Reviews

Dissociative recombination of electrons and molecular ions

G. V. Golubkov, M. G. Golubkov, S. V. Drygin, and G. K. Ivanov*

N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 4 ul. Kosygina, 117977 Moscow, Russian Federation. Fax: +7 (095) 938 2156

The existing techniques for the calculation of the dissociative recombination (DR) of electrons and molecular ions were compared. The advantages of the method of multichannel quantum defect (MQD), in which equations are formulated directly for the **T**-matrix of collisions and the unitarity of the scattering S-matrix is thus ensured, were demonstrated. The effect of molecular rotation and of the nonadiabatic electron-rotation coupling on the $e^- + H_2^+ \rightarrow H^* + H$ reaction was investigated. A procedure was suggested based on the use of the adiabatic approximation (with respect to the nuclear rotation) in the near-threshold area while taking into account the contributions of the excited vibronic states of the Rydberg complex formed in an intermediate stage of the reaction. It is notable that the partial rate constants (and the corresponding cross-sections) are very sensitive to the initial rotation excitation. However, the temperature-averaged rate constants under equilibrium conditions are only slightly affected by rotation.

Key words: dissociative recombination, Rydberg states, rotation motion, configuration interaction, cross-section, rate constant.

Introduction

Dissociative recombination (DR) of electrons and molecular ions, *i.e.*, the formation of neutral fragments,

$$XY^+ + e^- \rightarrow X + Y, \qquad (1)$$

is one of the fundamental phenomena of atomic and molecular physics. The DR reactions are known to play an important role in the chemical processes occurring in the upper layers of the Earth atmosphere and during combustion and thermonuclear synthesis, in the phenomena characterizing the properties of steady-state and decaying weakly ionized plasma, and also in the chemical processes occurring in gas lasers. It is these facts that account for the considerable interest of researchers in DR reactions. In recent years, particular attention has been concentrated on the study of the processes occurring in the hydrogen plasma and in the noble gas plasma, which is due to the necessity to solve such problems as transformation of electrical and nuclear energy into light, the search for new active media, and the development of a new generation of recombination lasers.

Researchers who study ionized states have to solve problems relating to various fields of physics. Many of these problems are associated with the microscopic properties of plasma, *i.e*, with the states of atomic and

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 6, pp. 1336—1348, June, 1996.

1066-5285/96/4506-1265 $15.00

molecular species and with the elementary processes involving them. These properties depend substantially on the presence of positively charged molecular ions, since reactions involving these species even at low concentrations can lead to a noticeable increase in the rate of disappearance of the volume charge in a decaying plasma. The latter is accompanied, as a rule, by the formation of excited atomic fragments followed by emission. Thus, the recombination of electrons and ions determines the ionization structure of a plasma, and the recombination spectrum, in turn, provides the necessary information on the physical conditions in the medium in which the emitting species are located.

The history of the investigation of DR reaction (1) dates back several decades. By now extensive information on this subject has been accumulated in the literature;[1–18] nevertheless, many important aspects still remain scarcely studied. This refers, for example, to the question of the effect of the vibrational and rotational excitation of ions on the rate of the DR.

The experimental studies dealing with electron-ion recombinations can be divided conventionally into two main types: determination of the rate constant for the recombination based on the observations of the decay of separate components of the plasma and the measurement of the cross-section of the process using the technique of intersecting beams.[7] However, the measurement of partial cross-sections of recombination is complicated by the fact that, for beams, no reliable methods for detecting the initial and final states of a recombining system exist. Therefore, the cross-sections observed are averaged over the energy spread in electron beams and over the initial distribution of ions over vibrational and rotational states, which hampers the direct comparison of experimental and theoretical results.

