

# Study of ionization in slow collisions of atomic particles

V. B. Leonas and A. P. Kalinin

*Institute of Space Research, USSR Academy of Sciences  
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The review is devoted to presentation of experimental and some theoretical results of the study of ionization processes in collisions of atomic particles of low energy. One of the main purposes of the review is to attempt to systematize the numerous results and methods of the experimental study of processes of formation of charged particles in collisions with energies below the characteristic ionization potentials (so-called chemi-ionization processes). The main attention in the review is devoted to studies carried out in recent years on the dynamics, energetics, and the electronic mechanism of processes involving particles in reliably identified states. Detailed discussions are given of questions of chemi-ionization with dissipation of electronically excited particles (Penning ionization), processes with transfer of an electron, and associative ionization of atomic particles of thermal energies. In conclusion some promising features of further studies of chemionization processes are discussed.

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## INTRODUCTION

The present review is devoted to presentation of the experimental results and certain theoretical results of the study of ionization processes in collisions of atomic particles of low energies. These processes are usually called chemi-ionization.

The principal attention in the review will be devoted to discussion of new directions in the physics of atomic collisions formulated in recent years. We have in mind studies of electron removal processes aimed at a detailed investigation of the dynamics, energetics, and electronic mechanism of processes utilizing particles in reliably identified states.

One of the main purposes of the review is to attempt a critical analysis of new results and new methods of the experimental study of charged-particle formation in collisions with energies less than the characteristic ionization potentials. A detailed discussion of earlier experimental studies can be found in Ref. 1.

From the phenomenological point of view chemi-ionization processes fall into two large classes—collisions with removal of an electron and collisions with formation of a pair of ions—positively and negatively charged heavy particles. These two classes differ qualitatively from the point of view of theoretical description, since before and after a collision with formation of a pair there are two particles, and transitions are accomplished between the discrete levels of the electronic energy—the terms of the quasimolecule arising from the colliding particles. In the case of electron removal we are deal-

ing with a transition to the continuum, and in the exit channel in addition to heavy particles there is a new particle—a free electron. The theory of transitions between discrete levels has been developed intensively in recent decades, while the theory of transitions of quasimolecular systems to the continuum has been inadequately developed.

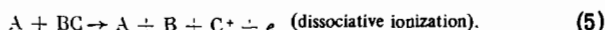
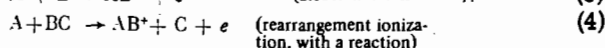
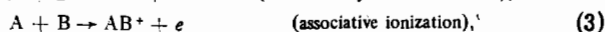
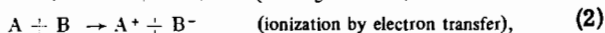
The possibility discovered experimentally of studying in detail the dynamic and kinematic characteristics of an elementary chemi-ionization event proceeding through the crossing of terms and of the decay systematics of quasistationary molecular states with characteristic lifetimes  $10^{-15}$ – $10^{-17}$  sec is of obvious interest for the theory. A basic simplifying circumstance of the quantitative theoretical analysis is the fact that in chemi-ionization the interaction of the particles in the exit channel turns out to be a Coulomb interaction. In technical respects the study of chemi-ionization processes utilizes the fact that the products of atomic collisions turn out to be "labelled" by charge and relatively easy to detect and to analyze in mass and energy. The appearance of new experimental information provides a stimulus for development of the concepts relating to these processes.

Thus, the study of ionization processes essentially opens a new direction in the physics of atomic collisions which will take the place of the already highly advanced study of charge exchange, excitation, and such processes.

Chemi-ionization processes have attracted considerable attention in recent years also as the result of ap-

plied problems, since ionization is one of the most important elementary processes determining the macroscopic behavior of gaseous systems, both natural (for example, the upper atmosphere of the Earth and the planets) and artificial (gas-discharge plasmas, plasmas in MHD installations, the gas behind the intense shock wave on entry of space craft into dense layers of atmosphere, and so forth). The practical necessity of assuring the functioning of apparatus in such media and the use of these media in physics and power installations as working materials explains the heightened interest in the processes discussed here.

We will include in chemi-ionization processes those described by the following symbolic equations,



A characteristic feature of the collision processes (1)–(5) discussed here is that the energy of radial motion of the nuclei at the distances where the electronic transition occurs is below the ionization energy of any of the particles involved.

This statement essentially means that the energy necessary for ionization (an electronic transition) is supplied not from the translational degrees of freedom of the atoms composing the quasimolecule, but is due either to the presence of initial excitation or to the possibility of excitation of the system as the result of approach of an initial term to the term of an ionic state. Accordingly, ionization of the quasimolecule arising can be accomplished by two principal means. If a term  $V^*$  of the initial quasimolecular state  $AB$  is located in the continuum, the lower limit of which is the ground term  $V^+$  of the quasimolecular ion  $AB^+$ , then the process corresponds to autoionization decay—a vertical electronic transition from state  $AB$  to the ionic state  $AB^+$ . This case (reaction (1)) is realized in the case of collisions of atoms  $A$  excited to a level with energy exceeding the ionization potential of atom  $B$  (or in the case of existence of excitation in both particles, the total energy of which exceeds the ionization potential of  $A$  or  $B$ ).

From comparison of the characteristic lifetimes of an electronically excited molecular system (the ionization decay time is  $10^{-15}$  sec, and radiative decay time— $10^{-9}$  sec) it is clear that the ionization channel will always have priority.

If interaction of the colliding particles occurs by means of the term  $V_0$  approaching the term  $V^+$  of the ionic state of the quasimolecule and penetrating the continuum corresponding to various energies of the elec-

tron, the nuclear motion will induce transitions between the terms; here the transitions induce both radial motion and rotational motion—rotation of the internuclear axis,<sup>[2]</sup> leading to the possibility of appearance of ions (reactions (3), (4), and (5)).

A qualitative picture of the terms in the situation discussed is shown in Fig. 1.

In the case of formation of a pair of ions, the initial term of the quasimolecule  $AB$  (the covalent term, in the terminology of quantum chemistry) crosses the term of the final state (the ionic term)  $A^+B^-$  (see, for example, Fig. 19 below), leading to the possibility of formation of free particles—the ions  $A^+$  and  $B^+$ .

For a known behavior of the terms, the Franck-Condon principle (conservation of the relative position and momenta of the nuclei in an electronic transition) provides a simple instrument for determination of the dynamics and energetics of the collision, i. e., the distribution of momenta and energy between the collision partners and the electrons which appear. The quantitative determination of the transition probabilities and the behavior of the corresponding terms has formed the principal goal of most of the experimental studies of chemi-ionization processes which are discussed in what follows.

The intensive experimental and theoretical investigations of chemi-ionization collisions encompass three types of processes, which differ in the initial state of the particles and in the type of particles which are produced.

1. Study of chemi-ionization with participation of electronically excited (metastable) particles with excitation energy exceeding the ionization potential of the second partner (process (1)).
2. Study of the process of electron transfer—formation of a pair of ions (positive and negative) (process (2)).
3. Studies of associative ionization in collisions of atomic particles which are in the ground electronic state (processes (3)–(5)).

These studies are carried out with an extensive collection of methods, with use of the newest experimental techniques. As a crude classification the methods used

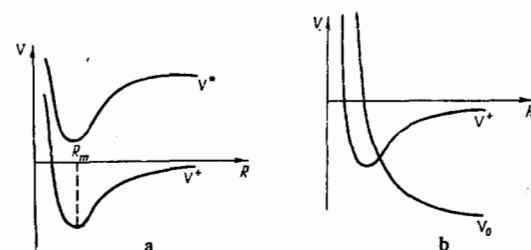


FIG. 1. Qualitative term pattern, explaining the two types of chemi-ionization.  $V_0$  corresponds to interaction in the system  $A-B$ ,  $V^*$  corresponds to interaction in the system  $A^+B^-$ , and  $V^+$  corresponds to interaction in the system  $A-B^+$ ;  $R_m$  is the position of the minimum potential.

<sup>1)</sup>The asterisk denotes an excited atom.

can be divided into two groups—kinetic methods and methods using beams.

Kinetic methods include the decaying-plasma method (stationary<sup>[3]</sup> and in a flow—the flowing-afterglow method<sup>[4]</sup>) and the kinetic spectroscopy method.<sup>[5]</sup>

However, various forms of studies with beams have become the main experimental tool: they provide experimental information which to a considerable degree avoids averaging over various characteristics of the collisions. Measurements of the angular and energy distributions of the electrons produced (electron spectroscopy) have provided an important addition to the measurement of total and differential cross sections for chemi-ionization in the range of thermal and superthermal ( $E \geq 10-10^2$  eV) energies traditional for studies with beams. In the general discussion of chemi-ionization processes, special attention is deserved by the study of processes involving highly excited atoms, i. e., atoms which are in high Rydberg levels with a principal quantum number  $n > 10$  (see the papers cited in Ref. 6). These states are characterized by a sharp reduction in the binding energy and ionization potential of the outer electron [ionization potential (IP)  $\sim n^{-2}$ ], and therefore for thermal collisions of highly excited atoms it is easy to achieve the condition  $E > IP$ . This circumstance takes collisions of highly excited particles outside the scope of the processes considered here. However, it must be emphasized that in this case we are encountering a qualitatively new type of collision.

A theoretical analysis of ionizing collisions of particles in Rydberg states has been carried out in Refs. 6 and 7, and a basic aspect of it is the treatment of collisions of  $A^{**}$  with B as interactions with atom B of a highly distant electron (the radius of a Rydberg orbit is  $\sim n^2$ ) in the presence of the "inert" ionic core of the excited atom  $A^{**}$ . Accordingly, an attractive consequence of the theoretical analysis is the promise of development of a new method of study of electron-atom collisions at ultralow energies ( $E_{el} \sim 10$  meV) based on study of the interaction of beams of highly excited atoms with various partners.

In collisions of highly excited particles, record values of ionization cross sections<sup>[6,7]</sup> up to  $10^{-11}$  cm<sup>2</sup> are achieved, which may give them an important role in the evolution of a recombining plasma; interest is also presented by the potential applied aspect of use of processes involving highly excited particles, in particular, in the electrical separation of isotopes.

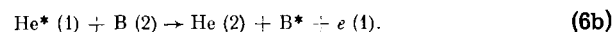
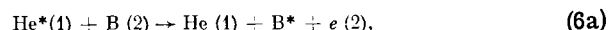
## 1. CHEMI-IONIZATION WITH PARTICIPATION OF ELECTRONICALLY EXCITED PARTICLES

In slow collisions of electronically excited particles  $A^*$  with particles B in the ground state the ratio of the excitation energy of  $A^*$  to the ionization potential of B can be greater or less than unity. These two cases differ fundamentally in the ionization mechanism; they also differ in the extent to which they have been studied. The greatest advances have been achieved in study of chemi-ionization involving metastable atoms of He and other noble gases; in what follows we will discuss only

these atoms. Studies of collisions of excited particles at high energies ( $1-10^3$  eV) has been assigned until recently to the category of measurements of cross sections for quenching of metastable states. However, the values of these cross sections,<sup>[8]</sup> which indicate that the "quenching" is accomplished in interaction at rather large internuclear distances, and the development of the theory<sup>[9]</sup> now permit them to be treated completely from the same point of view as collisions in the thermal region.

Before discussing the most recent experimental results, it is appropriate to present a brief exposition of the main theoretical ideas regarding the process of chemi-ionization by excited particles, described by the symbolic equation (1).

Well known alternative treatments of the electronic mechanism of the process can be given formally in the case of the following two reactions of metastable helium atoms:



Here the index 1 designates an excited electron of a metastable atom, and the index 2 designates one of the outer electrons of the ionized atom B.

Processes (6a) and (6b) can be called respectively photoionization reactions and electron-transfer reactions, respectively. In the first case it is assumed that the perturbation due to the approach of the particles leads to emission by the helium of a photon which is absorbed by particle B, which also leads to its ionization. This mechanism of the process has been discussed by Firsov and Smirnov (see Ref. 10) and has been considered also by Watanabe and Katsuura.<sup>[11]</sup> In the second mechanism, reaction (6b), the process is accomplished by tunneling of the outer electron (2) of atom B into the vacancy (the 1s shell) of the He atom, and as a result of the filling of this shell the 2s electron (1) of the He turns out to be free. We can expect that for collisions involving  $\text{He}(2^3S)$  the electron-transfer mechanism should be dominant, since the probability of a radiative transition is small in view of the spin forbiddenness (for  $\text{He}(2^1S)$  this forbiddenness is absent).

