IONIZATION CONSTANT IN THE PENNING PROCESS

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The Penning effect (ionization of an atom on collision with a metastable atom) is investigated for the most widespread case, when the probability of the ionization per collision is small. A general expression is obtained for the ionization constant. It follows from this expression that in the limit of low temperatures the constant is inversely proportional to the square root of the temperature, and in the limit of high temperatures it is independent of the temperature. The spectrum of the ionization electrons is independent of the temperature in the limits of low and high temperatures. The relative number of molecular ions produced in the Penning process decreases with increasing temperature, and in the low-temperature limit it is independent of the temperature. Some of the results are experimentally confirmed.

THE Penning effect^[1-2] is a process of ionization of an atom colliding with a metastable atom, the ionization potential of the destroyed atom being lower than the excitation energy of the metastable atom. Investigations^[3-5] have shown that the cross section of the Penning process is in most cases much smaller than the gas-kinetic cross section, i.e., the ionization probability is small when the particles come close together. In the present article we obtain information concerning the constant of the Penning process for just this case.

We introduce the quantity w(R)—the frequency of decay per unit time of a quasimolecule made up of a metastable atom and an impurity atom with a distance R between their nuclei. Then the probability of ionization of the impurity atom in collisions with a given impact parameter ρ is equal to

$$P_{i} = 1 - \exp\left\{-\int_{-\infty}^{+\infty} w \, dt\right\} \approx \int_{-\infty}^{+\infty} w \, dt = \frac{2}{v} \int_{r_{0}}^{\infty} w(R) \, dR \left(1 - \frac{\rho^{2}}{R^{2}} - \frac{U}{E}\right)^{-\psi},$$
(1)

where v is the relative velocity of collision of the particles, E is their energy in the c.m.s., $r_0(\rho)$ is the shortest distance between them, and U(R) is the potential of the interaction of the metastable atom with the impurity atom at a given total spin of the quasimolecule.

The cross section of the Penning process is $\sigma_i = \int P_i d\sigma$, where $d\sigma = 2\pi\rho d\rho$ is the differential cross section of the collision. Substituting (1) in this formula, changing the order of integration, and integrating with respect to $d\rho$, we reduce the cross section to the form

$$\sigma_{i} = \frac{4\pi}{v_{R}} \int_{min}^{\infty} R^{2} w(R) \sqrt{1 - \frac{U(R)}{E}} dR, \qquad (2)$$

where R_{min} is the minimal approach distance in the case of frontal impact $U(R_{min}) = E$.

Practical interest attaches to the experimentally obtained rate constant of the Penning process $k_i = \langle v\sigma_i \rangle$, where the averaging is over a Maxwellian distribution of the atoms. It is equal to

$$k_{i} = 8 \gamma \overline{\pi} \int_{0}^{\infty} e^{-x} dx \int_{R_{min}}^{\infty} R^{2} w(R) \sqrt{x - \frac{U(R)}{T}} dR, \qquad (3)$$

where x = E/T; T is the temperature of the system. The interaction potential of a metastable atom with an impurity atom has the form of a well so that when $R \le R_0$ the potential $U(R) \ge 0$, i.e., it corresponds to repulsion, and when $R \ge R_0$ the interaction potential $U(R) \le 0$, i.e., it corresponds to attraction $(U(R_0)$ = 0). The minimum value of the interaction potential is -D, where D is the dissociation energy of the molecule made up of the metastable atom and the impurity atom. The interaction potential has only one minimum.

Using the foregoing properties of the interaction potential, let us calculate the ionization constant (3), changing the integration limits in this formula. We obtain

$$k_{i} = 4\pi \int_{0}^{R_{0}} R^{2} w(R) e^{-U(R)/T} dR + 4\pi \int_{R_{0}}^{\infty} R^{2} w(R) \sqrt{1 - \frac{4U(R)}{\pi T}} dR.$$
 (4)

In the second term, the integral of the form

 $\int_{0}^{\infty} \sqrt{x + t} e^{-x} dx$ was replaced here by the function

 $\sqrt{1/4\pi + t}$, which gives the correct values of this integral at large and small values of the parameter and approximates this integral well in the intermediate region. We note that in the first term $U \ge 0$ and in the second $U \le 0$. Thus, using the assumption that the probability of the Penning process is low, we have obtained a rather simple expression (4) for the constant of this process. An analysis of formula (4) makes it possible to obtain information concerning this constant.

We introduce $a = |w'(R_0)/w(R_0)|$ and $\beta = |U'(R_0)/D|$, so that $1/\alpha$ and $1/\beta$ are characteristic distances over which the given quantities vary noticeably $(\alpha \gtrsim \beta)$. The quantities α and β are of the order of atomic dimensions. As follows from (4), at low temperatures the constant of the Penning process is

$$k_{i} = \frac{8 \gamma \overline{\pi}}{\gamma \overline{T}} \int_{R_{a}}^{\infty} R^{2} w(R) \gamma \overline{[-U(R)]} \, dR, \quad T \ll \frac{\beta}{\alpha} D. \tag{5}$$

The ionization occurs here in the region of attraction between the metastable atom and the impurity atom. It is interesting that the constant for the capture of the metastable atom by the impurity atom is proportional at low temperatures to $T^{1/6}(U(R) = -C/R^6 \text{ as } R \to \infty)$. At temperatures at which these constants are of the same order, formula (5) no longer holds, since the probability of ionization in these collisions is of the order of unity. At lower temperatures, the constant of the Penning process coincides with the capture constant.

At high temperatures $T \gg \beta D/\alpha$, the ionization occurs predominantly in the region of repulsive interaction of the particles, and the ionization constant is determined by the first term in (4). The constant of the Penning process increases with increasing temperature, reaching as $T \rightarrow \infty$ the value

$$k_i = 4\pi \int_{\alpha}^{R_0} R^* w(R) dR, \quad T \gg \frac{\beta}{\alpha} D.$$
 (6)

As before, we have assumed that the ionization probability is low.

Formula (4) also gives information concerning the distribution of the energies of the ionization electrons. Indeed, this formula makes it possible to determine the probability of autoionization at a given distance between nuclei, when the energy of the electrons liberated at a given distance between nuclei is strictly fixed. As follows from (4), the spectrum of the ionization electrons does not vary with temperature in the limits of low and high temperatures.

According to (4), when the temperature is increased, a contribution to the constant of the Penning process is made by ever decreasing distances between nuclei. Therefore the relative number of molecular ions produced in the Penning effect increases with decreasing temperature. When $T \ll \beta D/\alpha$, their relative number does not vary with temperature. This result was confirmed experimentally. Hotop and Niechaus^[6] deter-

mined, from the ionization-electron spectrum, the relative number of the produced molecular ions at temperatures of 90° and 320°K for collisions between metastable helium atoms and atoms of argon, krypton, and xenon. In some cases it is noticeably higher at low temperature, and in others it hardly varies with temperature. In particular, in the case of He(2³S)-Ar collisions, this number is practically independent of the temperature region $T \ll \beta D/\alpha$. In this region of temperature, the ionization constant varies in proportion to $T^{-1/2}$. This result is confirmed by an experimental measurement of the cross section for this pair^[7], carried out in the temperature region 192–500°K.

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