LETTER TO THE EDITOR

Collisional ionisation of high-Rydberg atoms. Diffusive mechanism

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Abstract. The ionisation of highly excited Rydberg atoms in collisions with ground-state atoms is considered. The stationary diffusion-like mechanism of the ionisation is presented. The investigation is based on the Fokker–Planck equation. Analytical expressions for the probabilities of stationary diffusive ionisation are obtained and applied for the explanation of experimental results on the ionisation of highly excited Rydberg states of caesium in collisions with ground-state Cs atoms. It is concluded that the diffusive mechanism is the main mechanism for collisional ionisation of Rydberg atoms with $n \gtrsim 25$-30.

Recently ionisation probabilities of high-Rydberg atoms ($n \gtrsim 20$) in thermal collisions with ground-state atoms have been measured (Niemax 1983, Švedas and Stakišaitis 1984, Weiner and Boulmer 1986, Herrmann *et al* 1986, Švedas 1987). Contrary to the collisional ionisation of states with small and moderate principal quantum numbers ($n \lesssim 15$) (Devdariani *et al* 1978, Klucharev *et al* 1980, Boulmer *et al* 1983, Zagrebin and Samson 1985), recent results cannot be explained by the theory of direct collisional ionisation (Duman and Shmatov 1980, Mihajlov and Janev 1981). In the present work we show that the multistep (diffusion-like) mechanism for collisional ionisation of high-Rydberg atoms (Kaulakys *et al* 1984) can explain experimental results on the ionisation of caesium with $n \gtrsim 20$ in collisions with ground-state Cs atoms (Herrmann *et al* 1986, Švedas 1987).

The ionisation rate constants K_i of alkali Rydberg atoms with $n \gtrsim 20$ by thermal collisions with ground-state parent atoms are of the order of or less than 10^{-9} cm^3 s^{-1}, i.e. $K_i \lesssim 0.2$ au (Weiner and Boulmer 1986, Švedas 1987). Thus the ionisation rate constants are considerably smaller than the l-mixing rate constants of alkali Rydberg atoms, which are of the order of 100 au (see Hugon *et al* 1983 and references therein). Collisions of ground-state atoms with the Rydberg atom may also induce transitions between the hydrogenic manifolds $n \to n'$. For $2vn^2 \ll 1$ (i.e. $n \lesssim 30$-50 for thermal collisions) the dominant transitions are $n \to n \pm 1$, and the rate constant of such transitions was given by Kaulakys (1986) as

$$K_{n,n \pm 1} = 4\pi\sigma_e(p_t)\langle v \rangle^4 n^7 \qquad 2vn^2 \ll 1 \qquad (1)$$

where $\langle v \rangle$ is the average collision velocity and $\sigma_e(p_t)$ is the cross section for elastic scattering of an electron given an impulse $p \gtrsim p_t = (2vn^3)^{-1}$ by the ground-state atom. The rate constant $K_{n,n+1}$ as a function of n reaches its maximum value $K_{n,n+1}^{\max} \simeq 0.13\sigma_e(p_t)\langle v \rangle^{1/2}$ at the point $n_{\max} \simeq \langle v \rangle^{-1/2}$ (Kaulakys 1986). The cross sections for elastic scattering of slow electrons by alkali atoms are of the order of $(0.5$-$1) \times 10^4$ au (see Hugon *et al* 1983, Kaulakys 1986). According to equation (1), $K_{n,n+1} \gtrsim K_i$ if

$n \gtrsim 20$ and $K_{n,n\pm1}$ exceeds K_i by about two orders of magnitude if $n \sim 40\text{--}80$. In such a case collisional redistribution of the population of the Rydberg levels is strong and the process of multistep transitions between the Rydberg states is diffusion-like. In such a manner, some of the Rydberg electrons can reach the ionisation continuum and give rise to the ionisation of Rydberg atoms.

Under the stationary conditions the diffusive ionisation flow is (see e.g. Lifshitz and Pitayevsky 1979)

$$j = D(\varepsilon)\frac{\mathrm{d}}{\mathrm{d}\varepsilon}\frac{f(\varepsilon)}{f_0(\varepsilon)}\bigg|_{\varepsilon=0} \tag{2}$$

where $f_0(\varepsilon) = \varepsilon^{-5/2}\exp(\varepsilon/T)$ is the Boltzmann distribution with T the temperature of the gas, $D(\varepsilon) = B(\varepsilon)f_0(\varepsilon)$ and $B(\varepsilon)$ is the diffusion coefficient of electrons in the energy space of the Rydberg atom, given by

$$B(\varepsilon) = \tfrac{1}{2}N\sum_{n'} K_{n,n'}(\Delta\varepsilon_{n,n'})^2. \tag{3}$$

