref. 7), 2) Na (Ref. 7), 3) Cs (Ref. 7), 4) Rb (Ref. 7), 5) Li (Ref. 8), 6) He(2^1P) (Ref. 9), 7) Ar($3p^54s$) (Ref. 10), 8) Kr($4p^55s$) Ref. 11), 9) H(B I), and 10) H(B II).

for transitions between any states of both atoms and molecules in the case when the magnitude of the electron energy ε is sufficiently small. In this case the type of transition and the sort of particle determine only the value of the derivative entering into this expression.

3. Let us determine the values of the indicated derivative in the case of a resonantly excited state from which a radiative dipole transition into the ground state is possible. In the limit of high incident-electron energies the cross section for excitation of such a state of an atom or a molecule by electron impact is equal to

$$\sigma_{0n}(\varepsilon)=\frac{4\pi}{\Delta E_{0n}}\frac{|(D_x)_{0n}|^2}{a_0}\varphi\left(\frac{E}{\Delta E_{0n}}\right)=\frac{2\pi e^4}{(\Delta E_{0n})^2}f_{0n}\varphi\left(\frac{E}{\Delta E_{0n}}\right). \tag{5}$$

Here D_{0n} is the matrix element of the dipole moment of the transition, ΔE_{0n} is the transition energy, and f_{0n} is the oscillator strength. Further, following Ref. 5, we shall assume that the formula (5) with some universal function $\varphi(x)$ $(x=E/\Delta E_{0n})$ is valid in the entire energy range. This assumption can be verified, using experimental data. The values of the function $\varphi(x)$ found on the basis of the relation (5) from the experimental data should accord closely. The results obtained with the aid of the indicated procedure for a number of atoms and transitions are shown in Fig. 1. As can be seen, the $\varphi(x)$ functions obtained from experiment for the various atoms and transitions coincide with reasonable accuracy in the region of their maximum values.

The most suitable approximation for the universal function $\varphi(x)$ is

$$\varphi(x)=(C_2+x)^{-1}\ln\left[1+C_1(x-1)^{1/2}\right]. \tag{6}$$

The function (6) then gives the correct dependence of the cross section in the region of high incident-electron energies, where $\varphi(x)=x^{-1}\ln x$, and in the near-threshold region $x-1\ll 1$, where $\varphi(x)\propto(x-1)^{1/2}$. The most suitable values of the parameters of this formula, which were found from Fig. 1, are $C_1=0.5$ and $C_2=3$. Hence we obtain for the sought derivative the value

$$\left.\frac{d\sigma_e}{d(E-\Delta E)^{1/2}}\right|_{E=\Delta E}=\frac{2\pi e^4 f_{0n}}{(\Delta E_{0n})^{5/2}}\frac{d\varphi}{d(x-1)^{1/2}}=\frac{2\pi e^4 f_{0n}}{(\Delta E_{0n})^{5/2}}a, \tag{7}$$

where

$$a=\frac{d\varphi}{d(x-1)^{1/2}}=\frac{C_1}{1+C_2}\approx 0.125.$$

It is clear that the experimental data used previously can give only an approximate value for the parameter a of interest to us. Indeed, the measurements were performed in the region of the cross section peak and at higher electron energies, whereas we are interested in the excitation cross section in the near-threshold region. To determine the parameter a, we used the cross sections experimentally obtained by Korchevoĭ and Przhonskiĭ[8] and Zapesochnyĭ[10] for the excitation of the resonance levels of the alkali metal atoms by electron impact in the near-threshold region. The results of the analysis of the indicated data are given in Table I. Also given in this table are the values, necessary for the subsequent computations, of the transition wavelength λ and the radiative lifetime τ_{0n}.

As can be seen, the approximation (6), which describes correctly the energy dependence of the cross section near the peak of this quantity, is suitable also for the description of the near-threshold energy dependence, since the spread in the a values obtained on the basis of the experimental data is significantly smaller than the errors in the experimental data used. Statistical averaging of the a values given in the table yields the quantity

$$a=0.13\pm0.007,$$

which is in accord with the indicated value $a=0.125$.