The assumption of some scheme or other is essential in the problem of calculating the transition probability. However, regardless of the electronic mechanism assumed for the ionization, the description of the energetics and dynamics of a chemi-ionization collision is based on consideration of the process as a vertical transition from a decaying quasimolecular state AB to a lower state of the electronic continuum, which corresponds, as a rule, to the ground-state term of the ion  $\text{AB}^+$ . This physically clear model of vertical transitions between quasimolecular terms for the processes considered was first suggested by Čermák<sup>[12]</sup> (see also Ref. 13); the complete formalization of this model in the classical, quasiclassical, and quantum approximations is contained in the article by Miller.<sup>[9]</sup>

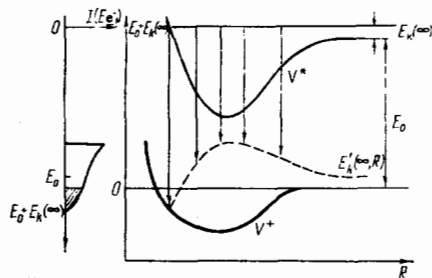


FIG. 2. Qualitative term diagram explaining the regularities in the distribution of energy between the atomic particles and the electron in the autoionization of a quasimolecule.

We shall consider qualitatively the process in thermal collisions with energy  $E(\infty)$ . In Fig. 2 in the upper part we have shown the term  $V^*$ , and below it the term  $V^+$ .

Since the angular momentum carried away by the liberated electron is negligible in comparison with the orbital angular momentum of the nuclei, the rotational energy of the nuclei remains unchanged. This fact, together with the Franck-Condon principle, permits us to relate the initial and final relative energies of the nuclei,  $E(\infty)$  and  $E'(\infty, R)$ , and the energy of the liberated electron  $E_{el}$  for a vertical transition at any point  $R$ ,

$$E_{el}(R) = V^*(R) - V^+(R), \quad (7)$$

$$E(\infty) = [V^*(\infty) - V^+(R)] = E'(\infty, R) + [V^+(\infty) - V^+(R)]. \quad (8)$$

From this, designating the asymptotic distance between the terms  $V^*$  and  $V^+$  by  $\Delta E$  ( $\Delta E = V^*(\infty) - V^+(\infty)$ ), we arrive at the relation

$$E'(\infty, R) = [E(\infty) + \Delta E] - E_{el}(R). \quad (9)$$

Since  $\Delta E$  and  $E(\infty)$  are known constants, the final relative energy of the nuclei, aside from a constant, coincides with the energy of the liberated electron.

Equation (9) is useful in analysis of the possible effects of a collision in the thermal region. In Fig. 2 the dashed curve shows values of the final energy  $E'(\infty, R)$  for vertical transitions at various  $R$  (see Eq. (9)). As can be seen from the diagram, the values of  $E'(\infty, R)$  can be both positive and negative. These two cases correspond to the usual division of process (1) into Penning ionization and associative ionization with formation of a bound state  $AB^*$  ( $E'(\infty, R) < 0$ ). The energies of the electrons which appear are given by the lengths of the vertical arrows in Fig. 2; the form of the electron spectrum (shown qualitatively in the left part of Fig. 2) will be determined by the dependence of the transition probability on the distance.

The transition probability per unit time (or the transition frequency  $\nu$ ) at an internuclear distance  $R$  is determined by the width of the autoionization level  $\Gamma(R)$  ( $\nu = \Gamma/\hbar$ ). The probability density of decay  $P(R, b)$  at a given internuclear distance  $R$  in motion along a trajectory with a radial velocity  $v_R$  ( $v_R = (2\{[E - V^*(R)] - E(b^2/R^2)\})^{1/2}/\mu$ , where  $b$  is the impact parameter and  $\mu$  is the reduced mass) is related to the transition

frequency by the expression

$$P(R, b) dR = \frac{\Gamma(R)}{\hbar v_R} dR. \quad (10)$$

Since transitions to the continuum can originate in any trajectory beginning with  $R = \infty$ , the probability of decay in a portion of the trajectory  $dR$  near  $R$  must depend on the previous history of the system, i.e., on whether the quasimolecular system could live long enough to approach the point  $R$ .

The description of scattering accompanied by transitions to the continuum is simplest in the case of the classical treatment of collisions (for a quasiclassical and quantum description, see Ref. 9). Since interaction in accordance with the term  $V^*$  corresponds to elastic scattering, the differential cross section for elastic scattering of excited particles can be written in the form

$$\sigma_{\text{elast}}(\theta) = \sigma_{\text{pot}}(\theta) W(\theta), \quad (11)$$

where  $\sigma_{\text{pot}}$  is the cross section for potential scattering for the term  $V^*$ , and  $W(\theta)$  is the probability of survival in a trajectory corresponding to deflection by an angle  $\theta$ . The scattering of particles in collisions with transitions is described by  $\sigma_{\text{inel}}(\theta)$ , which can be found, since in this case the point of the transition  $R$  corresponds to a completely determined deflection angle  $\theta_R$  determined by the relative energy  $E$ , the impact parameter  $b$ , and the compound potential of the interaction (the change  $V^* - V^+$  at the point of the vertical transition)

$$\sigma_{\text{inel}}(\theta) = \sum_{i=1}^N \sigma_{\text{pot}}^i(\theta) P_i(\theta), \quad (12)$$

where  $N$  is the number of combinations of  $R_i$  and  $b_i$  corresponding to the deflection angle  $\theta$  in potential scattering in accordance with the compound potential,  $P_i(\theta)$  is the probability corresponding to the point  $R_i$  of a transition, for a given  $b_i$ , leading to a deflection angle  $\theta$ . In the same classical approximation, if we assume that  $E_{el}$  (see Eq. (7)) is a single-valued function of  $R$ , it is easy to arrive at the expression for the differential energy spectrum of the electrons,

$$P(E_{el}) = \int_{R_0}^{\infty} P(E_{el}, b) b db; \quad (13)$$

here  $R_0$  is the distance of closest approach, which depends on the initial relative energy.

In view of the identity relation  $P(b, E_{el}) dE_{el} = P(b, R) dR$  we can write down the following expression:

$$P(b, E_{el}) = P(b, R) \left[ \frac{d[V^*(R) - V^+(R)]}{dR} \right]_{R=R(E_{el})}^{-1}. \quad (14)$$

Thus, the electron energy spectrum  $P(E_{el})$  should have singularities for points where  $d(V^* - V^+)/dR = 0$  (similar to the rainbows in elastic scattering) and  $v_R = 0$  (the turning point). The integration over impact parameters and the finite resolution will spread out the singularities in the observed spectrum (the discrepancies indicated

are removed in a more rigorous quantum discussion).

Expressions such as (11), (12), and (13) form the practical basis for interpretation of the observations of chemi-ionization processes involving excited particles. Depending on the nature and extent of the available experimental information, it is possible by means of these relations to solve effectively the inverse problem of determination of the terms  $V^*$  and  $V^+$  and the width  $\Gamma(R)$ .

#### A. Electron spectroscopy of chemi-ionization processes

The study of electrons has actually become in recent years an extremely efficient instrument for determination of the main characteristics of the ionization process. This is accomplished by analysis of a) the energy distribution, b) the angular distribution, and c) the spin state of the liberated electrons.

Measurements of electron energy spectra have been carried out both with beams of thermal energies (in Fig. 3 we have shown a diagram of the apparatus) and at high energies ( $10\text{--}10^2$  eV).<sup>[14,15]</sup> Figure 4 illustrates the experimental results characteristic of thermal collisions (the system  $\text{He}(2^3\text{S})\text{--Na}$ , Ref. 16) and comparison of calculations of the spectrum for various functional descriptions of the width of the autoionization level  $\Gamma(R)$  with the measured spectrum. For the assumed dependences  $V^*(R)$  and  $V^+(R)$ , as can be seen from Fig. 4, the fit provides the possibility of a semiempirical determination of  $\Gamma(R)$ , although only for a narrow range of distances  $R$ . Analysis of electron spectra in the case of high energy beams encounters difficulties in separation of the chemi-ionization electrons from the complete spectrum recorded. For thermal collisions the minimal approach distances  $R_0$  determined from the relation  $V^*(R_0) = E_{\text{rel}}$  are large. For large internuclear distances the following inequality is satisfied:

$$V^+(R) < V^{**}(R) < V^*(R) < V^A(R), \quad (15)$$

where  $V^{**}$  and  $V^A$  are terms which converge to different excited states of the particles forming the quasimolecule:  $V^{**}$  is the excitation of the ion  $\text{B}^+$ , and  $V^A$  is the autoionization state of atom B. In collisions of particles of an energetic beam, small  $R$  values also turn out to be accessible. On such close approaches the condition of noncrossing of the terms (15) may turn out to be violated, and on the electronic autoionization spec-

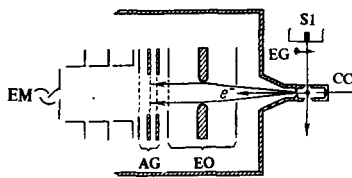


FIG. 3. Arrangement for measurement of electron spectra from chemi-ionization with participation of metastable helium atoms.<sup>[13]</sup> S1—source of He atom beam, EG—electron gun for excitation of  $2^1,3\text{S}$  states of helium, CC—collision chamber, EO—electron-optical system, AG—analyzing grids (retarding-potential method), EM—electron multiplier.

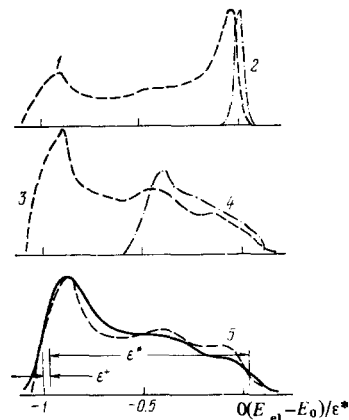


FIG. 4. Comparison of measured and calculated (dashed line) electron spectra from chemi-ionization in the system  $\text{He}(2^3\text{S})\text{--Na}(2^3\text{S})$ .<sup>[16]</sup> The calculations were made for various forms of functions describing the width of a level: 1— $\Gamma \sim \exp(-3R/R_m)$ , 2— $\Gamma \sim \text{const}$ , 3— $\Gamma \sim \exp(-12R/R_m)$ , 4— $\Gamma \sim \delta(R - R_{c1}^*) \exp(-6R/R_m)$ , 5— $\Gamma \sim \exp(-6R/R_m)$ ;  $R_{c1}^*$  is the classical turning point.

trum of the quasimolecular state there may be superimposed contributions from transitions to excited ionic states, from autoionization decays of the atoms, and even contributions from double ionization. This effect can be seen clearly in the example of the spectra of the system  $\text{He}(2^3\text{S})\text{--Xe}$ ,<sup>[15]</sup> taken at various energies (Fig. 5). Because of the uncertainty arising in the interpretation, the information content of the measurements of chemi-ionization electron spectra falls off as the collision energy increases, and in practice the upper limit of relative energies for these measurements hardly can be much greater than  $E_{\text{rel}} = 10$  eV (extension of the energy range will be justified only for the condition of simultaneous recording of the energy loss of the beam particles). Of no less interest are the possibilities of studying the angular distributions of the electrons arising in chemi-ionization collisions.<sup>[17,18]</sup> Results obtained in the thermal range of collision energy for the system  $\text{He}^*\text{--Ar}$  are shown in Fig. 6, where we can clearly see the anisotropy, characteristic also for other systems, in emission of the electrons with respect to

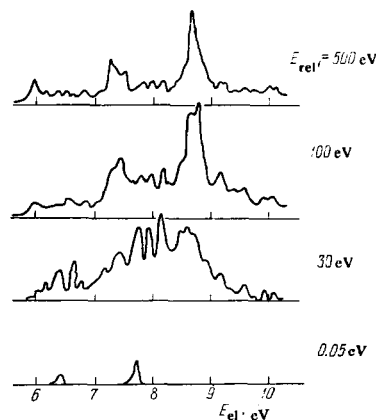


FIG. 5. Appearance of electron spectra for collisions  $\text{He}(2^3\text{S}) + \text{Xe} \rightarrow \text{He}(1^1\text{S}) + \text{Xe}^* + e$  (Ref. 15) for various relative energies  $E_{\text{rel}}$ . The spectrometer energy resolution is  $\delta E = 0.08$  eV.

the direction of the relative velocity vector (the photoelectrons arising in irradiation of Ar by the resonance line of He at 584 Å do not show such anisotropy in these same experiments). Previously, in discussing the frequency of autoionization collisions, we used the width  $\Gamma(R)$  averaged over the directions of electron emission. Actually there is a quite definite probability of emission of an electron with a polar angle  $\gamma$  and azimuthal angle  $\varphi$  relative to the internuclear axis of the quasimolecule, and the differential cross section for emission of such electrons is described by the width  $\Gamma(R, \gamma, \varphi)$ .<sup>[19]</sup>

Like the scattering amplitude, the quantity  $\Gamma(R, \gamma, \varphi)$  is described by an expansion in partial widths with an angular dependence given by the spherical functions. Thus, for theoretical prediction of the electron angular distribution it is necessary to calculate the partial widths occurring in the expansion.

