SELECTIVE IONIZATION OF ATOMS AND MOLECULES BY ELECTRIC AND LIGHT FIELD. AUTOIONIZING RYDBERG RESONANCES IN HEAVY ATOMS

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Within a consistent quantum mechanical approach we have studied the selective resonance excitation of atoms by laser radiation into the states near ionization limit and further autoionizing decay of the excited states under external electric field. We have carried out the accurate numeric calculation of the atom autoionizing under external electric field. The numeric data for the Rb atom autoionization states with n=7-12 in the 10^4 V/cm electric field are presented. We have carried out the theoretical study of the autoionizing resonances (AR) in the multielectron heavy atoms (rare earth atoms: Yb, Tm etc.) in the external electric and laser fields. An unusual behavior of AR in the field was predicted. The effect of giant AR widths broadening at relatively weak external field is found. Two AR decay channels (a traditional Beutler-Fano channel and a new reorientation decay channel) are examined. An appreciable dependence of the reorientation decay velocity at the moderately weak (~100 V/cm) electric field is analyzed. Detailed information about AR is required to optimize the excitation and ionization of atom. The optimal scheme presumes the compromise between high excitation probability and high decay rate that determines lower and upper limits for the AR decay rate.

1. The method of selective ionization of atoms, based on the selective resonance excitation of atoms by laser radiation into the states near the ionization limit and further photo-ionization of the excited states by additional laser radiation, was been first proposed and realized by Letokhov [1, 2]. This method is of great interest for laser separation of isotopes and nuclear isomers [3, 4]. The significant disadvantage of the two-step selective ionization of atoms by laser radiation method is a great difference between cross-sections of resonant excitation and photo-ionization ($\sigma_{exc}/\sigma_{phion} > 10^{+4...8}$). The application of very intense laser radiation for the excited atom ionization is required. The situation is more simplified for the autoionizing levels, but detailed data regarding these levels are often absent. The authors of ref. [5] have considered the possibility of selective ionization of atoms, based on selective resonance excitation of atoms by laser radiation into the states near the ionization limit and further ionization decay of excited atoms by external electric field. Electric field changes the electron spectra so that the part of discrete spectral levels (near the ionization limit) moves into continuum and other levels become autoionizing. The probability of their autoionizing decay quickly increases with the growth of the principal quantum number. The most optimal situation is when the atom is excited to a state, which has higher autoionizing probability than the radiation decay probability. To obtain the exact information about the optimal scheme for selective ionization of atom by the light and electric field, it is necessary to carry out the accurate calculation of the process of sequential excitation of atoms by laser field (it is a trivial task) and the probability of ionization of the highly excited atoms by the electric field. Epy robability of ionization for highly excited atoms by electric field is given by the known expression [5]

$$W = 1/n^3(4/\varepsilon n^2)^{2n2+|m|+1}[1/n2!(n2+|m|)!]\exp\{-2/3\varepsilon n^3 + 3(n1-n2)\}\ .$$

In the case of atomic ionization by the pulsed field, the probability of the process is determined by the following expression:

$$W(nlm) = \sum_{n2}(a^{nlm}_{n1n2})^2 W(n1n2m)$$

where $W(n1n2m)$ is the probability of Ψ_{n1n2m} states decay; a are the coefficients of expansion of the ψ(nlm) functions on the parabolic functions $\psi(n1n2m)$. To achieve the effective optimal situation, it is necessary to switch on the field for the time which is small in comparison with the excited state radiation decay time. In order to find the expansion coefficients, we have elaborated the numerical procedure for the calculation of the corresponding matrix elements and the matrix diagonalization. In a real multi-electron atom it is necessary to take into account the influence of the electron shells which results in the change of the potential barrier and wave functions. To determine the wave functions and the electron state energies in the external electric field one should diagonalize the energy matrix, calculated between the states with the same n. The exact procedure is given by the operator perturbation theory method, developed in [7–10]. In Table 1 we present the calculated values for the characteristics of the most rapidly decaying states for the Rb atom (the field strength 3 10^{+4} V/cm; n=7–12).

Table 1. The characteristics of the most rapidly decaying states for the Rb atom (the field strength 3 10^{+4} V/cm; n=7–12).

n	7	8	9	10	11	12
E, cm(-1)	31405	31904	32229	32456	32614	32761
n_2^*	4.7	5.8	7.0	8.0	8.9	9.0
a_f^2	0.26	0.25	0.13	0.13	0.011	0.13
a_s^2	$<10^{-6}$	$<10^{-6}$	$<10^{-5}$	$<10^{-5}$	$6\ 10^{-5}$	0.028
a_p^2	$<10^{-6}$	$8\ 10^{-6}$	$2.5\ 10^{-5}$	0.0002	0.0026	0.16
a_d^2	0.00028	0.0009	0.0036	0.015	0.045	0.008

With the growth of the number n, all the characteristics increase. The influence of the electron shells leads to more sharp dependence of the decay probability upon the number n. Thus, one can realize a scheme of the selective photoionization of atoms by means of the resonance excitation into the states near the ionization limit (the optimal scheme requires the accurate estimates of the atomic characteristics); then these states undergo autoionizing decay in a weak electric field (< 30 kV/cm). The problem of calculation of the autoionizing resonances and their characteristics in external field requires separate consideration.