Here N is the density of the ground-state atoms, $\Delta\varepsilon_{n,n'} = \varepsilon' - \varepsilon$ and $\varepsilon = \tfrac{1}{2}n^{-2}$ is the binding energy of the Rydberg electron. In stationary conditions the probability density $f(\varepsilon)$ of the electrons in the energy space of the Rydberg atom is the solution of the stationary Fokker–Planck-type diffusion equation (Lifshitz and Pitayevsky 1979, Kaulakys *et al* 1984)

$$\frac{\partial}{\partial\varepsilon}\left(D(\varepsilon)\frac{\partial}{\partial\varepsilon}\frac{f(\varepsilon)}{f_0(\varepsilon)}\right) + \gamma\delta(\varepsilon - \varepsilon_0) - W(\varepsilon) = 0 \tag{4}$$

where γ is the rate of generation of Rydberg atoms with energy ε_0 and $W(\varepsilon)$ is the quenching rate of the Rydberg atoms.

For Rydberg atoms with sufficiently high n, the dependences of f_0, B and W on the energy are the power-type dependences

$$f_0(\varepsilon) = C\varepsilon^{-r} \qquad B(\varepsilon) = A\varepsilon^s \qquad W(\varepsilon) = f(\varepsilon)\varepsilon^q/\tau \tag{5}$$

where C, A, τ, r, s and q are constants. In reality, the exponential in the Boltzmann distribution may be neglected when $\varepsilon \lesssim T$. The expression for the diffusion coefficient (3) reduces to the result of Pitayevsky (1962) (see Kaulakys 1986)

$$B(\varepsilon) = (2^{9/2}/3\pi)N\sigma_t(p_t)v_T^2\varepsilon^{3/2} \qquad \varepsilon \lesssim v_T = (2T/\mu)^{1/2} \tag{6}$$

where $\sigma_t(\approx\sigma_e)$ is the momentum transfer cross section for electron–perturber elastic collisions and μ is the reduced mass of the colliding atoms. The quenching rate of the Rydberg atoms caused by radiative relaxation follows from the Kramers formula (see e.g. Sobel'man *et al* 1981) and may be written as

$$W(\varepsilon) = f(\varepsilon)\varepsilon^{5/2}/\tau \qquad \tau = \tfrac{3}{64}\sqrt{3}\,\pi c^3/\ln(n_2/n_g^*). \tag{7}$$

Here $c = 137.036$ au is the velocity of light, n_g^* and n_2 are the effective principal quantum numbers of the ground state and a certain Rydberg state (see below), respectively.

The substitution of equations (5) into equation (4) yields

$$\varepsilon^2\frac{\mathrm{d}^2\varphi}{\mathrm{d}\varepsilon^2} - (r-s)\varepsilon\frac{\mathrm{d}\varphi}{\mathrm{d}\varepsilon} - \frac{\varepsilon^{2-s+q}}{A\tau}\varphi = -\frac{\gamma\varepsilon^{2+r-s}}{A}\delta(\varepsilon - \varepsilon_0) \tag{8}$$

where $\varphi(\varepsilon) = f(\varepsilon)/f_0(\varepsilon)$. The solution of the homogeneous equation may be written as (Kamke 1959)

$$\varphi(\varepsilon) = C_1 \varepsilon^P I_\nu(y) + C_2 \varepsilon^P K_\nu(y). \tag{9}$$

Here C_1 and C_2 are constants,

$$y = 2\varepsilon^{m/2}/m(A\tau)^{1/2} \qquad \nu = 2p/m \qquad p = (r-s+1)/2 \qquad m = 2-s+q \tag{10}$$

I_ν and K_ν are modified Bessel functions of the first and second kind, respectively. The general solution of equation (8) may be obtained in the usual way. Taking into account that the Wronskian $W\{K_\nu(z), I_\nu(z)\} = K_\nu(z) I'_\nu(z) - K'_\nu(z) I_\nu(z) = 1/z$ (Abramowitz and Stegun 1972) we have

$$\varphi(\varepsilon) = \begin{cases} C_1 \varepsilon^P I_\nu(y) + C_2 \varepsilon^P K_\nu(y) & \varepsilon \leqslant \varepsilon_0 \\[2mm] \dfrac{2\gamma(\varepsilon\varepsilon_0)^P}{Am} \Big(I_\nu(y_0) K_\nu(y) - K_\nu(y_0) I_\nu(y) \Big) + C_1 \varepsilon^P I_\nu(y) + C_2 \varepsilon^P K_\nu(y) & \varepsilon \geqslant \varepsilon_0. \end{cases} \tag{11}$$