The development and perfection of lasers that can be modified and the development of new methods for the measurements suggest that the microscopic parameters of reaction (1) will be studied in detail in the near future. This imposes heavy demands on the existing theory, and, especially, on the studies of processes involving simple diatomic ions XY^+. The positive ion H_2^+ is the most promising in this respect, since the hydrogen molecule has only one low-lying doubly excited repulsive state $^1\Sigma_g^+(2p\sigma_u)^2$, whose term intersects the ion potential near the equilibrium state. In addition, the molecular ion of hydrogen is apparently one of the few objects for which precise quantum-mechanical calculations are possible. Note that before the development of the methods of intersecting beams, it has been extremely difficult to obtain reliable experimental data concerning the reactions involving H_2^+, because this ion is chemically reactive and efficiently forms heavier cluster ions H_n^+ ($n \geq 3$) in a plasma.[7] Therefore, the chemical nature of the ions participating in reactions should be specially checked.

The overall cross-sections of the $e^- + H_2^+$ recombination have been measured repeatedly using the beam method;[19–24] the results obtained[19–22] differed from one another within an order of magnitude and did not reflect the resonance structure of the energy dependence typical of reaction (1). The latter was discovered for the first time in more recent studies,[23–24] carried out using the technique of combined beams. To explain this effect, it has been suggested[25] that the resonance structure is due to the indirect DR process, whose model description has been reported in a number of known studies.[26–28] According to these views, an incident electron loses its energy due to the vibrational excitation of the ion core and is captured to the Rydberg state of the neutral molecule, which can either become autonomous (inelastic electron scattering), or predissociate (DR reaction). In later studies,[29,30] it has been shown that narrow resonances are formed within the energy dependence of the cross-section of DR, their widths being much less than the distance between the Rydberg levels.

A further important feature of reaction (1) is the jumpwise decrease in the cross-section on passing over the threshold of the vibrational excitation. This effect is due to the crowding of resonance levels near the threshold of the closed channel and is associated with the disappearance of the resonance contribution on going to the open channel, which is typical of Coulomb interaction.[31–35] Experimental evidence for this effect has been reported more recently.[36]

An alternative approach to the description of the $e^- + H_2^+$ recombination, corresponding to a direct mechanism of trapping of the electron to the diabatic repulsive state of the neutral molecule, has been suggested by O'Malley.[37] Since the repulsion term intersects the set of Rydberg states, the latter are predissociative states and can be treated as resonances, *i.e.*, they can be described within the framework of the theory of resonance scattering.[38–42] This fact is very significant for the elucidation of the mechanism of the DR reaction and, in particular, for the determination of relative probabilities of the formation of final states. However, the approach developed by O'Malley[37] can be regarded as acceptable only in the case where the coupling of the Rydberg states with the ionization continuum is extremely weak and self-ionization occurs *via* the dissociative state (double transition).

In the general case, the DR reaction occurs both as the direct transition to the dissociative continuum and *via* the formation of intermediate complex XY^{**} followed by its decomposition to the dissociative state. The amplitudes corresponding to these transitions interfere with one another, which results in a fairly complex dependence of the reaction cross-section on energy. If the molecular ion XY^+ exists in the ground vibrational state ($v = 0$), the nearest closed channel ($v = 1$) plays the crucial role in the formation of the resonance structure of the dissociation spectrum in the energy region below the threshold of its vibrational excitation. Due to the states of this channel, an infinite set of Fano-

Feshbach resonances arise, which are described by the following equation (near an nth resonance E_n^r):

$$\sigma(E) = \sigma_0(E)\frac{(x+q)^2}{1+x^2}, \quad x = \frac{2(E-E_n^r)}{\Gamma_n}. \qquad (2)$$

Here Γ_n is the width of this resonance and q is the profile index. The sequence of the resonances is clearly regular: the same multiplier n^3 characterizes the decrease in the widths Γ_n, in the intensities $I_n = (\pi/2)q^2\sigma_0(E_n^r)\Gamma_n$, and in the distances between the resonances following an increase in the number n of the level of the closed channel. This regularity can be violated due to resonances of far Rydberg series ($v > 1$) or of the quasidiscrete states of valent (non-Rydberg) configurations. The channels of self-ionization and predissociation compete with each other.