The difficulties in a nonempirical calculation of the width  $\Gamma(R, \gamma, \varphi)$  are comparable with the difficulty of calculating the behavior of the terms  $V^*$  and  $V^+$ , and such a calculation has been carried out only for the case of the system with the simplest electron structure,  $H(1^2S)-He(2^3S)$  (see Ref. 19). Dalidchik<sup>[20]</sup> has given a theoretical discussion of the electron angular distributions for the case of chemi-ionization with formation of the ions in excited electronic states.

The difficulties cited in calculation of the partial widths lead to development of semiempirical approaches to description of the angular distributions of the liberated electrons.<sup>[18,21]</sup> In the thermal range of collision energies this recipe is simplest in the case when the main contribution to the detected electron current is from approach distances corresponding to the turning point and one can therefore neglect the exact dependence of the partial widths on  $R$ . If, following Ebding and Niehaus,<sup>[18]</sup> we assume that the main contribution to  $\Gamma(R, \gamma, \varphi)$  is from the first terms of the expansion, then for electron emission symmetric relative to the molecular axis it is easy to arrive at an expression for the width which contains only the two parameters  $\xi$  and  $\delta$ :

$$\Gamma(R, \gamma) \sim (1 + 2\xi \cos \delta \cos \gamma + \xi^2 \cos^2 \gamma) \exp(-\beta R), \quad (16)$$

where  $\beta$  is the rate of falloff of the averaged width,

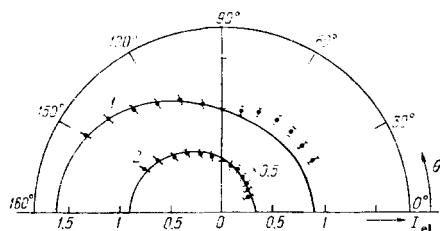


FIG. 6. Angular distribution of flux  $I_{e1}$  of emitted electrons in chemi-ionization  $He^* + Ar \rightarrow He + Ar^* + e$  relative to the direction of the  $He^*$  beam, which is shown by the arrow. The dots with error bars show the experimental points: 1— $He(2^1S)$ , 2— $He(2^3S)$ ; the solid lines are a semi-empirical calculation<sup>[18]</sup> with use of the following values of the variable parameters: 1— $\xi = 1.4$ ,  $\cos \delta = 0.6$ ; 2— $\xi = 1.4$ ,  $\cos \delta = 0.4$ .

TABLE I. Comparison of degree of polarization of  $He(2^3S)$  atoms  $P_m$  with degree of polarization  $P_e$  of electrons arising in chemi-ionization collisions of  $He(2^3S)$  with various targets.<sup>[23]</sup>

Target	$P_e$	$P_m$
Ar	0.28	0.30
H <sub>2</sub>	0.29	0.30
N <sub>2</sub>	0.31	0.30
CO	0.22	0.30
CO <sub>2</sub>	0.30	0.30
N <sub>2</sub> O	0.27	0.30
Brass surface	0.27	0.30

which is assumed known. Numerical values of the parameters  $\xi$  and  $\delta$  can be found by fitting the calculated distributions to the measured values.

The efficiency of the fitting procedure can be seen in Fig. 6, where the solid lines represent the theory and the error bars show the spread in the measured values. Using this procedure, Ebding and Niehaus<sup>[18]</sup> were able to give a good description of the measurements for the systems  $He(2^3S)-Ar$ , Kr, Xe, CO, N<sub>2</sub>, and a satisfactory description for the systems  $He(2^1S)-Ar$ , N<sub>2</sub>. For the systems  $He(2^3S)-Hg$ ,  $He(2^1S)-CO$ , Xe, and Hg an isotropic distribution was observed in the measurements.<sup>[18]</sup>

The calculation carried out by Micha and Nakamura<sup>[21]</sup> of the angular distribution for the system  $He^*-Ar$  with use of the radial dependence  $\Gamma(R)$  from Olson<sup>[22]</sup> also gave good agreement with experiment.

These first advances and the state of the theoretical development of this problem permit us to conclude that measurements of the electron angular distributions already can be used as an additional source of quantitative information on the quasimolecule interaction terms  $V^*(R)$  and the width  $\Gamma(R, \gamma, \varphi)$ .

Experiments on spin analysis of the electrons have a fundamental value for understanding the Penning ionization process (process (1)). In fact, for the exchange mechanism of chemi-ionization (process (6a)) the liberated electron is capable of retaining the "label" attached before "turning on" the interatomic interaction, i. e., before formation of the quasimolecule. The two chemi-ionization mechanisms discussed above, (6a) and (6b), are not mutually exclusive; they can compete, and their actual weight can be established immediately in experiments with use of electrons labelled in spin. It is possible to attach the label by orienting in spin the  $He(2^3S)$  atoms in optical pumping by circularly polarized monochromatic light in a uniform magnetic field. Studies of the effects of collisions of such oriented  $He(2^3S)$  atoms with various partners have been carried out by Keliher *et al.*<sup>[23]</sup> by the decaying-plasma method in a flow, by measurement of the degree of electron polarization  $P_e$ . Results of the measurement of  $P_e$  ( $P_e = (n_+ - n_-)/(n_+ + n_-)$ ;  $n_{\pm}$  are the populations of states with  $m_s$  equal to  $\pm 1/2$ , respectively) are given in Table I (the error is estimated by the authors as  $\pm 0.1 P_e$ ).

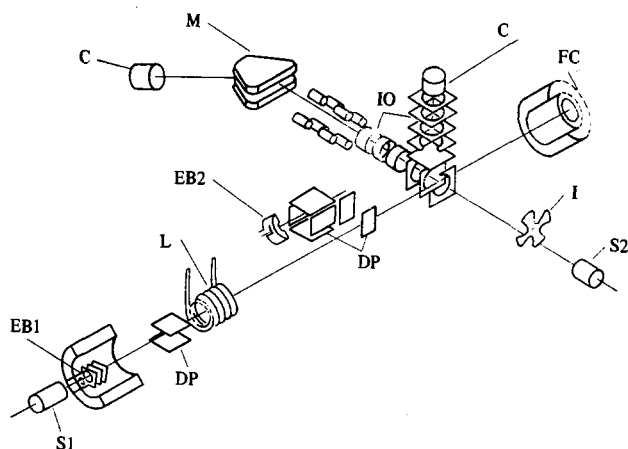


FIG. 7. Diagram of apparatus for measurement of absolute cross sections for chemi-ionization with use of intersecting beams. S1 and S2 are the sources of the beams, EB1 is the electron beam for excitation of He atoms, DP is a set of deflecting plates, L is a lamp for quenching the  $2^1S$  state of He, EB2 is the electron beam for absolute calibration, FC is a Faraday cup, I is a mechanical interrupter of the target-particle beam, C are ion collectors, IO are ion-optical systems for transportation of the charged products, and M is an analyzing magnet.

A characteristic feature of the data given in Table I is the constancy of  $P_e$ , i. e., the fact that the degree of electron polarization is practically independent of the nature of the partner. In addition, as can be seen from Table I, the values of  $P_e$  are in essential agreement with the values measured in the same experiment for the degree of polarization  $P_m$  of He( $2^3S$ ) atoms ( $P_m = (N_+ - N_-)/(N_+ + N_- + N_0)$ , where  $N_+$  and  $N_0$  are the populations of the levels with  $M_s = \pm 1$  and 0. The equality of  $P_e$  and  $P_m$  permits us to conclude that spin polarization is conserved for the chemi-ionization collisions studied. The measurements discussed confirm the predictions of the theoretical analysis carried out by Drukarev *et al.*<sup>[24]</sup> According to these authors the initial polarization of the metastable atoms should be transmitted to the reaction products completely, without any depolarization.

The preservation of the polarization label ( $P_e = P_m$ ) unambiguously favors a dominant role of the electron-transfer mechanism relative to the photoionization mechanism for the systems studied. The small observed deviation of  $P_e$  from  $P_m$  for the CO system (see Table I) can be explained, following Keliher *et al.*,<sup>[23]</sup> by the existence of a resonance for the lower vibrational level of the excited state of the ion  $CO^+$  ( $B^2\Sigma$ )—the additional transition channel to this state arising as the result of the close location of the terms evidently can produce a depolarizing effect.

We note that a byproduct of these studies is the promise of use of chemi-ionization processes as the basis of a method of obtaining polarized electron beams for studies in atomic and nuclear physics.<sup>[25]</sup>

In regard to the photoionization mechanism, direct manifestations of this mechanism have apparently been observed in the recent work of Kubota *et al.*<sup>[5]</sup> devoted

to chemi-ionization of He atoms in the  $3^1P$  state, from which an optical transition is allowed. For the pairs He( $3^1P$ )—Ne, Ar, Kr, and Xe the chemi-ionization cross sections measured by the method of kinetic spectroscopy agree with the photoionization cross sections calculated from formulas of the type proposed in Refs. 10 and 11 (see also Ref. 6). The difference in the calculated and measured cross sections does not exceed 20%; only in the case of Xe does it reach 100% (this discrepancy is outside the limits of the possible inaccuracies of the calculation and deserves special attention).

## B. Measurements of the total cross sections for chemi-ionization by excited particles

Although the number of individual measurements of total cross sections  $Q$  for chemi-ionization by metastable atoms (Penning and associative ionization) amounts to the order of thirty or more,<sup>[6]</sup> systematic measurements of the energy dependence  $Q(E)$  have been carried out only very recently. In Fig. 7 we have shown the arrangement of apparatus for direct measurement of absolute cross sections for chemi-ionization for a fixed collision energy in the thermal range. This apparatus has been used to study the interaction of He( $2^3S$ ,  $2^1S$ ) with Ar, Kr, Xe,  $N_2$ ,  $O_2$ , NO, CO,  $CO_2$ ,  $N_2O$ , and  $CH_4$  and of metastable atoms of the inert gases (Ne, Ar, Kr) with Ar, Kr, Xe,  $N_2$ ,  $H_2$ ,  $O_2$ , NO, CO,  $CO_2$ , and  $N_2O$ .<sup>[26,27]</sup> The  $Q$  values obtained differ substantially from those published previously (see Ref. 6). However, the discrepancy, which appeared discouraging, is completely explainable when the subsequently observed strong dependence of  $Q$  on energy is taken into account; a common deficiency of all previous cross-section measurements was an uncertainty in the relative energy of the collisions. The first reliable experimental indications of a strong dependence  $Q(E)$  were obtained in kinetic measurements with the method of a decaying plasma in a flow.<sup>[28]</sup> This method, developed and perfected by Ferguson and Fehsenfeld,<sup>[4]</sup> has for the last ten years given quantitative data on the rate constants of neutral and ion-molecular reactions in more than one hundred cases. In application to chemi-ionization processes involving He( $2^3S$ ) the measurements reduced to determination at various temperatures of the dependence of the concentration of excited atoms in the flow on the pressure (the frequency of quenching collisions) of the gas studied. Measurements interpreted in terms of the reaction rate constant  $k(T)$  were carried out in Ref. 28 in the temperature range 300–900 °K, which permitted use of standard methods to find  $\epsilon_A$ —the exponent (activation energy)—and  $A$ —the pre-exponential factor of the Arrhenius relation

$$k(T) = A \exp\left(-\frac{\epsilon_A}{kT}\right). \quad (17)$$

In Fig. 8 we have shown the functions obtained, and in Table II we have given values of  $\epsilon_A$  for the systems studied in Refs. 28 and 29. The phenomenological nature of Eq. (17) does not permit us to deduce the nature of the observed activation barrier. In terms of the scheme of chemi-ionization by excited particles discussed

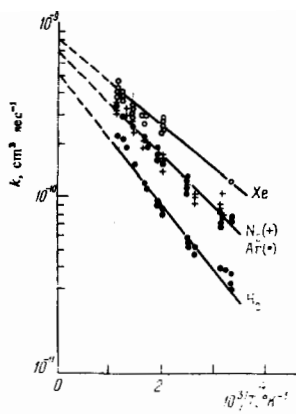


FIG. 8. Typical temperature dependences of the rate constant of chemi-ionization reactions involving He( $2^3S$ ).<sup>[28, 29]</sup> The linearity of the behavior for the coordinates used indicates that the Arrhenius dependence  $k(T)$  is satisfied and permits determination of the activation energy (see Table II).

above, two sources for the appearance of an effective activation barrier are conceivable.