The solution (11) must be suplemented by the boundary conditions corresponding to the process of ionisation of the Rydberg atom. The condition implying the absence of free electrons and, consequently, the absence of electrons with very small binding energy ($\varepsilon \to 0$), is $\varphi(0) = 0$. Using the limiting forms of the Bessel functions

$$I_\nu(y) = y^\nu/2^\nu \Gamma(\nu+1) \qquad K_\nu(y) = 2^{|\nu|-1} \Gamma(|\nu|) y^{-|\nu|} \qquad y \to 0 \tag{12}$$

we can show from equations (2) and (11) that the ionisation flow $j \neq 0$ only if $p > 0$ and $m > 0$. In such a case the boundary condition $\varphi(0) = 0$ according to equations (11) and (12) forces $C_2 = 0$. The probability (efficiency) P_i of diffusive ionisation of Rydberg atoms under stationary conditions is the ratio of the diffusive ionisation flow j to the rate of generation of the Rydberg atoms γ. Substitution of equation (11) into equation (2) according to equations (10) and (12) yields

$$P_i = C_1 A/\gamma m^{\nu-1} \Gamma(\nu)(A\tau)^{\nu/2}. \tag{13}$$

The constant C_1 depends on the second boundary condition for certain values of $\varepsilon_2 > \varepsilon_0$. The condition implying the absence of electrons with binding energy $\varepsilon \geqslant \varepsilon_2$ due to quenching of Rydberg atoms with small principal quantum numbers is $\varphi(\varepsilon_2) = 0$. From equation (11) this condition yields

$$C_1 = \frac{2\gamma\varepsilon_0^P}{Am} \left(K_\nu(y_0) - I_\nu(y_0) \frac{K_\nu(y_2)}{I_\nu(y_2)} \right)$$

$$y_{0,2} = \frac{2\varepsilon_{0,2}^{m/2}}{m(A\tau)^{1/2}}. \tag{14}$$

The condition which implies the absence of a flow of electrons for certain values of $\varepsilon_2 > \varepsilon_0$ (as a consequence of the large intervals between neighbouring energy levels of the Rydberg atom) gives

$$C_1 = \frac{2\gamma\varepsilon_0^P}{Am} \left(K_\nu(y_0) + I_\nu(y_0) \frac{K_{\nu-1}(y_2)}{I_{\nu-1}(y_2)} \right). \tag{15}$$

Substitution of equations of (14) and (15) into equation (13) gives

$$P_i = \frac{2^{1-\nu}y_0^\nu}{\Gamma(\nu)}\left(K_\nu(y_0) - I_\nu(y_0)\frac{K_\nu(y_2)}{I_\nu(y_2)}\right) \qquad \varphi(\varepsilon_2) = 0 \qquad (16)$$

$$P_i = \frac{2^{1-\nu}y_0^\nu}{\Gamma(\nu)}\left(K_\nu(y_0) + I_\nu(y_0)\frac{K_{\nu-1}(y_2)}{I_{\nu-1}(y_2)}\right) \qquad \left.\frac{d\varphi}{d\varepsilon}\right|_{\varepsilon=\varepsilon_2} = 0. \qquad (17)$$

For $y_2 \gg 1$ or $\varepsilon_2 \gg \varepsilon_0$ equations (16) and (17) reduce to

$$P_i = 2^{1-\nu}y_0^\nu K_\nu(y_0)/\Gamma(\nu). \qquad (18)$$

Thus, the ionisation probability is not very sensitive to the second boundary condition. The limiting forms of P_i according to equation (18) are

$$P_i = 1 - \frac{\Gamma(1-\nu)}{\Gamma(1+\nu)}\left(\frac{y_0}{2}\right)^{2\nu} + \frac{1}{1-\nu}\left(\frac{y_0}{2}\right)^2 + \ldots \qquad y_0 \ll 1 \qquad \nu \neq 1 \qquad (19)$$

$$P_i = \frac{\sqrt{\pi}}{\Gamma(\nu)}\left(\frac{y_0}{2}\right)^{\nu-1/2} \exp(-y_0)\left(1 + \frac{4\nu^2-1}{8y_0} + \ldots\right) \qquad y_0 \gg 1. \qquad (20)$$