4. Thus, the cross section for quenching of resonantly excited atoms and molecules, in the case when the controlling mechanism is the direct mechanism of quenching, is given in terms of the atomic particle and transition parameters by the expressions (4) and (7). A parameter that is more convenient for the analysis of the properties of a low-temperature plasma is the electron-impact-quenching rate constant of excited atoms and molecules, which is given by the relation

$$k=\langle(2\varepsilon/m)^{1/2}\sigma_g(\varepsilon)\rangle. \tag{8}$$

Here the angle brackets denote averaging over the energy (ε) distribution function of the electrons. Averaging the expression (4) with allowance for (7), we obtain

$$k_g=\frac{g_n}{g_0}\left(\frac{2}{m}\right)^{1/2}\Delta E\left.\frac{d\sigma_e}{d(E-\Delta E_{0n})^{1/2}}\right|_{E=\Delta E_{0n}}=1.1\,[\text{см}^{-1/2}]\,\frac{\lambda^{7/2}}{\tau_{0n}},$$

$$\frac{1}{\tau_{0n}}=\frac{g_e}{g_0}\frac{f_{0n}8\pi^2e^2}{mc\lambda}. \tag{9}$$

TABLE I. Values of the parameter a determined on the relation (5) from measurements of the cross section for resonance excitation of atoms of the alkali metals in the near-threshold region.

Atom	$K(4^2P_{1/2},\ {}^3/_2)$		$Rb(5^2P_{1/2},\ {}^3/_2)$		$Cs(6^2P_{1/2},\ {}^3/_2)$	
ΔE_{0n}, eV	1.61;	1.62	1.56;	1.59	1.45;	1.39
λ, Å	7699;	7665	7948;	7800	8521;	8943
τ_{0n}, nsc	26.7;	27.2	29.3;	26.7	34;	30.2
a	0.11(Ref. 8)	0.12 (Ref. 10)	0.12 (Ref. 10)	–	0.14(Ref. 10)	0.15 (Ref. 8)

TABLE II. Quenching rate constants of excimer molecules.

Molecule	Ar_2	Kr_2	Xe_2	ArF	KrF	XeF	XeBr	XeCl
λ, Å	1261	1457	1720	1933	2484	3521	2820	3080
τ, nsec	5±0.6	6±2	5.7±1.1	4	8±1	16±2	15±3	11±1
k_g, 10^{-8} cm^3/sec	0.13	0.15	0.23	0.9 23 [2]	1.1 3.1(Ref.12) 20(Ref. 2)	1.8 6.2(Ref.12) 40(Ref. 3)	0.8	1.4

Here λ is the wavelength of the transition in question and τ_{0n} is the lifetime of this transition. The expression (9) obtained for the quenching rate constant depends neither on the distribution function nor on the mean electron energy. This fact is directly connected with the energy dependence of the quenching cross section (4) and the near-threshold square-root dependence of the atomic-particle excitation cross section (3).

The quenching-rate-constant values computed on the basis of the expression (9) for the same excimer molecules are compared in Table II with the results of measurements[2,3] and computations carried out in the Born approximation.[12] The radiative lifetimes given in Table II are the result of a statistical processing of the published data.[13]

Comparing the results of our calculation with those obtained by Jobe and St. John[12] in the Born approximation, we note that the discrepency between them is quite natural. The Born approximation usually overestimates the excitation cross section in the peak region by a factor of two to three (see Refs. 1 and 14). The same thing can be expected in the near-threshold region. The disagreement between our results and the experimental data indicates the presence of an additional quenching mechanism for halogen-containing molecules. Our next problem is the determination of this mechanism and the investigation of the characteristics associated with its manifestation.

5. Let us construct the pattern of potential terms for those states of the excited halogenous molecule which participate in the transition in question. As an example, in Fig. 2 we show the terms of the system KrF*. The analysis performed below is based on this particular system. The excimeric molecule KrF* has three states with an ionic chemical bond ($Kr(^2P) + F^-(^1S)$), which are customarily denoted by $B_{1/2}$, $C_{1/2}$, and $D_{3/2}$, where the subscript characterizes the component of the total angular momentum of the electron along the axis joining the nuclei. The electronic terms of these states were taken from Ref. 15. Let us note that the energy of dissociation of the $B_{1/2}$ state, which corresponds to the disintegration of the molecule into Kr^+ and F^-, is[15] 5.30 eV. From this it follows that the lowest vibrational level of this molecule is located 1.2 eV below the $Kr(^3P_2) + F^-$ term in the case of infinite separation between the particles.