The first of these is the existence of a potential barrier in the long-range part of the term  $V^*$ , similar to that which exists, for example, for the  $a^3\Sigma$  term of the  $He_2$  system. If the level width  $\Gamma(R)$  is small up to the barrier, then only particles with a relative collision energy greater than the barrier height can overcome it and approach to distances where  $\Gamma(R)$  is large.

On the other hand, an effective barrier may be due simply to the nature of the function  $\Gamma(R)$ , which rises rapidly with increase of the internuclear distance. The problem of the nature of the activation barrier we shall consider again below in discussion of measurements of the differential scattering of the system He( $2^3S$ )-Ar, having noted that carrying out additional measurements of  $Q(E)$  in the low-energy region ( $T \leq 10^2$  °K) would undoubtedly clarify this question.

Another simple and effective means of measuring  $Q(E)$  over a wide energy range in the thermal region is to use the time-of-flight method. The method is based on detection of the prompt fluxes  $i(t)$  from a short pulse—a packet of particles with different velocities, produced for example by mechanical interruption of a beam and spreading apart as the result of traversing a drift path (from the interrupter to the detector) of known length  $L$ .

As a result of the spatial spread of the packet in the time interval between  $t$  and  $t + dt$  after the cutoff, particles with velocity in the interval between  $v$  and  $v - dv$  will reach the detector ( $v = L/t$ ). Thus, a beam directed to a target appears to break up into a set of successively arriving monokinetic beams whose intensity is easily

TABLE II. Values of activation energy  $\epsilon_A$  for the chemi-ionization reactions He( $2^3S$ ) + X  $\rightarrow$  He( $1^1S$ ) + X\* (Refs. 28 and 29).

X	$\epsilon_A$ , meV*	X	$\epsilon_A$ , meV*	X	$\epsilon_A$ , meV*	X	$\epsilon_A$ , meV*
Ne	112	O <sub>2</sub>	36	CO	33*	N <sub>2</sub> O	28*
Ar	39	CO <sub>2</sub>	19	NO	37*	C <sub>2</sub> H <sub>6</sub>	37*
Ne	48	NH <sub>3</sub>	12	D <sub>2</sub>	76*	C <sub>2</sub> H <sub>8</sub>	34*
H <sub>2</sub>	72	Kr	53*	CH <sub>4</sub>	47*	C <sub>2</sub> H <sub>10</sub>	28*
N <sub>2</sub>	59						

\*) Values marked with asterisks (\*) were obtained by estimation from the data of Ref. 29.

measured. If we now make the time of flight of the ions arising in the target exceptionally small and known (by accelerating them), then recording the time spectra of intensity of the metastable beam  $i^*(t)$  and of the ions  $i(t)$  will permit us to find the relative magnitude of the cross sections  $Q(v)$  and  $Q(E)$  from the values of  $i^*(t)/i(t)$  for times synchronized with respect to the cutoff. Utilization of the entire set of velocities in the beam permits determination of  $Q(E)$  over a wide range of relative energies from 20 to 600 meV.<sup>[30]</sup> In Refs. 30 and 31 this method of measurement was used for beams of He\*, Ne\*, and Ar\* with detection of both the total fluxes of ions<sup>[30]</sup> and the fluxes of positive ions of Penning or associative ionization, analyzed separately by a quadrupole mass spectrometer.<sup>[31]</sup> In Fig. 9 we have shown the arrangement of the apparatus<sup>[30]</sup> in which the most extensive measurements have been made of the functions  $Q(E)$  for the systems He( $2^1S$ ), He( $2^3S$ )-Ar, Kr, Xe, N<sub>2</sub>, Hg; Ne( $3P_{0,2}$ )-Kr, Hg; and Ar( $3P_{2,0}$ )-Hg. The relative magnitudes of the measured cross sections were calibrated by independent measurements.<sup>[28]</sup>

The results obtained are characterized by an excess by about an order of magnitude of the total cross sections for parahelium  $Q_1$  over the cross sections  $Q_3$  for orthohelium at low collision energies ( $\sim 20$  meV) and the approach of the values of  $Q_3(E)$  and  $Q_1(E)$  at energies  $\geq 10^2$  meV (Fig. 10). For systems which include Hg (Hg-Ar\*, He\*, Ne\*) a falloff of  $Q_3(E)$  and  $Q_1(E)$  with energy is characteristic.

The functions  $Q(E)$  obtained (typical ones are shown in Fig. 10) can be used to determine the characteristics of the interaction  $V^*(R)$  and  $\Gamma(R)$ , on the basis of the formalism developed.<sup>[9]</sup> This information permits us to understand the causes of the striking differences in the experimental dependences for the two forms of metastable helium.

For measurements of the total cross sections for chemi-ionization in the superthermal energy region ( $E_{rel} > 0.1$  eV) attractive possibilities are offered by the original method of overtaking (merging) beams, proposed at the end of the sixties by Belyaev and co-workers<sup>[32]</sup> (see also Ref. 33). In this method, small values of relative energies are achieved by organization of the col-

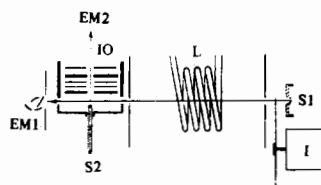


FIG. 9. Schematic representation of apparatus with intersecting beams for determination by the time-of-flight method of the dependence of chemi-ionization total cross sections on energy.<sup>[30]</sup> S1 is the source of the beam of metastable He\* atoms, S2 is the source of the target beam, I is a mechanical beam interrupter, L is a gas-discharge lamp for quenching the  $2^1S$  state of He, IO is an ion-optical system for extraction and acceleration of the chemi-ionization products, EM1 and EM2 are electron multipliers for counting the atoms of He\* and the chemi-ionization products, respectively.



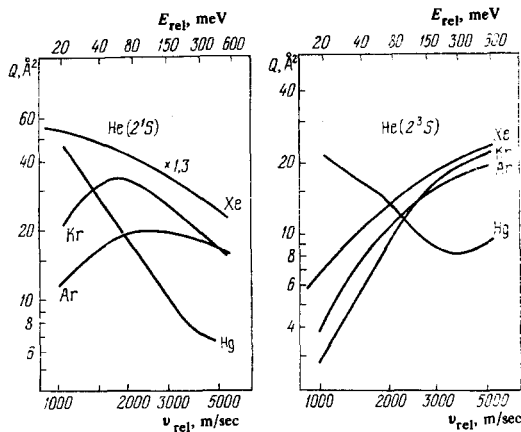


FIG. 10. Smoothed experimental dependences<sup>[30]</sup> of total cross sections for chemi-ionization involving metastable atoms He\* as a function of relative velocity and energy. The cross sections of the system He\*-Hg are given in arbitrary units.

lisions of particles of monokinetic beams of high energies ( $\sim 10^3$  eV) laterally displaced into the interaction region. The relative energy of a collision is related to the kinetic energy in the laboratory system of one of the beams  $E_1$  and the difference in the energies of the beams  $\Delta E = E_2 - E_1$  by the relation  $E_{rel} = (\Delta E)^2 / 8\sqrt{E_1 E_2}$ .

It can be seen from this that displacement, for example, of two beams with energies  $E_1 = 1000$  eV and  $E_2 = 1010$  eV permits study of collisions with  $E_{rel} = 0.0125$  eV. The quasimolecular term can turn out to be imbedded in the continuous spectrum in the case when both colliding particles are in excited states. Such collisions are most conveniently studied by the overtaking-beam method, since by choice of appropriate partners of charge exchange of the initial ion beams it is possible to prepare the particles in different excited states. Very recently such experiments have been carried out<sup>[34]</sup> for the system He( $2^1,3S$ )-Ne( $3P_{2,0}$ ) in the relative collision-energy range  $10^{-2}$ -10 eV.

Figure 11 shows a diagram of the apparatus used<sup>[33]</sup> to measure chemi-ionization total cross sections for

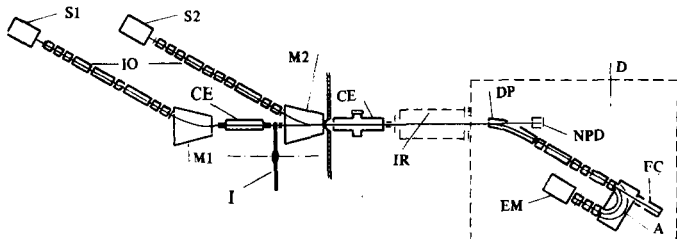


FIG. 11. Schematic form of apparatus for study of atomic collisions in overtaking beams of neutral particles.<sup>[33]</sup> S1 and S2 are ion sources, IO are ion-optical systems for formation and transportation of the beams, CE is the charge-exchange chamber, M1 and M2 are the magnets which analyze and superimpose the beams, I is the mechanical interrupter of beam 1, IR is the interaction region of the particles of the superimposed beams, D is a mobile detecting apparatus, DP is the set of separating deflecting plates, FC is a Faraday cup, A is a hemispherical analyzer for the ion energies, EM is an electron multiplier, and NPD is a neutral-particle detector.

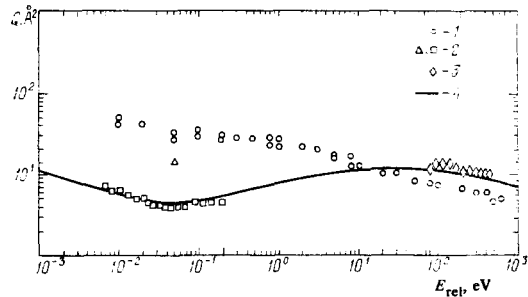


FIG. 12. Summary of results on determination of the total cross section for chemi-ionization of the system Ne\*-Ar as a function of relative energy. 1—overtaking-beam method,<sup>[35]</sup> 2—measurement of quenching cross section with use of Ne\* beam of thermal velocities, according to Refs. 27 and 41, respectively; 3—measurements of cross sections for quenching with use of a fast beam,<sup>[8]</sup> 4—theoretical calculation from Ref. 42.

the systems Ne\*-Ar,<sup>[35]</sup> He\*-H, D,<sup>[36]</sup> He\*-N, O,<sup>[37]</sup> Ne\*-Kr,<sup>[38]</sup> and dissociative ionization cross sections for He\*-H<sub>2</sub>.<sup>[39]</sup> The deficiency (although it is one that can be overcome) of the measurements carried out previously is the indistinguishability of the excited states—the results obtained are an average over the population of  $2^3,1S$  states in the case of He atoms and  $3^3P_{2,0}$  states in the case of Ne atoms. At the present time, using available laser sources,<sup>[40]</sup> it is possible to selectively quench any states and in this way to avoid the averaging mentioned above. In Fig. 12 we have shown results of cross-section measurements in the energy interval  $E_{rel} = 10^{-4}$ - $10^3$  eV for the system Ne\*-Ar. The astonishing feature of the dependence of Fig. 12 is the slow drop of the cross section (only by a factor of six) as the energy changes by five orders of magnitude. In the same figure we have shown a comparison between three independent measurements of  $Q(E)$  (Refs. 8, 41, and 27) and a semiempirical calculation<sup>[42]</sup> aimed at description of the data of Refs. 8 and 41 by a single function. This comparison permits some doubt as the accuracy of the measurements of absolute values in Ref. 41 and allows us to conclude that  $V^*$  and  $\Gamma(R)$  have not been correctly chosen in the semiempirical calculation of Ref. 42. A similar comparison of the cross sections measured in Ref. 36 for the system He( $2^3S$ )-H, D with nonempirical calculations<sup>[19]</sup> showed very good agreement.