2. The effect of electric field on the autoionizing states (AS) is interesting from several points of view (see [2, 5–8, 11]). Study of decay processes for Rydberg states (RS), in particular, multistage ionization method [1, 2] and its applications, is very important for laser spectroscopy. A great role is played by AS in many processes in plasma and gases. Their account is important for correct determination of the rates of excitation and de-excitation of ions in dense plasma and in the examination of dielectron recombination in plasma [2]. Especially interesting effects occur in a complex heavy atom when its broad autoionizing resonances mix with much narrower resonances of op-

posite parity by means of the external electric field. Such effects are of great importance for laser spectroscopy. The interest to the problem of the AR decay of complex atoms is recently enhanced due to new properties which appear under the resonant or non-resonant interaction of an autoionizing level with strong laser field. Here we consider Tm atom, which represents an undoubted interest for experimental spectroscopy, in controlling the population and decay kinetics of excited states or the selective ionization under laser radiation [5–9]. The authors of [11] have studied new effects related to the behaviour of the Tm AS in a weak electric field and predicted an effect of drastical broadening of the reorientation type AR already in a weak electric field. Here we obtain more accurate numeric data. The main autoionizing decay channels for Tm states are illustrated in Fig.1. The availability of two pairs of close-lying ionization limits (with vacancy states $4f7^1/2$ and $4f5^1/2$) provides two main types of AD :

(BFD) $4f^1_{5/2}\ 6s1/2\ (J12)\ nl$ –
$4f^1_{7/2}\ 6s1/2\ [J12']\ Tm^+ + leje$,
$n>7$, $J12=2; 3$, $J12'=3; 4$

(ROD) $4f^1j\ 6s1/2\ (J12)\ nl$ –
$4f^1j\ 6s1/2\ [J12']\ Tm^+ + leje$,
$n>25$ $J12=3$, $J12'=2;4$
$j=5/2,7/2$,

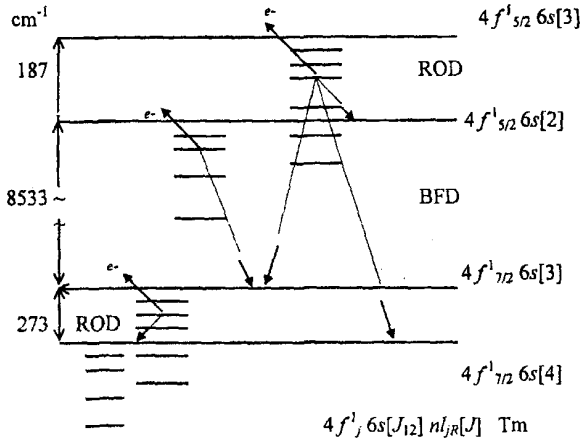

Fig 1. Position of the near lying first ionization limits $4f^16snl$ Tm and scheme of the autoionizing decay of $4f^{13}6snl$ Tm autoionizing Rydberg states.

These AR decay channels are discussed in detail in [5–8, 11]. ROD means the reorientation AR decay, and BFD means Beutler-Fano AR decay. The $4f^1_{5/2}\ 6s_{1/2}(J12=3)nl$ states undergo simultaneously both BFD and ROD. Remember that contrary to BFD, ROD is a low-energy process preserving all the single electron quantum numbers of atomic core: $4f^1j$ and $6s1/2$. ROD can be of monopole or quadruple character. We mean here the multipolarity of the inter-quasi-particle interaction causing AD. The states with $J12=2;4$ do not undergo ROD. Nevertheless, their admixing with states undergoing ROD can significantly enhance the monopole ROD. In Table 2 we present the calculated values of the energy E, autoionizing width of the $4f7^1/26s(3)ns,np$ Tm states ($n=25$). For Rydberg series, the only possible AS decay is the reorientation one. Any two states of different parity can be mixed by the external electric field. The mixing leads to the redistribution of the autoionizing widths. In the case of degenerate or near-degenerate resonances this effect becomes observable even at a moderately weak field. In the case of Tm we deal with reorientationally decaying ns and np series, converging to the same ionization limit, i.e. they are nearly degenerate states of different parity. Among them one can find some pairs of ns and np states with widths Γ, differing by several orders. We consider the $f^1_{7/2}\ 6s(3)25s[5/2]$ state, decaying due to the quadruple interaction and $f^1_{7/2}\ 6s(3)25p_{1/2}[5/2]$ undergoing the monopole ROD. Regarding the calculation procedure, we note that the general approach to the calculation of atomic characteristics of multi-electron systems in electric field is presented earlier [11, 12]. Here we only note that the diagonalization of the complex energy matrix leads to the complex energy correction: $\mathrm{Re}\ E - i\Gamma/2$, where $\mathrm{Re}\ E$ is the level shift, Γ is the level width, including the radiation and autoionizing widths simultaneously. If the effects of AR decay are included only into the matrix M, then Γ presents only the autoionizating width of the state. Only $\mathrm{Re}\ M$ is diagonalized. The imaginary part is converted by means of the matrix of eigen-

