ASSOCIATIVE IONIZATION INVOLVING HIGHLY EXCITED ALKALI METAL ATOMS

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Papers on collisional ionization of excited alkali metal atoms by atoms in their ground states are briefly analyzed. The main premises behind the theoretical models of the process and some experimental findings for a number of atoms during the optical excitation of an effusive atomic beam are described.

There is great interest in low temperature plasma physics and chemistry in the ionization processes during the thermal collisions of atoms and molecules such as the processes involving excited-state and ground-state alkali metal atoms:

$$A^*(nl) + B \begin{cases} \nearrow AB^+ + e, & (1a) \\ \searrow A + B^+ + e, \quad n \gg 1, & (1b) \end{cases}$$

where n and l are the principal and the orbital quantum numbers. The reaction (1a) is called associative ionization (AI), and the process (1b) we will call Penning ionization (PI). Alkali atoms are commonly used in a number of physicotechnical instruments and are relatively convenient subjects of investigation for experimentalists and theorists.

A rigorous quantum mechanical approach to the collisional ionization problem is only possible for the very simplest systems; therefore, in order to solve such problems, the simplest model concepts are used.

The model developed in [1, 2] is used most widely. The authors of this model assumed that process (1) takes place at large internuclear distances. With this assumption the asymptotic theory [3] can be used to describe the terms of the system in its initial and final states. The perturbation theory was used to calculate the effective cross section for the process. The model does not take into account the multiple crossings of the initial term with the grid of adjacent terms. It also assumes a small autoionization probability of quasimolecules at the intersection point of the initial and final terms.

In [4], the diffusion ionization mechanism of highly excited atoms (HEA) during multiple collisions with atoms in their ground-state was considered. Another model [5], also called diffusional, considers the ionization process as a diffusion along the energy states of quasimolecules during one collision act. Reference [6] proposed an ionization mechanism of highly excited atoms that involves a charge transfer to a self-ionizing state of the negative ion.

For subthermal velocities – for example, those encountered with effusive atomic beams, in which catch-up collisions take place – the capture ionization mechanism might be efficient [7].

In the past 10-12 years the widespread use of beam methods in conjunction with laser excitation made it possible to obtain the data on the collisional ionization process that had been theretofore unobtainable. The most intensive studies have been conducted in a number of U.S. and French laboratories. The majority of the investigations were devoted to symmetric collisions (A and B atoms of the same kind). The data that had been published prior to 1989 were collected in the review [8].

A collision chamber with an atomic beam or intersecting beams, tunable die-lasers, and a mass-analysis and recording system for charged reaction products are essential elements of the modern experimental apparatus. In order to correctly analyze the experimental data it is essential to take into account the following:

1) the difference of the relative velocity distributions of colliding particles in different types of experiments (cell, beam, intersecting beams) [9];

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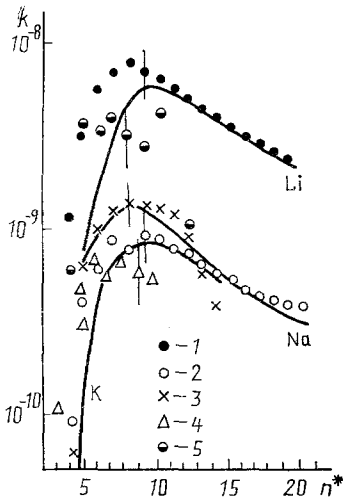

Fig. 1. Dependence k(n*): 1) Li (T = 1100 K) [12]; 2) Na (T = 720 K) [13]; 3) K (T = 660 K) [14]; 4) Sr (T = 1000 K) [15]: 5) Na (nP) + K (4S) (T = 750 K) [16]. k in cm^3/sec.

2) the collisional mixing of highly excited atoms with regular atoms [10];

3) the ionization of highly excited atoms by thermal radiation [11]; and

4) the ionization of cascade-populated low-lying states.

The figure shows the dependence of rate constant k for process (1) on the effective principal quantum number n* for a number of nP-states [12-16]. The results were obtained on one apparatus with a single effusion beam, which makes it proper to compare them. The temperatures of atomic sources are indicated. The results of the calculations using the models of [1-2] (continuous lines) correspond to experimental conditions. The data on strontium are also shown. The mass-analysis for sodium has shown that the AI channel (1a) is dominant even for the maximal values of n* in this experiment. It can be assumed that this is valid for all symmetric collisions investigated here. The agreement between experiment and theory is fully satisfactory. The calculations employing the models of [1, 2] are also in qualitative, and in many cases quantitative, agreement with the experimental results for other types of experiments on symmetric collisions of alkali atoms. Calculations based on the model of [6] predict a substantial rise of k for $n^* \geq 20$; however, this has not yet been confirmed experimentally.

There have been individual studies devoted to investigating nonsymmetric collisions, such as those for sodium–calcium [16], lithium–sodium [17], and calcium–rubidium [18] pairs. The AI rate constants for these experiments are similar to those for symmetric collisions. On the basis of these results, Djerad, Cheret, and Gounand [18] concluded that there are no basic differences between the mechanisms of these processes. The results of calculations based on the model of [2] strongly disagree with the experimental data of [17] and [18].