For the case considered above (equations (5)-(7)) we have $r = \frac{5}{2}$, $s = \frac{3}{2}$, $q = \frac{5}{2}$. Therefore, equations (10) give $m = 3$, $p = 1$, $\nu = \frac{2}{3}$ while equations (18)-(20) yield

$$P_i = -3^{1/3}\Gamma(\tfrac{1}{3})\text{Ai}'(\eta) \qquad\qquad \eta = (\tfrac{3}{2}y_0)^{2/3} = \varepsilon_0/(A\tau)^{1/3} \qquad (21)$$

$$P_i = 1 - 1.18y_0^{4/3} + 0.75y_0^2 + \ldots \qquad\qquad y_0 = \tfrac{2}{3}\varepsilon_0^{3/2}/(A\tau)^{1/2} \lesssim 0.5 \qquad (22)$$

$$P_i = 1.17y_0^{1/6}\exp(-y_0)(1 + \tfrac{7}{72}y_0^{-1} + \ldots) \qquad y_0 \gtrsim 1. \qquad (23)$$

Here the relationship $K_{2/3}(y_0) = -\pi 3^{1/2}\eta^{-1}\text{Ai}'(\eta)$ between the Bessel function $K_{2/3}(y_0)$ and the derivative of the Airy function $\text{Ai}'(\eta)$ was used (Abramowitz and Stegun 1972).

From equation (6) we have $A = \frac{32}{3}\sqrt{2}\sigma_t p/\pi\mu$ with p being the pressure (in atomic units) of the ground-state atoms. Using equations (7) and (10) we can write

$$y_0 = [\mu \ln(n_2/n_g^*)/c^3\sigma_t p]^{1/2}/3^{5/4}n_0^{*3} \qquad (24a)$$

in atomic units or

$$y_0 = 10^5[\mu \ln(n_2/n_g^*)/\sigma_t p]^{1/2}n_0^{*-3} \qquad (24b)$$

where p is in mTorrs, μ is in atomic mass units, σ_t is in atomic units and $n_0^* = (2\varepsilon_0)^{-1/2}$ is the initial effective principal quantum number.

In figures 1 and 2 plots of theoretical ionisation probabilities for Rydberg states of caesium in collisions with ground-state Cs atoms are shown together with experimental results. The values of the parameters n_g^*, n_2 and σ_t have been taken as follows. $n_g^* = (2\varepsilon_g)^{-1/2} = 1.87$ with ε_g being the binding energy of the electron in the ground-state Cs atom. $n_2 = 20$, hence the diffusive ionisation of the Rydberg states with $n^* \lesssim 20$ is hardly probable. Note that the ionisation probability is very insensitive to n_2 (see equations (21)-(24)). The momentum transfer cross section $\sigma_t = 8.5 \times 10^3$ au for elastic scattering of electrons by the ground-state Cs atom was chosen for fitting the theoretical ionisation probabilities of Rydberg atoms with $n^* \gtrsim 30$ to the experimental results of Herrmann *et al* (1986) and Švedas (1987). Such a value of σ_t is close to the value used by Hugon *et al* (1983) and Kaulakys (1986) for the description of inelastic collisions between Rydberg and ground-state Rb atoms. One can affirm that equations (21)-(24) describe rather well the dependences of the ionisation probabilities on the
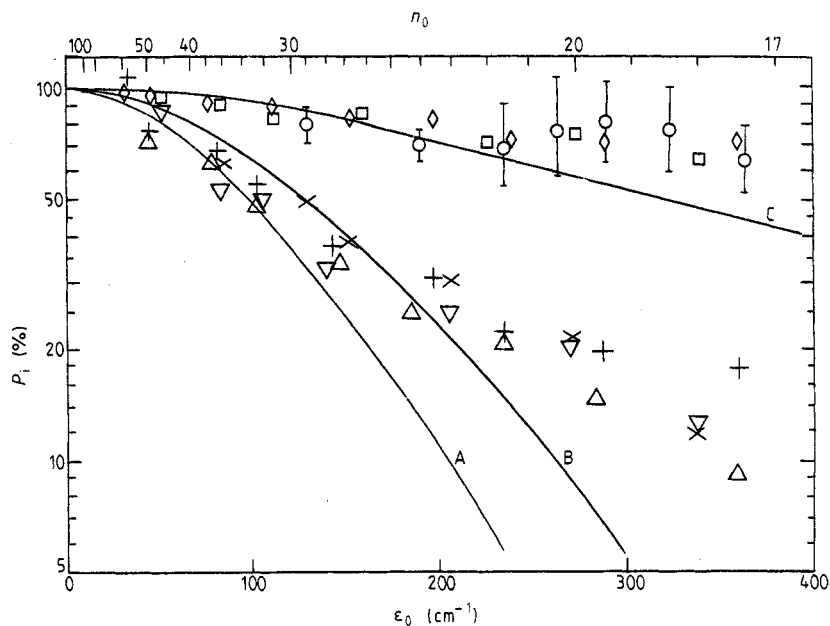
Figure 1. Collisional ionisation probabilities P_i for Rydberg states of caesium in collisions with ground-state Cs atoms plotted against the binding energy of the Rydberg electron ε_0. Experiment: ∇, $nS_{1/2}$ states; $\triangle$, $nD_{5/2}$ states, $p = 0.17$ mTorr; $\times$, $nS_{1/2}$ states; $+$, $nD_{5/2}$ states, $p = 0.37$ mTorr; $\square$, $nS_{1/2}$ states; $\diamond$, $nD_{5/2}$ states, $p = 5.4$ mTorr, Herrmann *et al* (1986); $\dot{\bigcirc}$, nP states, $p = 5.6$ mTorr, Švedas (1987). The curves A, B and C show the theoretical calculations of diffusive ionisation probabilities, equations (21)-(24), for $p = 0.17$, 0.37 and 5.5 mTorr, respectively, with $n_g^* = 1.87$, $n_2 = 20$ and $\sigma_t = 8.5 \times 10^3$ au.
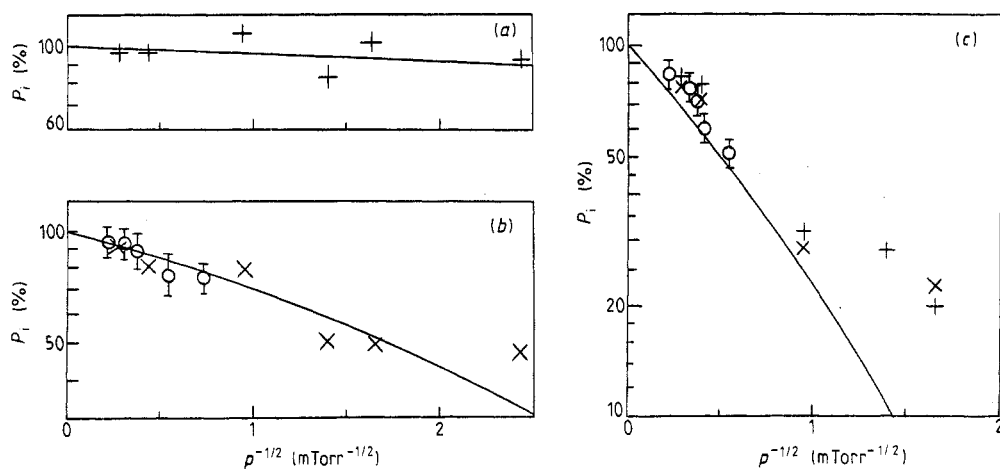