### C. Measurements of differential cross sections for chemi-ionization by metastable particles

We can assume that it will be possible by means of the differential-cross-section measurements begun very recently to reveal the true causes of the sharp differences in the behavior of  $Q_3(E)$  and  $Q_1(E)$ , and to establish reliably the form of the dependence  $\Gamma(R)$ . Several variants of the study of chemi-ionization differential cross sections have been worked out in various energy regions and with various means of detecting the effect.<sup>[43-45, 46]</sup>

Figure 13 shows schematically the apparatus for measurements in the thermal region of the differential elastic scattering in intersecting beams of the atoms

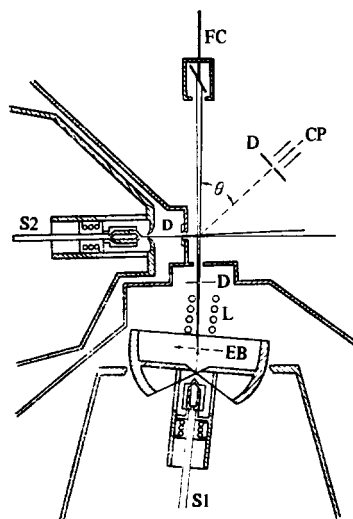


FIG. 13. Diagram of apparatus employing intersecting beams for study of the differential elastic scattering of He\* atoms.<sup>[43]</sup> S1 and S2 are sources of molecular beams, EB is the electron beam for excitation, L is a lamp for quenching of the 2<sup>1</sup>S state, D are collimating diaphragms, FC is a Faraday cup, CP is a channel-plate electron multiplier for detection of scattered He\* atoms; the cross-hatched regions represent diaphragms which separate differentially pumped volumes.

He(2<sup>1,3</sup>S)-Ar, Ne.<sup>[43,44]</sup> Detection of the fluxes of elastically scattered metastable atoms was carried out on the basis of the secondary-electron emission produced by them in a molybdenum-beryllium plate; for discrete counting use was made of subsequent acceleration of the electrons, directed toward a scintillator placed in front of the entrance window of a photomultiplier tube. Separate detection of singlet and triplet atoms was accomplished by the usual quenching of the 2<sup>1</sup>S state by the radiation of a helium discharge lamp [He(2<sup>1</sup>S) + hν - He(2<sup>1</sup>P) - He(1<sup>1</sup>S)].

The measured differential cross section for scattering of the system He(2<sup>3</sup>S)-Ar is shown by the solid line in Fig. 14. The pattern of the differential cross section can be interpreted in terms of a complex potential  $V_R = V^* + iV$ ,<sup>[47]</sup> which includes a potential  $V^*$  and a width  $\Gamma = -V/2$ , but the dependence in Fig. 14 has a feature predicted by Chen *et al.*<sup>[44]</sup> by a simpler method of analysis of the measurements. In fact, beginning with an angle  $\theta_{lab} \sim 40^\circ$ , an appreciable change is visible in the behavior of the dependence, which appears in a rapid decrease of the flux of scattered particles. The only channel for loss of metastable particles is the chemi-ionization process, and it is therefore natural to conclude that up to this angle the dependence  $\sigma_{el}(\theta)$  describes purely elastic scattering, while for  $\theta \geq 40^\circ$  an inelastic channel for disappearance of particles is turned on. Then the initial portion of the dependence can be used to establish the term  $V^*$ , using known means of solution of the inverse problem.<sup>[48]</sup>

After determination of the interaction potential  $V^*$  (the complexity in the behavior of  $V^*$  required for its description 15 parameters, some of which were taken from other studies, and some of which were determined

in solution of the inverse problem) it can be used to obtain  $\sigma_{pot}(\theta)$ —the behavior of the cross sections in the range of angles  $\theta > 40^\circ$  unperturbed by chemi-ionization. This behavior is shown in Fig. 14 by the dashed line. The subsequent analysis of the measurements, following Ref. 49, is based on use of the so-called optical model. The measured scattering cross section  $\sigma_{el,ast}(\theta)$  can be related to the cross section for pure elastic scattering by means of an opacity function  $O(\theta)$  which effectively describes the absorption and disappearance of the particles and which is related to the survival probability,  $O(\theta) = 1 - W(\theta)$ .

In the region of angles beyond the rainbow peak  $\theta > \theta_r$  (where the classical deflection function  $\theta(b)$  is single valued) the opacity function  $O(E, b)$  for fixed energy  $E$  permits calculation of the chemi-ionization total cross section

$$Q(E_0) = 2\pi \int O(E_0, b) b db, \quad (17')$$

and for the value  $E_2 = 65$  meV used in the measurements of Ref. 44 the calculations give for He\*-Ar the values  $Q_3 = 15 \text{ \AA}^2$ ,  $Q_1 = 31 \text{ \AA}^2$ , which are roughly twice the values given in Fig. 10. Haberland *et al.*<sup>[43]</sup> also attempted to find the dependence  $Q(E)$  on the basis of the obtained opacity function  $O(E_0, b)$ . However, the means used to construct the universal function  $O(E, b)$  from  $O(E_0, b)$  cannot be regarded as correct. Therefore the conclusion drawn by Haberland *et al.*<sup>[43]</sup> that there is a chemi-ionization energy threshold ( $E_{thr} = 0.02$  eV) and that the cross section  $Q(E)$  is constant in the region  $E \geq 0.1$  eV cannot be considered reliable; furthermore, they are inconsistent with the direct measurements of  $Q(E)$  shown in Fig. 10. The energy threshold obtained in this way cannot be related to the activation energy actually observed previously (see Table II).

Another method of studying differential scattering with detection of the ionized products of the reaction He(2<sup>1</sup>S)-Ar has been used by Leu and Siska.<sup>[45]</sup> Analysis of the products (Ar<sup>+</sup> and HeAr<sup>+</sup>) was carried out by a quadrupole mass spectrometer which provided rotation with respect to the region of intersection of the beams; discrete counting of ions was performed at the

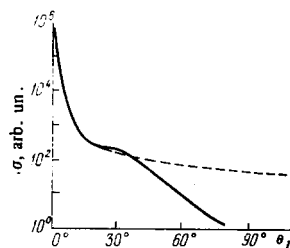


FIG. 14. Pattern of differential elastic scattering of a beam of He(2<sup>1</sup>S) in Ar at  $E = 0.65$  eV (the L system).<sup>[44]</sup> The solid curve is the smoothed experimental dependence; the dashed curve is a calculation with use of  $V^*(R)$  determined from the initial portion of the experimental dependence. Beginning with  $\theta_L = 35^\circ$ , a suppression of the flux of elastically scattered particles is distinctly visible, which is related to the disappearance of He(2<sup>1</sup>S) in the chemi-ionization process.

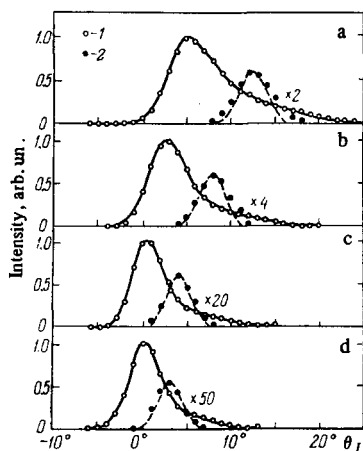


FIG. 15. Angular distributions of products of the reaction  $\text{He}(2^1\text{S}) + \text{Ar} \rightarrow \text{He}(1^1\text{S}) + \text{Ar}^* + e$ : 1— $\text{Ar}^*$ , 2— $\text{HeAr}^*$ , for various initial relative energies  $E$  (eV): a) 0.068, b) 0.086, c) 0.156, and d) 0.248. The angle  $\theta = 0$  corresponds to the direction along the beam of Ar. The dashed curves are the calculated distributions of the velocity vectors for the motion of the center of mass  $\bar{v} = (m_{\text{Ar}}\bar{v}_{\text{Ar}} + m_{\text{He}}\bar{v}_{\text{He}}) / (m_{\text{Ar}} + m_{\text{He}})$ . The displacement of the  $\text{Ar}^*$  peak with respect to  $\theta = 0$  is due to scattering in the approach to distances  $R$  where the quantity  $\Gamma(R)$  becomes appreciable.

exit of the mass spectrometer. The elastic-scattering measurements carried out here give results in agreement with those obtained by Haberland *et al.*<sup>[43]</sup> In Fig. 15 we have shown the characteristic appearance of the angular distributions (in the laboratory system) for various  $E_{\text{rel}}$ . We can distinctly see a suppression of the contribution of the associative channel with increase of  $E_{\text{rel}}$ . The distribution of  $\text{Ar}^*$  ions is concentrated in the forward direction, near the initial beam axis, which is quite explainable in terms of the scheme of vertical transitions between the terms  $V^*$  and  $V^+$ , which have shallow potential wells. A kinematic analysis of the  $\text{Ar}^*$  distributions by means of Newton diagrams<sup>[50]</sup> permits establishment of a value of recoil energy compatible with the observed distribution. It turned out that the observed distributions can be described by taking the ratio of the initial and final relative energies  $E/E^1$  equal to 0.34, 0.61, 0.85, and 0.9 for the four measurements shown in Fig. 15. The differential cross sections obtained from analysis of the primary data for scattering of the products in the center-of-mass sys-

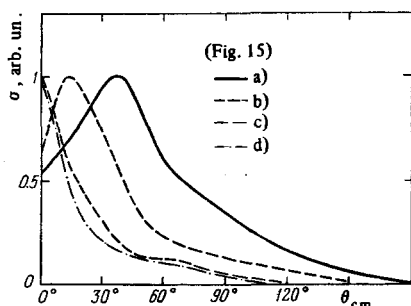


FIG. 16. Differential cross sections in the C system, found from analysis of the data of Fig. 15, for the process  $\text{He}(2^1\text{S}) + \text{Ar} \rightarrow \text{He}(1^1\text{S}) + \text{Ar}^* + e$ .

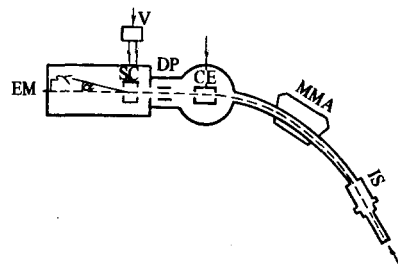


FIG. 17. Schematic form of apparatus for study of differential chemi-ionization with use of fast beams.<sup>[46]</sup> IS is an ion source of the Nier type, MMA is a magnetic mass analyzer, CE is a charge-exchange chamber, DP are deflecting plates, SC is a scattering chamber, V is a solenoid valve providing admission of gas alternately either into the scattering chamber or into the vacuum region, and EM is an electron multiplier.

tem are shown in Fig. 16, and their form gave Leu and Siska<sup>[45]</sup> a basis for concluding that there is a potential barrier in the region  $R > R_m$  in the long-range part of the  $V^*$  term.

It is not possible to obtain information on the behavior of  $V^*$ ,  $V^+$ , and  $\Gamma(R)$  in the region of small distances in experiments with thermal beams. Collisions with close approach have been achieved and the differential chemi-ionization studied with use of fast  $\text{He}(2^3\text{S})$  beams by Kalinin and Leonas.<sup>[46]</sup> Scattering of beams with energies  $E = 400, 600, 1200,$  and  $2000$  eV was studied in the apparatus shown in Fig. 17. An investigation was made of the region of small scattering angles corresponding to approach to a distance where the energy of interaction of the repulsive type has values from tenths to units of electron volts.