vectors $\{C_{mk}\}$ The eigenvectors are obtained by the diagonalization of ReM:

$$\mathrm{Im}\, M_{ik} = \sum_{ij} C^*_{mi}\, M_{ij} C_{jk}\,.$$

This procedure is correct to terms of the order of Im M / Re M. The field matrix element is

$$V_{12} = \varepsilon \langle ns_{1/2} \mid r \mid np_{1/2} \rangle.$$

This matrix element for the highly excited states under investigation can be approximated with the acceptable degree of accuracy by the following expression: V_{12} [cm^{-1}] = $10^{-5}\, n^2\, \varepsilon$ [$V\cdot$ cm^{-1}], where ε is the field strength. The results of calculation of the widths of the states under investigation are presented in Table 2 for different values of the field strength. One can see that even at weak electric field, a strong change of the width of the autoionization resonance occurs. Detailed spectroscopic information about the RS levels is required to optimize the excitation and ionization of the atom. An optimal scheme presumes a compromise between high excitation probability and high decay rate that determines the lower and upper limits for the AD rate. The use of the ROD channel, investigated here, essentially increases the possibilities of such a compromise.

Table 2. Autoionization widths Γ, energies E for some values of the field strength ε ($V\cdot$cm^{-1}).

State	$4f^{13}{}_{7/2}\,6s1/2\,(3)\,25s\,[5/2]$	$4f^{13}{}_{7/2}\,6s1/2\,(3)\,25p_{1/2}\,[5/2]$
E, $\varepsilon = 0$	49854.7 cm^{-1}	49865.3 cm^{-1}
Γ, $\varepsilon = 0$	1.10D – 05	1.204D - 01
Γ, $\varepsilon = 50$	1.20D – 04	1.207D - 01
Γ, $\varepsilon = 100$	4.30D – 04	1.22D - 01
Γ, $\varepsilon = 150$	9.200D – 04	1.30D - 01

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СЕЛЕКТИВНА ІОНІЗАЦІЯ АТОМІВ ТА МОЛЕКУЛ ЕЛЕКТРИЧНИМ ТА СВІТЛОВИМ ПОЛЕМ. АВТОІОНІЗАЦІЙНІ РІДБЕРГОВІ РЕЗОНАНСИ У ВАЖКИХ АТОМАХ

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На основі послідовного квантово-механічного підходу розглянуто процес селективного резонансного збудження атомів лазерним випромінюванням у стани біля межі іонізації та подальшого автоіонізаційного розпаду збуджених станів під дією зовнішнього електричного поля. Виконано чисельний розрахунок автоіонізаційних характеристик атома в зовнішньому полі. Представлено чисельні дані для автоіонізаційних станів атома Rb з головним квантовим числом n=7–12 в електричному полі ~10^4 В/см. Проведено розрахунок характеристик автоіонізаційних резонансів у багатоелектронних атомах (рідкоземельні атоми Yb, Tm) у зовнішньому електричному полі. Передбачено незвичайну поведінку автоіонізаційних резонансів у полі, зокрема, ефект гігантського збільшення їх ширин у відносно слабкому електричному полі. Розглянуто два основних канали автоіонізаційного розпаду: традиційний типу Бейтлера-Фано та новий реорієнтаційний канал. Проаналізовано залежність швидкості реорієнтаційного розпаду у достатньо слабкому електричному полі (~100 В/см). Докладна інформація стосовно автоіонізаційних резонансів необхідна для оптимізації процесів збудження та іонізації атомів. Зокрема, оптимальна схема передбачає компроміс між високою імовірністю збудження та високою швидкістю розпаду, яка визначає нижню та верхню межі швидкості розпаду автоіонізаційних резонансів.