Let us consider the intraction between Kr* and F^-. Since the excited krypton atom has the electron shell $Kr(4p^55s)$, it follows that at sufficiently large distances between the nuclei, while the inner-shell electrons do not participate in the interaction, there is a single interaction potential for the atoms. Indeed, this interaction stems from the interaction of the 5*s* electron of the krypton atom with the negative fluorine ion, which has a closed electron shell. This system is characterized by a single electronic term, so that, for large distances between the nuclei, the electronic terms of the system $Kr^* + F^-$ that correspond to the various multiplet states of $Kr(4p^55s)$ run parallel to each other. Therefore, below we shall consider only the lowest of these terms.

In the region of interaction energies of the order of tenths of an electron volt, the major role is played by the exchange interaction corresponding to the overlap of the electron shells of the interacting particles. So long as the 5*s* shell of the krypton atom is distorted slightly, this interaction corresponds to repulsion. Estimates in which the measured interaction potentials for negative halogen ions and light inert-gas atoms in the ground state are used[16] show that, if we continue this interaction into the region of small distances, then it will correspond in the region above the bottom of the $KrF(B_{1/2})$ well to a Kr^*-F^- repulsion with an energy of nearly 1 eV, i.e., the Kr^*F^- term will lie above the bottom of th $KrF(B_{1/2})$ well at a distance of roughly 2 eV. In fact, such a continuation is inadmissible. An effective ion-ion interaction occurs in the system in question in the region of Kr^*-F^- separations where this terms approaches the $KrF(B_{1/2})$ term. This implies that the 5*s* shell undergoes drastic distortion. This electron shifts in the direction of the negative ion. In this configuration, it only partially screens off the positive krypton ion. The resulting ion-ion coupling leads to attraction between the particles. As to the valence 5*s* electron, its link with the krypton ion weakens as the orbit distortion increases, and at some distance between the nuclei

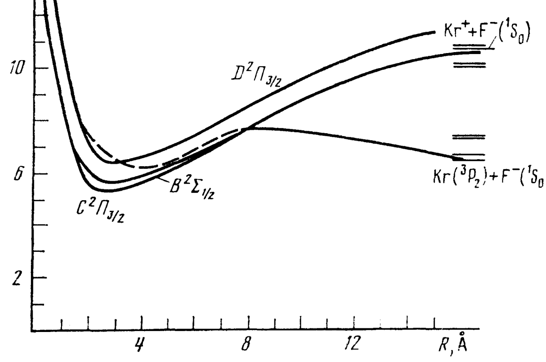

FIG. 2. Terms of the quasimolecule composed of a krypton ion or excited atom and a negative fluorine ion.

it vanishes. The state Kr^*-F^- becomes an auto-ionized state. Figure 2 depicts the behavior of this term.

6. The appearance of the auto-ionized state of Kr^*F^- leads to the appearance of a new quenching mechanism for molecules of the type under consideration. This process proceeds according to the scheme

$$KrF^* + e \to Kr^*F^-, \tag{10}$$

$$Kr^*F^- \to Kr + F + e. \tag{11}$$

The second stage of the process is similar to the Penning process in the case of the interaction of a metastable krypton atom with a negative fluorine ion from which an electron is detached.

Let us examine the quenching rate constant of an excimer molecule for the quenching mechanism (10), (11). The rate constant for electron capture by the excimer molecule, i.e., for the process (10) is equal to[1]

$$k_c = \frac{(2\pi)^{3/2}\hbar^2}{(mT)^{3/2}} \sum_n \langle \Gamma_1(R) e^{-U_n/T} \rangle, \tag{12}$$