In real experiments with high energy beams the measurement of differential cross sections at small angles has encountered difficulties due to the finite size of the beam, the detector slit, and so forth. Actually the measured quantity turned out to be not the differential cross section itself, but its fold  $I(\alpha)$  with the angular aperture of the detector, which was set at an angle  $\alpha$  to the beam.<sup>[51]</sup>

In Fig. 18b we have given typical experimental dependences (reduced coordinates  $I\alpha^2$  and  $\alpha E$  have been used);

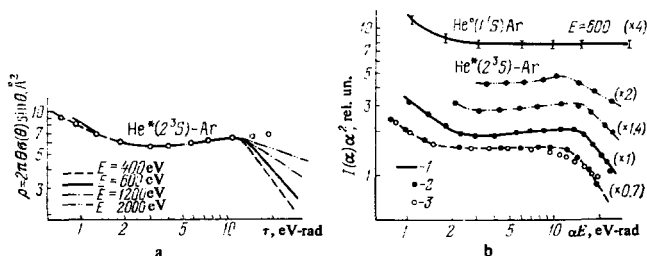


FIG. 18. Differential scattering of He atoms in Ar.<sup>[41]</sup> a) Reduced differential cross sections  $\rho(T)$  (the circles show the elastic differential cross section calculated from  $V^*$  (Ref. 46)); b) dependence of the scattered-particle flux in reduced coordinates: 1) smoothed experimental curves, 2) calculation with use of  $\Gamma(R)$  and  $V^*(R)$  from Ref. 46, 3) calculation with use of  $\Gamma(R)$  from Ref. 42; the vertical bars show the typical spread of the experimental values.

TABLE III. Parameters  $B$  and  $\beta$  of the exponential approximation of the level width  $\Gamma(R)$  of the system  $\text{He}^*-\text{Ar}$ .

$B$ , eV	$\beta$ , $\text{\AA}^{-1}$	Reference
$2.01 \cdot 10^5$	5.3	30
$1.09 \cdot 10^5$	5.25	31
$1.98 \cdot 10^6$	5.55	53
$2.72 \cdot 10^4$	2.84	22
$1.24 \cdot 10^3$	5	46

in Fig. 18a we have shown the reduced differential-scattering cross sections  $\rho(\tau)$  of the  $\text{He}^*-\text{Ar}$  system, obtained by inversion of the fold  $I(\alpha)$ . From comparison of the behavior of  $I\alpha^2$  ( $\rho(\tau)$ ) for systems including the atoms  $\text{He}(1^1\text{S})$  and  $\text{He}(2^3\text{S})$ , it is evident that the differential scattering of metastable helium is characterized by distinct features—a sharp drop for  $\alpha E$ ,  $\tau > 12$  eV-rad and a dependence of the steepness of fall-off on energy. It is natural to relate these features to the appearance of effects of autoionization decay of the quasimolecules and to consider them as a potential source of information on the characteristics of the decaying system. An additional interesting feature of the observed dependences  $I\alpha^2$  and  $\rho(\tau)$  is the fact that for values  $\tau \leq 12$  they lie on a single curve for each of the systems studied ( $\text{He}^*-\text{Ar}$ ,  $\text{Kr}$ , and  $\text{Xe}$ ). This provides a basis for assuming that the scattering in this range of reduced angles is independent of velocity, and therefore is not perturbed by decays, and for use of the dependences  $I\alpha^2$  and  $\rho(\tau)$  for determination of  $V^*(R)$ . In choice of the behavior of  $V^*(R)$  we took into account the need for a smooth joining of the values of the trial  $V^*(R)$  with the potentials determined in measurements with beams of thermal energies.<sup>[44]</sup>

The results of choice of the potential  $V^*$  (Ref. 46) are illustrated by the agreement shown in Fig. 18a of the elastic differential cross sections  $\rho_{el}(\theta)$  calculated from  $V^*$  (the circles) with the measured cross sections.

In the region of reduced angles  $\alpha E$ ,  $\tau > 12$ , where perturbation by autoionization transitions appears, the scattering pattern will be determined not only by the potential  $V^*$  but also by the curve of the ionic state of the quasimolecule. If information is available<sup>[52]</sup> on  $V^*$  and  $V^+$ , we can determine  $\Gamma(R)$  on the basis of a quantitative calculation of the scattering pattern with trial functions  $\Gamma(R) = B \exp(-\beta R)$  and compound potentials formed from  $V^*$  and  $V^+$ . Such calculations permitted choice of values of  $B$  and  $\beta$  which describe the measurements (the solid circles in Fig. 18b); the values found are given in Table III.

For the system  $\text{He}^*-\text{Ar}$  there is the possibility of comparing the total cross sections for destruction of  $2^3\text{S}$  states, calculated for the values of  $B$  and  $\beta$  in Table III, with the values measured in Ref. 8. The results of a calculation in accordance with the expression  $Q(E) = 2\pi \int P(b, E) b db$  and the data of Ref. 8 give good agreement in the interval  $E = 100-2000$  eV.

For the most widely studied pair  $\text{He}(2^3\text{S})-\text{Ar}$  we have

given for comparison in Table III the values of  $B$  and  $\beta$  determined by other authors. The first thing which catches our attention is the sharp difference in the parameter values of the individual determinations. A second feature is due to the fact that  $B$  and  $\beta$ , as determined from measurements with thermal beams,<sup>[30, 31, 53]</sup> in contrast to the values from Refs. 46 and 22, give unacceptably large values of the total cross sections  $Q(E)$  in the high-energy region. The total cross sections  $Q(E)$  calculated from the data of Refs. 30, 31, and 53 are greater than the experimental values by two to three times. Thus, there is a distinct discrepancy in the results, which cannot be explained in terms of the simple concepts considered above. A compromise between the results under discussion is possible only in the case when the behavior of  $\Gamma(R)$  has a steepness which changes rapidly with distance of approach. In this case it is possible to match the values of  $\Gamma(R)$  obtained for thermal collisions (and corresponding to large distances of approach) with the values obtained in fast beams and which correspond to small distances of approach. Just how realistic such a behavior of  $\Gamma(R)$  is can be determined only by reliable calculations of  $\Gamma(R)$  or by additional measurements with beams of intermediate energies, 1–10 eV. An additional possibility of explaining the observed discrepancy may involve the existence of a dependence of  $\Gamma(R)$  on energy. Observation of such a dependence is also a problem for experiments of the near future.

## 2. PROCESSES WITH ELECTRON TRANSFER

The low ionization potential, i. e., the weak binding of the outer electron, in alkali-metal atoms ( $M$ ) in collisions with partners ( $X$ ) possessing a substantial electron affinity ( $EA$ ) leads to an effective lowering of the threshold energy for appearance of ions and to large cross sections for the production of a pair  $M^+-X^-$ . A typical pattern of quasimolecular terms, shifted toward infinity by an amount  $\Delta E (=IP - EA)$ , shown in Fig. 19, makes clear what we have been saying. A characteristic feature of the behavior of the terms is the crossing of the covalent term of the  $M-X$  system and the ionic term of the  $M^+-X^-$  system at the point  $R_c$  for which we have

$$\Delta E - \frac{e^2}{R_c} \approx \frac{C}{R_c^6}, \quad (18)$$

since at large distances the covalent term corresponds

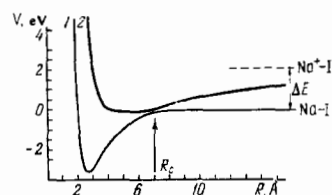


FIG. 19. Behavior of the  $1\Sigma^+$  adiabatic covalent and ionic terms of the system  $\text{Na}(2^1S_{1/2})-\text{I}(2^3P_{3/2})$  (curve 1) and of the system  $\text{Na}^+(1^1S_0)-\text{I}^-(1^1S_0)$  (curve 2). The value shown for the asymptotic difference in energy of the terms 1 and 2,  $\Delta E$ , is equal to the energy threshold for formation of an ion pair;  $R_c$  is the point of pseudocrossing of the terms.

mainly to a dispersive attraction  $\sim C/R^6$ , and the ionic term corresponds to a Coulomb attraction  $\sim e^2/R$ . Since at large distances the energy of dispersive attraction is only a small fraction of the Coulomb energy, it can be neglected and from Eq. (18) it follows that  $\Delta E = e^2/R_c$ . For  $\Delta E = 2-3$  eV it is easy to arrive at an estimate  $R_c = 7-5 \text{ \AA}$  and correspondingly to an upper limit of the cross section  $Q = \pi R_c^2 \approx 10^2 \text{ \AA}^2$ .

Manifestations of electron-transfer effects have been observed in studies in intersecting beams of alkali-metal atoms and molecules  $X_2$  containing halogens ( $X = \text{Br, I, and so forth}$ ) of the dynamics of chemical reactions (see Ref. 54), whose measured cross sections turned out to be very large (up to  $10^2 \text{ \AA}^2$ ). To explain these results the physically understandable "harpoon" model<sup>[54]</sup> based on the phenomenon of electron transport has been proposed.

In collisions with the reaction  $M + X_2 \rightarrow MX + X$ , the "harpoon" is the weakly bound electron of atom M; this harpoon is thrown to the molecule  $X_2$  (in traversal of the point of crossing by the system  $M-X_2$ ). Reaching the point  $R_c$  signifies the onset of a short-lived ion pair—an intermediate association product  $MX_2$  ( $M^+-X_2^-$ ), which immediately decays into  $MX$  and  $X$ . The magnitude of the cross section is determined by the length  $R_c$  of the harpoon line, and the cross section turns out to be large, roughly equal to  $\pi R_c^2$ . However, at thermal collision energies, reaching the point of crossing of the terms  $R_c$  (Fig. 19) does not necessarily lead to formation of a free pair  $M^+, X^-$ , since for separation of these products an energy in the center-of-mass system equal to or greater than the reaction threshold  $E_{\text{thr}} = \Delta E$  is necessary.

The necessary energy can be derived not only from the initial kinetic energy; thus, according to Ref. 55 in chemi-ionization in thermal collisions of a dimer  $K_2$  with molecules containing halogen atoms ( $\text{Br}_2, \text{I}_2$ , and so forth), separation of the ionic products is accomplished by utilization of the separation energy of the dimer bond.

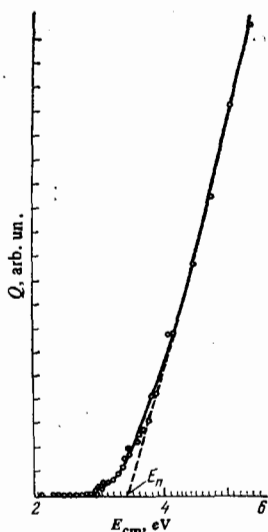


FIG. 20. Example of removal of instrumental effects in determination of the threshold behavior of the excitation function of the process  $\text{Cs} + \text{O}_2 \rightarrow \text{Cs}^+ + \text{O}_2^-$ . The circles are the experimental points, and the solid curve is a fold calculated with the trial function shown by the dashed line.

For a negative value of  $\Delta E$  ( $IP < EA$ ) the asymptote of a covalent term of  $M-X$  turns out to be higher than the asymptote of the term  $M^+-X^-$ , and the possibility of a crossing disappears. For molecular reagents  $X_n$  the relative position of the asymptote of the term  $M^+-X_n^-$  is determined by the level of excitation of  $X_n^-$  (electronic or vibrational). Therefore the absence of a crossing for the term corresponding to the ground state of  $X_n^-$  does not exclude a crossing of the terms corresponding to excited states of  $X_n^-$ . These effects have been observed experimentally<sup>[16]</sup> in study of pairs including  $M$  and the fluorides of metals  $\text{XF}_6$  ( $X = \text{Mo, W, Ir, Re}$ ). For these systems with  $\Delta E \leq 0$  the detection of ionic products in thermal collisions can be explained only by the appearance of excited negative ions.

The magnitude of the electron affinity in the case of molecules depends on the initial vibrational state ( $v$ ) or, more precisely, on the instantaneous internuclear distance at the moment of the transition. Thus, even for the ground vibrational states of molecules  $X_2^-$  and  $X_2$ , two measured affinity values are possible, depending on the direction of the transition  $X_2^- \rightleftharpoons X_2 + e$  (usually the adiabatic value of the affinity, which corresponds to the ground vibrational levels of the molecules  $X_2$  and  $X_2^-$ ,  $v=0, v'=0$ , and the vertical value of the affinity are different).