The next important aspect, whose investigation is needed to understand the mechanisms of the DR reactions, is the dependence of the cross-section on the initial vibrational excitation of the XY^+ ion. The picture of the phenomenon depends substantially on the mutual arrangement of the ionic and dissociative terms and is largely determined by the behavior of the Franck—Condon factors, incorporated in the expression for the amplitudes of the direct transition. Thus, the task of the theory amounts to adequate description of these two mechanisms of recombination, *i.e.*, to a correct calculation of the main parameters included in expression (2). This problem can be solved most systematically in terms of two approaches to the DR theory, namely, the method of configuration interaction (CI)[40,41] (and its subsequent generalization[43,44]) and the method of multichannel quantum defect (MQD). In the latter case, two principally different variants should be distinguished: the two-step procedure[29,45] and its modifications[46—48] and the procedure of the collision T-matrix.[49—54] The latter method, as shown below, is much simpler for calculations and combines the advantages of the two above approaches. At first glance, the approaches developed are not related to one another, or a relationship can be followed only between some of them. To develop a unified concept, these approaches need to be analyzed from a certain general standpoint.

The present paper is devoted to a comprehensive description of reaction (1) and to the study of the effects of various factors on the dynamics of this process. The existing theories are discussed in detail, and a rigorous correlation between them is established. In view of the necessity to take into account a large number of rovibronic closed channels of motion, a special procedure has been used that allows successive refinement of the results obtained by including additional closed channels. Note that none of the theories considered took into account the rotational motion of the XY^+ ions, which is especially significant for hydrogen-containing systems. Investigation of the temperature dependence of the rate constant of this reaction under essentially nonequilibrium conditions, in which rotation is significant, is no less important for understanding the physics of the processes occurring in the low-temperature plasma. The main attention is devoted to these problems. It should also be noted that our calculations (unlike those carried out previously[47]) take into account both the direct transitions caused by the dependence of the quantum defect on the interatomic distance and the transitions *via* the dissociative continuum. The latter were found to be fairly significant for the $e^- + H_2^+$ system. Our results obtained for this system are compared with the numerical data obtained previously by other researchers[43,44,47] and with experimental results.[23—24]

The integral variant of the MQD theory

The general properties of scattering processes and reactions are normally described using the S-matrix relating the initial i-states of the system (when the colliding species are separated by an infinite distance) to the final f-states corresponding to the removal of reaction products to infinity. The modules of the elements of this matrix squared $|\langle i|S|f\rangle|^2$ determine the probabilities of transitions from states i into states f. The sum of the probabilities of all the possible transitions is strictly equal to 1, which is ensured by the condition of unitarity of the S-matrix ($SS^+ = 1$).

Along with the S-matrix, for the description of reactions (or inelastic transitions), it is convenient to introduce the T-operator of collisions, related to the matrix by the expression $S = I - 2iT$. The T_{fi} elements, like S_{fi}, are symmetrical with respect to the i and f indices and do not depend on the choice of the coordinate. They are related to a physically observable value, *viz.*, the effective cross-section of the reaction (or scattering), which is defined as the ratio of the number of transitions per unit time to the density of the flux of the incident species (in the system of the center of inertia), *i.e.*,

$$\sigma_{fi} = \frac{\pi}{k_i^2}|S_{if}|^2,$$

where k_i is the initial momentum of the colliding species.

In the quantum theory of collisions, two main mechanisms of the interaction of species, *viz.*, direct and resonance mechanisms, are clearly distinguished. The former is characterized by short times of interaction (of the order of time τ_r required for the flight through the characteristic reaction area). The latter (resonance) mechanism is accompanied by trapping the species by a target and is characterized by longer times $\tau \gg \tau_r$. In conformity with the uncertainty principle, the functional manifestations of these mechanisms, in particular, the dependences of the cross-sections on the energies of the colliding particles, are essentially dissimilar. The direct mechanism is described by a smooth energy dependence, whereas the resonance mechanism accounts

for sharp outbursts in the cross-sections, which is caused by the existence of special conditions for the formation of the intermediate complex.