Figure 2. Collisional ionisation probabilities P_i for different binding energies of the Rydberg electron ε_0 plotted against $p^{-1/2}$ where p is the pressure of ground-state Cs atoms. (a) $\varepsilon_0 \simeq 34$ cm^{-1}; (b) $\varepsilon_0 \simeq 130$ cm^{-1}; (c) $\varepsilon_0 \simeq 290$ cm^{-1}. Experiment: $\times$, $nS_{1/2}$ states; $+$, $nD_{5/2}$ states, Herrmann *et al* (1986); $\dot{\bigcirc}$, nP states, Švedas (1987). The curves show the theoretical calculations of diffusive ionisation probabilities, equations (21)-(24), with parameters as in figure 1.

binding energy of the Rydberg electron as well as on the pressure of the ground-state atoms if $n_0^* \geqslant 25\text{-}30$. For $n^* \leqslant 25$, direct ionisation of Rydberg atoms is efficient; and since observable ionisation is the sum of direct and diffusive ionisations the experimental values of the ionisation probabilities of states with $n^* \leqslant 25$ are larger than the diffusive ionisation probabilities. In addition, direct collisional ionisation may also become important for states with $n^* \geqslant 100$ (Kaulakys 1985).

It should be noted that time-resolved experimental measurements of collisional ionisation of impulsive excited Rydberg atoms are desirable. Observation of the delay time for the ionisation of Rydberg atoms would be direct proof of the diffusive ionisation mechanism. Theoretical investigation of non-stationary diffusive ionisation of Rydberg atoms has been carried out by Kaulakys and Čižiūnas (1987).

To summarise, the diffusion-like mechanism for the collisional ionisation of Rydberg atoms has been presented. Analytical expressions for the probabilities of stationary diffusive ionisation have been obtained and applied in order to explain experimental results for caesium. It has been concluded that the diffusive mechanism is the main mechanism for the collisional ionisation of Rydberg atoms with high principal quantum numbers.

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