Studies of collisions with transfer of an electron are carried out in two main directions—measurements of the excitation function (EF), i. e., of the dependence of the total cross sections for formation of pairs of ions on energy, and measurements of the differential elastic and inelastic scattering of atoms  $M$ . Practically all of these studies of chemi-ionization collisions have been carried out with beams of alkali-metal atoms. Studies of excitation functions have permitted development of a new method for determination of an important atomic characteristic—the electron affinity. Measurements of EF permit determination of  $E_{\text{thr}}$ —the energy threshold of the process ( $E_{\text{thr}} = \Delta E$ ; see Fig. 19) and thus for a known value  $IP(M)$  to find the energy of the electron affinity  $EA(X)$ .

Establishment of the true threshold behavior of the EF in this new technique for determining the affinity involves overcoming a series of experimental difficulties. In the first place, the smallness of the useful signal near threshold will lead to detection of an apparent threshold; second, the existence of a spread in the relative collision energies as a result of the nonmonokinetic nature of the beams used leads to a shift (toward lower energies) of the measured threshold. Effective methods for avoiding these effects<sup>[57,58]</sup> have been developed, based on calculation of the fold of a trial (model) excitation function with the known distributions of the dynamical parameters, and combination of the calculations with the experimental dependence.

In Fig. 20 we have shown an example of the combination for the  $\text{Cs}-\text{O}_2$  system, and it is evident that the method used gives a distinct location of the threshold  $E_{\text{thr}}$  and therefore a value of the EA. The informativeness of this new method is illustrated in Table IV,

TABLE IV. Summary of results on determination of electron affinity from excitation-function thresholds in chemi-ionization.

Atom or molecule	"Harpooner"	Electron affinity, eV	References
O <sub>2</sub>	Cs	0.46±0.06	57
NO	" "	0.4±0.1	58
NO <sub>2</sub>	" "	2.5±0.1	58
N <sub>2</sub> O	" "	-0.15±0.1*)	58
SF <sub>6</sub>	" "	0.65±0.2	56
TeF <sub>6</sub>	" "	3.2±0.2	56
SeF <sub>6</sub>	" "	3.0±0.2	56
WF <sub>6</sub>	" "	4.5	56
IrF <sub>6</sub>	" "	4.34	56
MoF <sub>6</sub>	" "	3.89	56
ReF <sub>6</sub>	" "	3.89	56
SF <sub>5</sub>	" "	2.8±0.2	56
Br <sub>2</sub>	" "	2.23±0.1	60
Br <sub>2</sub>	K	2.48±0.1	61
I <sub>2</sub>	K	2.6±0.1	62
" "	Na, Li	2.4±0.1	62
" "	Na <sub>2</sub>	2.5±0.2	62, 63
NO <sub>2</sub>	Cs	1.14±0.15	64
ClI <sub>2</sub> I	K, Na	0.2±0.1	65
CH <sub>3</sub> Br	K	0.4±0.1	65
CFCI <sub>2</sub>	" "	0.9	66
CFCI <sub>3</sub>	" "	1	66
CO <sub>2</sub>	Na, K, Cs	-0.6±0.2	67
COS	" "	0.46±0.2	67
CS <sub>2</sub>	" "	1±0.2	67
I	" "	3.2±0.1	60, 62
" "	Na	3.0±0.1	62
" "	Li	3.1±0.1	62
" "	K <sub>2</sub>	3.2±0.2	62, 63
SO <sub>3</sub>	Cs	1.7±0.15	62, 64
O <sub>3</sub>	Cs	2.14±0.15	64
Br <sub>2</sub>	Na	2.64	67
Br <sub>2</sub>	Li	2.49	67

\*)Negative values of electron affinity correspond to metastable ions.

where we have given a summary of the results on determination of EA by measurements of EF; for the most carefully carried out studies there is good agreement of the EA values with data obtained by other methods (photoejection, electron impact).

The new results were obtained with use of molecular partners; thus, in Ref. 65 the interesting observation was made of appearance of vibrational excitation of CH<sub>3</sub>Br molecules for the system K-CH<sub>3</sub>Br; it turned out that the EF at threshold are substantially more sensitive to the vibrational energy (which is controlled by the temperature of the CH<sub>3</sub>Br target) than to the relative energy of the collision (which is determined by the K beam energy).

For collisions with molecules, another channel for pair formation is possible—the dissociative chemi-ionization channel. In Ref. 62 a study of EF by mass-spectrometric detection of the products X<sup>-</sup> and X<sub>2</sub><sup>-</sup> (X<sub>2</sub> = Br<sub>2</sub>, I<sub>2</sub>) revealed a characteristic difference in the thresholds and in the behavior of the EF in the two cases. It has been possible to obtain<sup>[62]</sup> a qualitative description of the differences in behavior of the EF for M = Li, Na, and K on the basis of a scheme of crossing of the initial covalent term and the ionic terms corresponding to various quasimolecular systems composed of M and either molecular X<sub>2</sub><sup>-</sup> or the atomic ion X<sup>-</sup>.

The cause of the difference in the form of the EF is the possibility of asymmetry of the entrance and exit portions of the trajectory in the region to the left of the point of crossing. In fact, if the decay of X<sub>2</sub><sup>-</sup> occurs in the time between two successive passages of the crossing point, the interaction in the exit portion will corre-

spond to a term of the system M<sup>+</sup>-X<sup>-</sup>, and not to the term M<sup>+</sup>-X<sub>2</sub><sup>-</sup>. Using this reasoning and some additional assumptions, Mouthinho *et al.*<sup>[62]</sup> were able to reproduce the features of the behavior of the EF for systems including Na and K (atoms of Li in the interval studied have too high a velocity, and the condition of rapid decay of X<sub>2</sub><sup>-</sup> is not satisfied). Dissociative ionization of CO<sub>2</sub>, CS<sub>2</sub>, and COS have been studied,<sup>[67,68]</sup> and the relative weights of the decay channels with formation of various fragment negative ions were found. The thresholds of dissociative formation of pairs of ions for collisions of noble gas atoms (Ar, Xe) with molecules of CsBr and NaBr have been measured in Ref. 69, and those of Xe, Kr, and Ar, with CsCl<sub>2</sub> and Cs<sub>2</sub>Cl<sub>2</sub> in Ref. 70.

The informativeness of EF measurements is limited, and measurements of the differential cross sections for production of ion pairs are substantially more interesting. Such measurements have been carried out for the systems K-Br<sub>2</sub>, I<sub>2</sub>; Li-Br<sub>2</sub> (Ref. 71); K, Na, Cs-I<sub>2</sub> (Refs. 72 and 73); Na-I (Ref. 74); Li-Cl<sub>2</sub>, HBr, HCl, O<sub>2</sub>, SF<sub>6</sub> (Ref. 75); K-O<sub>2</sub> (Ref. 76) with detection of both elastically scattered atoms M and the ions M<sup>+</sup> which arise. These measurements make an important contribution to the intensive development in recent years of a new direction of research—so-called collision spectroscopy.<sup>[77]</sup> In contrast to ordinary spectroscopy, collision spectroscopy deals with quasistationary states and the corresponding transitions to quasimolecules.

The attractiveness of studies of differential scattering in the M-X system is due to the fact that at large distances the exact behavior of the ionic term is known beforehand, and this limits the number of free parameters in calculation of the scattering pattern and gives a fine object for application of the tool of collision spectroscopy which has been developed.<sup>[77]</sup>

We shall discuss in more detail only the results<sup>[74]</sup> for the system Na-I, since they correspond to a spherically symmetric interaction, while the assumption of central forces is a crude approximation in interpretation of measurements with molecules. In addition, measurements for the Na-I system are also distinguished by a high degree of perfection in method. In Fig. 21 we have shown a diagram of the apparatus used in Ref. 74, which is an example of the latest generation of apparatus. The measurements were carried out on-line with a small computer, which controlled the step motor for moving the detector, controlled the operation of the multichannel analyzer which accumulated the results of repeated traversals of the angular range of the measurements, monitored the experimental conditions, and accomplished the primary analysis of the data.

In Fig. 22 we have shown (in the center-of-mass system) the experimental measurements of the differential scattering of the Na<sup>+</sup> ions produced for a beam energy E<sub>lab</sub> = 18.2 eV; the abscissa shows the reduced angle τ = θE. In Fig. 22 we can see a well resolved rich structure which includes the so-called rainbow peaks at τ = 35 and τ = 250 and multiple rainbows (Stueckelberg oscillations). The rainbows are due to the features of scattering by the wells of the ionic and covalent intersect-

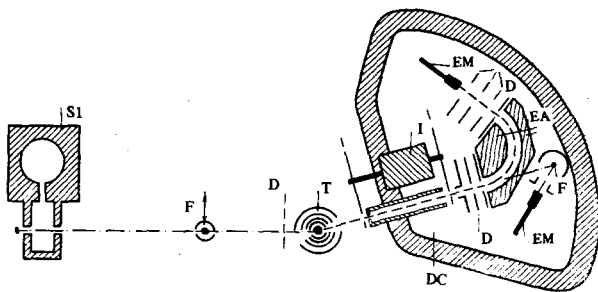


FIG. 21. Diagram of apparatus for study of differential scattering with electron transfer in the system Na-I. S1 is a source with charge exchange of fast Na atoms, T is a target with dissociated iodine vapor, DC is a differentially pumped moveable detection chamber, I is a mechanical beam interrupter, EA is an electrostatic analyzer of the products, EM are electron multipliers for detection of the elastically and inelastically scattered beams. F are hot filaments for surface ionization, and D are collimating diaphragms.

ing terms, and the oscillations are due to interference of the contributions from the two trajectories arising in the case of crossing of the terms. An analysis of the curve shown in Fig. 22, which with complete justification can be called a scattering spectrum, was accomplished by calculation of the scattering pattern in a system of two crossing terms  $U_{cov}$  and  $U_{ion}$ . These terms are described by the sum of the components of the dispersive attraction and the valence repulsion (for a covalent potential) and by the sum of the components of the valence repulsion and the electrostatic, induction, and dispersive attractions (for an ionic potential). The components of the attraction are determined by known atomic characteristics—charge, polarizability, Van der Waals' constant, and therefore it is easy to supply a numerical estimate; the components of the repulsion, which are approximated by exponential functions, are unknown and are to be determined by solution of the inverse problem.

The behavior of the adiabatic terms, i. e., the split terms  $U_{cov}(2)$  and  $U_{ion}(1)$ , is shown in Fig. 19; the probability of a single crossing 1-2 along the diabatic term is given for a given impact distance by the well-known exponential formula of Landau and Zener,<sup>[77]</sup> in which the argument includes the difference in the slopes  $dU/dR$  of the diabatic terms at the point  $R_c$ ,  $H_{12}$ —the value of the adiabatic splitting of the terms, and the radial velocity  $v_R$  at the point  $R_c$ . Like the exact behavior of the terms  $U_{cov}$  and  $U_{ion}$ , the value of the splitting parameter  $H_{12}$ , which is unknown in magnitude, can be found by fitting the calculated cross section to the measured dependence. The rich structure of the scattering spectrum guarantees uniqueness in determination of the corresponding parameters. In fact, the calculations carried out in Ref. 74 with use of a set of trial values of the decisive parameters permitted general agreement to be obtained between the observed and calculated structures of the scattering spectrum (the solid line in Fig. 22 shows the interference structure reproduced in the calculation, and the arrows show the reproduced positions of the oscillation maxima).

However, comparison of the measurements and cal-

culations revealed several characteristic discrepancies. For example, the period of the oscillations in the vicinity of  $\tau \sim 65$  is not reproduced, nor is the value of the cross section in the region of the minimum at  $\tau \sim 65$ , and the magnitude of the differences depends on energy in both cases.

The discrepancies found correspond to angles where the deflection function is determined mainly by the interaction near the region of crossing of the terms. Delvigne and Los<sup>[74]</sup> discuss the possible sources of the discrepancies, associated with various approximations used in the calculation. The authors conclude that the dependence of the discrepancies on energy requires taking into account the effect of transitions induced by rotation of the internuclear axis in the collision. Rotational transitions occur only between the crossing  $^1\Sigma^+$  ionic and  $^1\Pi^+$  covalent terms of the system (Landau-Zener transitions occur between terms of low electronic states of the system). It is well known<sup>[78]</sup> that the probability of such rotational transitions is described by an exponential whose argument has a linear dependence on the relative velocity; for a Landau-Zener probability the dependence is inverse.