The formation of the intermediate complex may be due to various reasons. On the one hand, the complexes are formed due to excitation of the inner degrees of freedom of the target by the incident species, so that the incident species is trapped by a potential well. In the literature, the state of these complexes is usually referred to as Feshbach-type resonance. On the other hand, this may be due to overcoming the tunnel barrier, which separates the reactants from the region in which the intermediate complex is formed. The state of the latter is referred to as shape resonance. In this case, the energy of the incident species should correlate with the energetic structure of the intermediate complex, and this finally leads to the sharp resonance dependence of the cross-sections of the processes.

The previously suggested[49–54] approach to the solution of the problem of movement of a slow (or weakly bound) electron in the field of the XY^+ ion can be called the integral variant of the MQD theory, since it is based on the rearranged Lippman—Schwinger equations for the collision T-operator. Owing to the separable structure of the Coulomb Green function, these integral equations are reduced to a set of algebraic equations for the elements of the T-operator, for which the dissociative channels are taken into account just as the scattering channels. These significant properties automatically ensure the unitarity of the scattering S-matrix in any basis set of the motion channels taken into account, which guarantees a controlled accuracy of calculations in the method of strong coupling.

In this case, the fundamental set of equations assumes the following form ($\hbar = m_e = e = 1$):

$$\mathbf{T} = \mathbf{t} - i\mathbf{t}\sum_{p}|p\rangle\langle p|\mathbf{T} + \mathbf{t}\sum_{c}|c\rangle\langle c|\frac{1}{\lambda(E)}\mathbf{T}, \qquad (3)$$

where $|p\rangle$ and $|c\rangle$ are wave functions for open (p) and closed (c) motion channels; E is the total energy of the system (with respect to the ground state of the XY^+ ion); $\lambda(E)$ is the diagonal matrix that specifies the spectrum of eigenvalues of the energy for closed channels and the discrete energy levels for isolated valence configurations, *i.e.*, $\lambda_{cc} = \tan\pi\nu_c(E)$ for the Rydberg channels and $\lambda_{cc} = E - E_c$ for the valence configurations (ν_c is the effective principal quantum number, and E_c are characteristic energies of the valence configuration levels). The $|p\rangle$ wave functions for the open channels are normalized by the conditions $\langle p|p'\rangle = \pi\delta(E - E)$. The real t-operator describes the electron scattering on the ion core with allowance for the interaction with valence (non-Rydberg) configurations and obeys the equation

$$\mathbf{t} = \mathbf{V} + \mathbf{V}\mathbf{G}_0(E)\mathbf{t}, \qquad (4)$$

in which the Green operator ($\mathbf{G}_0$) is a slow function of energy E and contains no pole features of a Coulomb center. The operator **V** includes the interaction with the ion core and configuration interaction.

It should be noted that equations similar to (3), both without and with allowance for the dissociative channel, have been obtained previously (see Refs. 49, 50 and Refs. 51—53, respectively). The spectrum of the eigenvalues of energy is specified by the poles of the T-matrix and is determined from a uniform equation whose right-hand side contains no free term t. In this case, the scattering T-matrix is replaced by the operator of the displacement of levels τ. The solution of Eq. (4) can be represented as follows:

$$\mathbf{t} = \mathbf{t}^{(0)} + \frac{1}{\pi}\mathrm{P}\int \mathbf{V}\frac{|\beta\rangle\langle\beta|}{E - E_\beta}\mathbf{V}\mathrm{d}E_\beta, \qquad (5)$$

(symbol P means integration in terms of the principal value). The $\mathbf{t}^{(0)}$ operator in Eq. (5) describes the electron scattering on an isolated ion core without allowance for the configuration coupling, and the wave functions $|\beta\rangle$ specify the adiabatic basis of the dissociative configuration.