Where T is the electron temperature, Γ_1 is the width of the auto-ionization level corresponding to the decay of the state into an electron and an excited molecule, and U_n is the excitation energy of the corresponding level. We shall assume that $U_n = U_0 + n\hbar\omega$, where U_0 is the excitation energy of the lowest auto-ionizing level and $\hbar\omega$ is the energy of the vibrational quantum for the auto-ionization state. Then

$$\sum_n e^{-U_n/T} = e^{-U_0/T}(1 - e^{-\hbar\omega/T})^{-1}.$$

Further, the probability for decay of the auto-ionizing state in the channel (11) is equal to $\Gamma_2/(\Gamma_1 + \Gamma_2)$, where $\Gamma_2(R)$ is the partial auto-ionizing level width corresponding to the decay channel (11). Hence we find the rate constant for quenching of the excimer molecule according to the scheme under consideration:

$$\begin{aligned} k_g &= \frac{(2\pi)^{3/2}\hbar^2}{(mT)^{3/2}} \sum_n \left\langle \frac{\Gamma_1(R)\Gamma_2(R)}{\Gamma_1(R)+\Gamma_2(R)} e^{-U_n/T} \right\rangle \\ &= \frac{(2\pi)^{3/2}\hbar^2 \exp(-U_0/T)}{(mT)^{3/2}[1-\exp(-\hbar\omega/T)]} \left\langle \frac{\Gamma_1\Gamma_2}{\Gamma_1+\Gamma_2} \right\rangle \end{aligned} \tag{13}$$

and in the limit $\hbar\omega \ll T$ we have

$$k_g = \frac{(2\pi)^{3/2}\hbar^2 e^{-U_0/T}}{m^{3/2}T^{1/2}\hbar\omega} \left\langle \frac{\Gamma_1\Gamma_2}{\Gamma_1+\Gamma_2} \right\rangle. \tag{14}$$

Let us compare the expression (14) obtained for the rate constant for quenching of excimer molecules through the above-considered mechanism with the experimental data given in Table II. Assuming that $\hbar\omega = 330\ \text{cm}^{-1}$ for the molecule KrF^* and that $T_e \sim 1$, in accordance with the estimates given in Refs. 2 and 3, we find after equating the measured and computed quenching rate constants for this molecule that

$$e^{-U_0/T} \left\langle \frac{\Gamma_1\Gamma_2}{\Gamma_1+\Gamma_2} \right\rangle \approx 0.02\ \text{eV}.$$

A typical value of the width of the Penning process for an internuclear separation ≈ 2.5 Å, which corresponds to the equilibrium separation in the excimer molecule KrF^*, is of the order of 0.1 eV (see Ref. 13). It is to be expected that the quantity Γ_2 will have the same order of magnitude. It follows from this and the above relation that $\Gamma_1 \ll \Gamma_2$. This condition leads to the relation

$$\langle \Gamma_1 \rangle \exp(-U_0/T) \approx 0.02\ \text{eV},$$

which, as can easily be verified, is not at variance with either the computational scheme or the assumptions made above about the orders of magnitude of the quantities Γ_1, U_0, and T_e. Thus, we can presume that the proposed mechanism of the quenching process is able to account for the experimental data. It should be noted that the formulated condition $\Gamma_1 \ll \Gamma_2$ leads to the important conclusion that the process of excitation by electron impact of the vibrational states of the excited molecules has an insignificant effect on the character of the quenching of these molecules.

7. Thus, the analysis performed above leads us to the conclusion that two mechanisms underlie the quenching of electron-excited molecules by electron impact. The first of these mechanisms (the "direct" mechanism) has a general character, and is connected with the interaction between the incident and weakly-bound electrons. The quenching rate constant characterizing this mechanism does not, at low electron energies, depend on either the form of the distribution function or on the mean electron energy, and is given by the relation (9). But if by chance the molecules contain atoms of the electronegative elements, then the "indirect" quenching mechanism connected with the capture of an electron in the auto-ionizing state of the negative molecular ion, with subsequent Penning-ionization-induced decay of this state, may turn out to be significantly more effective. The estimates carried out above show that the anomalously high quenching-rate-constant values experimentally observed for the excimer molecules can be attaines when the above-described quenching mechanism obtaines and reasonable assumptions are made about the values of the width of the auto-ionizing state with respect to capture and Penning ionization. It is to be expected that the indicated mechanism will play an important role in the quenching of a broad class of diatomic molecules (e.g., CO, O_2, CN, NO, etc.).

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