Calculations invoking both mechanisms of nonadiabatic transitions, although they did permit the agreement to be improved, nevertheless, did not completely remove the discrepancies. The reason for this was discussed in the later paper,<sup>[79]</sup> where a substantially more accurate calculation was made of the differential scattering in the Na-I system, the nonadiabatic transitions not being localized at the point  $R_c$ , but permitted in a finite region of distances (the splitting  $H_{12}$  depended on the distance). Comparison of the results of this calculation<sup>[79]</sup> with the measurements which we have discussed (Fig. 22) has permitted removal of the discrepancies and has shown that to obtain agreement with the measurements it is not necessary to take into account rotational transitions.

For the classical treatment of scattering in the M-X<sub>2</sub>

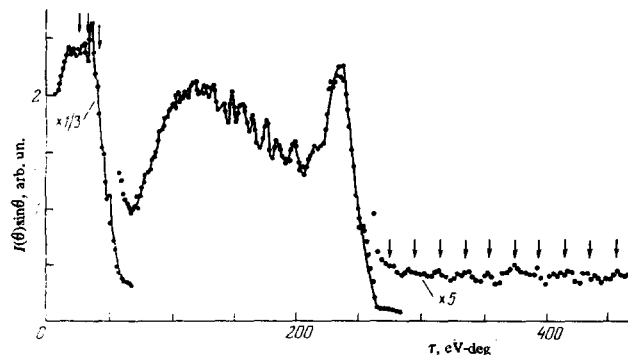


FIG. 22. Pattern of differential scattering in the process Na + I  $\rightarrow$  Na<sup>+</sup> + I<sup>-</sup> (relative collision energy 18.2 eV). The circles are the experimental values, the solid curve is the interference structure obtained in the calculation and due to the action of attractive forces in passing along the adiabatic terms. The arrows show the locations of the interference peaks obtained in the calculation and due to the repulsive branches of the terms.

system, a qualitative analysis of the effect of variations of the decisive parameters (the asymptotic splitting of the terms  $\Delta E$ , the magnitude of the splitting of the terms  $H_{12}$ , the depth of the ionic potential well, and the relative collision energy) has been carried out by Duren.<sup>[60]</sup> The results obtained are useful as a unique "instruction" in practical numerical fits to a measured scattering pattern.

### 3. ASSOCIATIVE IONIZATION OF ATOMIC PARTICLES OF THERMAL ENERGY

The associative ionization in collision of particles in electronic ground states and in the case when the excitation energy of one of them is below the ionization potential of the other (the Hornbeck-Molnar process) is an additional new and interesting object of studies of the physics of atomic collisions. The experimental appearance of associative ionization (AI) was observed long ago,<sup>[1]</sup> but only in recent years has a systematic study of this phenomenon begun. From the theoretical point of view these processes are interesting because of the fact that they involve the departure of a term of a discrete quasimolecular state into the continuous spectrum with a subsequent decay described, as in the case of Penning ionization, by a width. In a number of cases the model of slow decay is used, i. e., localization of the region of the transition from the quasimolecular state  $AB$  to the state  $AB^+$ . Study of the behavior of collision systems near the boundary of the continuous spectrum forms the physical content of the studies considered below.

We limit ourselves here to discussion of collisions of particles in electronic ground states. Interest in study of this process, in addition to the reasons listed in the introduction, has arisen recently as a result of the fact that, together with the inverse process of dissociative recombination



it can play a significant role in the chemical evolution—

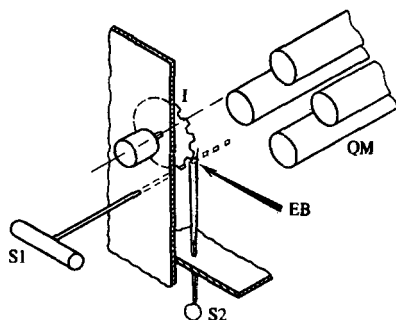


FIG. 23. Diagram of experiment for investigation of associative ionization in intersecting beams.<sup>[62]</sup> S1 and S2 are sources of beams of uranium atoms  $U(^5L)$  and oxygen atoms  $O(^3P)$ , I is a mechanical interrupter of the beam of uranium atoms, EB is an electron beam for ionization of the neutral reagents, QM is a quadrupole mass spectrometer for analysis of the ionic products, and the crosshatching shows the walls of the vacuum regions.

the establishment of an equilibrium molecular composition—of interstellar clouds.<sup>[61]</sup> Thus, study of one of the paths of reaction (19) and use of the principle of detailed balance enables us to obtain the necessary estimates of the characteristic rates of the chemical transformations. Study of associative ionization with participation of uranium atoms presents significant interest in connection with the search for new methods of electrical separation and enrichment of radioactive isotopes.

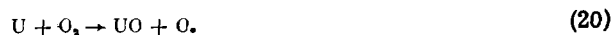
A study of associative ionization in collisions of atoms of U, Th, Gd, Zr, and Ti with atoms and molecules of oxygen has been carried out by Fite and his colleagues<sup>[62, 63]</sup> with use of the apparatus shown schematically in Fig. 23.

Significant cross sections for associative ionization can be expected for these systems on the basis of thermochemical data and the features of the electronic structure of the interacting atomic particles.

In fact, since the energy of the electronic ground state of the  $UO^+$  ion lies 2.7 eV below the asymptote of the  $UO$  molecule, the reaction  $U + O \rightarrow UO^+ + e$  is exothermic ( $\Delta E = 2.7$  eV).

The exothermal nature of a transformation, however, in no way indicates that it is probable in a collision; the high probability of a process even at thermal energies is due to the features of the electronic structure of the system. Approach of the atoms in their ground states,  $U(^5L)$  and  $O(^3P)$ , in accordance with the well-known rules for building of molecular terms,<sup>[64]</sup> is possible along 81 terms. The number of terms arising is larger by about a factor of two (153 terms), since the source of Fig. 23 is heated to 2000 °C for production of a beam of U, and the energy of the first excitation of the electronic state of  $U(^5K)$  is only  $7.7 \times 10^{-3}$  eV.

A similar diversity of terms occurs also in the case of the molecular ions; the ground states of the ion  $U^+$  ( $^4I$ ) and the atom  $O(^3P)$  correspond to 63 potential curves. The closest two excited states of  $U^+$ ,  $U^+(^6L)$  and  $U^+(^6K)$ , are separated from the ground state by 0.36 and 0.11 eV. Therefore the number of accessible ionic terms reaches 193. As a rough approximation we can assume that for half of the terms of the molecular and ionic states, mutual crossings are possible—this assumption gives us a basis for expecting high probabilities of associative ionization in the  $U-O$  system. The qualitative picture discussed is valid with small changes also in the case of other quasimolecular systems such as  $TiO$ ,  $GdO$ , and  $ThO$ . We note that for collisions involving  $O_2$  molecules, in addition to associative ionization, there is a competing channel consisting of the chemical reaction



The measurements carried out by Fite and co-workers<sup>[62, 63]</sup> have shown (Table V) that the cross sections for associative ionization of atoms under the conditions of thermal collisions actually can have the same values as the kinetic-theory cross section; this is in good agreement with the known experimental fact of a sharp rise in the conductivity of a flame on introduction of ad-



TABLE V. Cross sections for associative ionization in thermal collisions of particles in the electronic ground state.

System.	Cross section, Å <sup>2</sup>	Reference
U-O	16.2±0.44	82
U-O <sub>2</sub>	0.17±0.03	82
Ti-O	0.45±0.15	83
Gd-O	8.35±2.83	83
Th-O	10.3±3.2	83
Th-O <sub>2</sub>	0.15±0.03	83
Zr-O	12.9±3.8	83

ditions such as U, Mo, and La.<sup>[85]</sup>

Reaction (20) has a cross section of  $(17.8 \pm 0.45) \times 10^{-16}$  cm<sup>2</sup> and completely suppresses the associative ionization channel for this pair.

The complexity of the electronic structure of the systems given in Table V prevents the possibility of any serious quantitative theoretical analysis of the associative ionization process for these pairs. Such an analysis, however, has been carried out<sup>[86]</sup> for the simpler reaction



which presents significant interest in connection with the study of the mechanism of formation of one of the interstellar molecules (HCO<sup>+</sup>). The radio line of HCO<sup>+</sup> has been identified<sup>[87]</sup> only tentatively, since until recently radiofrequency spectroscopy of ions has not existed. Of the terms arising for a linear configuration of the system CH(X<sup>2</sup>Π)-O(<sup>3</sup>P), <sup>4,2</sup>Σ, <sup>4,2</sup>Π, and <sup>4,2</sup>Δ with the <sup>1</sup>Σ<sup>+</sup> ground state of the molecular ion HCO<sup>+</sup>, according to the rule of conservation of total spin, only the doublet terms can interact. Thus, in the approximation of a central interaction and prompt decay after crossing the boundary of the continuum, the cross sections  $Q_i$  for the associative ionization reaction occurring through the  $i$ -th crossing of different terms and the total rate constant  $k(T)$  can be calculated if information is available on the behavior of the potential curves (of the adiabatic terms), and the magnitudes of the splitting of the quasi-crossing terms. Calculations in this approximation, carried out by MacGregor and Berry,<sup>[88]</sup> have permitted estimates to be obtained both of the partial cross sections  $Q_i(E)$  and the rate constants, and of the total rate constants at various temperatures. In particular, it follows from these estimates that at a temperature  $T = 25$  °K (typical of a gas in an interstellar cloud) the rate constant of formation of HCO<sup>+</sup> can have values  $1.7 \times 10^{-11} - 9 \times 10^{-13}$  cm<sup>3</sup> sec<sup>-1</sup>. This estimate permits reaction (21) to be considered the most probable channel of formation and permits the observed content of HCO<sup>+</sup> molecules to be explained. The identification<sup>[87]</sup> of the radiation arriving from interstellar clouds has now been confirmed by an independent method, since the wavelength corrected for the Doppler shift turned out to be close to the laboratory value for HCO<sup>+</sup>, just observed for the first time,  $\lambda = 89188.65$  MHz.<sup>[88]</sup>

## CONCLUSION

In conclusion let us consider some of the problems of further studies of chemi-ionization which follow from the discussion given above.

An important problem is the further refinement of the technique of measuring the effects of atomic collisions and the systematic accumulation of information on the atomic parameters describing the interaction in collisions. Here it is necessary to attempt to formulate and carry out complex experiments with simultaneous detection of different effects—different manifestations of the chemi-ionization process.

In studies of the Penning ionization process it is necessary to clarify the relative role of the photoionization mechanism of destruction of metastable states and to remove the existing discrepancies in the values of the absolute cross sections for chemi-ionization processes involving metastable particles.

It is necessary to learn the true nature of the activation energy for chemi-ionization processes with participation of metastable atoms and the reasons for the discrepancy in determination of the width of a level for autoionization decay in measurements with thermal and fast beams. An important problem is the reliable determination of the real dependence of the width on interatomic distance and on the relative collision energy—this will permit advances to be made in the theoretical calculation of the widths.

We must expect a further expansion of study of chemi-ionization processes involving atoms in excited states, including processes with formation of the products in an excited state, of the regularities of two-fold ionization processes, and of the effect of vibrational-rotational excitation of the collision partners on the chemi-ionization efficiency.

As a result of the common basic nature of ionization in collisions of the keV range and associative ionization in the thermal range, we should expect development in all possible ways of electronic collision spectroscopy. Deciphering of the data from this source is the key to the improvement of our understanding of the behavior of quasimolecular systems near the boundary of the continuum.

The deciphering of electronic spectra depends critically on a knowledge of the behavior of the terms of the final and initial quasimolecules. Therefore the problems of further studies include a study of elastic scattering with interaction along terms, which presents interest in connection with autoionization decays of quasimolecules.

Some extremely interesting phenomena which remain almost unstudied experimentally are collisions of two excited particles, in particular, two metastable atoms of He.

The novelty of the phenomena and of the methods of investigation, together with the practical needs of contemporary technology, will undoubtedly stimulate not only the preservation of the achieved level but also the further development of studies in the region discussed.

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