Valuable information on the reaction mechanisms and coupling parameters of colliding particles can be obtained from the temperature dependence of rate constants (or even better, directly from the dependence of the effective cross section on velocity). However, there have been no systematic studies of processes (1) over wide temperature intervals.

In order to understand the reaction mechanism, the vibrational and rotational state distributions of the final product – the molecular ion – are of interest. Preliminary results were obtained by the time-of-flight spectroscopy of photofragments [19].

One important practical application of the collision ionization process is the possibility of its use in the working cycle of laser isotope separation. Therefore, it is important to explain the effect of the isotope composition of colliding atoms on the reaction yield efficiency. Experiments [20] for Rb atoms (11P) have shown that the ratio of ion signals during the laser excitation of different rubidium isotopes coincided with the ratio of the isotope contents of the original mixture.

LITERATURE CITED

1. E. L. Duman and I. P. Shmatov, Zh. Éksp. Teor. Fiz., **78**, 2116-2124 (1980).
2. A. A. Mihailov and R. K. Janev, J. Phys. B: At. Mol. Phys., **14**, 1639-1653 (1981).
3. B. M. Smirnov, Asymptotic Methods in the Theory of Atomic Collisions [in Russian], Moscow (1973).

4. B. P. Kaulakis, A. R. Chizhyunas, and V. I. Shvyadas, Litovskii Fiz. Sb., **XXIV**, No. 3, 48-58 (1984).
5. A. Z. Devdariani, A. N. Klyucharev, N. P. Penkin, and Yu. N. Sebyakin, Opt. Spektrosk., **64**, No. 3, 706-709 (1988).
6. L. P. Presnyakov and A. D. Ulantsev, Brief Reports on Physics, Moscow (1984), No. 1, pp. 38-43 (Sb. Nauch. Tr./Lebediev FIAN).
7. B. M. Smirnov, Excited Atoms [in Russian], Moscow (1982).
8. A. N. Klucharev and V. Vujnovic, Phys. Repts., **185**, No. 2, 55-81 (1990).
9. A. N. Klyucharev and N. N. Bezuglov, Excitation and Ionization Processes during Light Absorption [in Russian], Leningrad (1983).
10. V. S. Lebedev and V. S. Marchenko, Zh. Éksp. Teor. Fiz., **88**, 754-770 (1985).
11. B. P. Kaulakis, Pis'ma Zh. Éksp. Teor. Fiz., **47**, 300-302 (1988).
12. S. B. Zagrebin and A. V. Samson, Pis'ma Zh. Éksp. Teor. Fiz., **11**, 680-682 (1985).
13. S. B. Zagrebin and A. V. Samson, J. Phys. B: At. Mol. Phys., 11, L217-L220 (1985).
14. A. V. Samson, Opt. Spektrosk., **65**, No. 1, 242-243 (1988).
15. A. V. Samson, Opt. Spektrosk., **63**, No. 2, 440-442 (1987).
16. A. V. Samson, Khim. Fiz., **9**, No. 4, 573-575 (1990).
17. B. C. Johnson, M.-X. Wang, and J. Weiner, J. Phys. B: At. Mol. Phys., **21**, 2599-2607 (1988).
18. M. T. Djerad, M. Cheret, and F. Gounand, J. Phys. B: At. Mol. Phys., **20**, 3789-3799 (1987).
19. J. Keller, R. Bonanno, M.-X. Wang, M. S. de Vriens, and J. Weiner, Phys. Rev., **A33**, No. 3, 1612-1617 (1986).
20. B. V. Dobrolezh, A. N. Klyucharev, and A. B. Tsyganov, Proceedings of All-Union Seminar on "Ionization Processes Involving Excited Atoms," Leningrad (1988), pp. 22-23.

CHEMOIONIZATION IN A LOW TEMPERATURE PLASMA

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Ionization processes are considered in a low-temperature plasma which involve collisions of heavy particles leading to significant changes in the charged particle balance with ionization or recombination nonequilibrium. The possibilities for use of chemoionization processes in modern low temperature plasma physics applications such as gas laser active media, detection of oscillatory excitation in molecules, and optogalvanic spectroscopy are evaluated.

It follows from simple qualitative considerations that chemoionization processes will have the greatest effect on ionization kinetics in cases of alkali metals or atoms with a similar excited state term structure. For such systems, with their relatively uniform sequence of energy levels, excitation to a resonant level does not imply that the excited electron immediately enters the continuum – as a rule, the "tight spot" in these cases is located higher and the presence of an effective drain through the chemoionization channel from lower levels can have a significant effect on the net ionization rate. On the other hand, in the case of inert gas atoms the ionization rate is practically always limited by the rate of excitation of lower states with subsequent rapid ionization in electron–atom collisions.

It has been proposed previously that in a low temperature plasma chemoionization plays a significant role only in the initial stages of ionization development: in gas breakdown, in shock waves, etc. (see, for example, [1]). Dissociative recombination processes reduce the role of chemoionization. However there exists a situation in which chemoionization (through the molecular ion formation channel) is not accompanied by the reverse process of recombination; thus, at a temperature of the

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