Equation (3) are formally exact and describe all the types of nonadiabatic coupling in the Rydberg states of the XY^{**} complex. However, if the $|\langle c|\mathbf{V}|\beta\rangle| << 1$ inequality holds, which is the case for most diatomic molecules, and the $\xi = a_0/R_e$ parameter is small (a_0 is the amplitude of the zero vibrations, R_e is the equilibrium interatomic distance), one may restrict the consideration to a finite number of vibronic states in the set of Eq. (3) by using the method of strong coupling. The allowance for the relationship between the electron motion and rotation is, in the general case, quite cumbersome. Therefore, in the analysis of the solutions of Eq. (3), it is expedient to use methods involving the successive inclusion of the vibrational and rotational degrees of freedom into the general scheme, *i.e.*, to separate the problem into two stages. In the first stage, a traditional adiabatic statement of the problem should be considered, without account of the relationship with rotation, while in the second stage, the rotational motion should be included in the general scheme. On the basis of the characteristic features of the adiabatic picture of the phenomenon, the overall number of rovibronic channels of motion, needed for adequate description of reaction (1), can be efficiently reduced.

Comparison of various versions of the theory of MQD

To establish a relationship between the existing theories of MQD, it is convenient to use the integral variant outlined above. First of all, let us show how the correlation between the approaches of Seaton[35,55] and Fano[56] can be elucidated from Eqs. (3) and (4) and let us analyze the possible ways for combining these approaches. If we restrict ourselves, for convenience, to a single-channel case (the elastic scattering $e^- + XY^+$), the amplitude (which is related, by definition, to the t-matrix

by the equality $T = t(1 + it)^{-1}$) can be expressed in terms of the scattering phase δ:

$$T = -\sin\delta e^{i\delta}.$$

The known Seaton relationship between the scattering phase and the magnitude of the quantum defect $\delta = \pi\mu$[35] follows from the above expression.

To derive the Gaitilis—Seaton[34,55] equation, which relates the S-matrix to the generalized X-matrix for open channels

$$S_{oo} = X_{oo} - X_{oc}(X_{cc} - e^{-2i\pi\nu_c})^{-1}X_{co}, \qquad (6)$$

we introduce, by analogy, a generalized $T^{(o)}$-matrix, which can be written, using our designations, as follows

$$\mathbf{T}^{(o)} = \mathbf{t} - i\mathbf{t}\sum_q |q\rangle\langle q|\mathbf{T}^{(o)}$$

(all the q-channels of the system are assumed to be open). Using the general idea of modification of set (3)—(4), we obtain the following operator equation:

$$\mathbf{T} = \mathbf{T}^{(o)} + \mathbf{T}^{(o)}\sum_q |q\rangle\langle q|\cot\pi\nu_q + i|\mathbf{T}.$$

Then, if we use the relationship between the **X**-matrix and the collision **T**-matrix ($\mathbf{X} = \mathbf{I} - 2i\mathbf{T}^{(o)}$) and take into account the fact that the expression in square brackets is equal to $2i[1 - e^{-2\pi i\nu_q}]^{-1}$, it is an easy matter to obtain relationship (6).

By using the same formal expedient, the operator Eq. (3) and (4) can be replaced, on the other hand, by the equivalent set of equations:

$$\mathbf{T} = \mathbf{R} - i\mathbf{R}\sum_q^{N_o} |q^o\rangle\langle q^o|\mathbf{T},$$

$$\mathbf{R} = \mathbf{t} + \mathbf{t}\sum_q^{N_c} |q^c\rangle\langle q^c|\cot\pi\nu_c\mathbf{R}.$$

In this case, the summation is taken over both open (q^o) and closed (q^c) channels. The matrix **R** thus introduced coincides, to accuracy of the sign, with the reactance Seaton matrix.[55] Compiling then a sequence of relationships for the R_{oo}, R_{oc}, and R_{cc} matrices based on the second equation we obtain the expression

$$R_{oo}(E) = t_{oo} + t_{oc}[\tan\pi\nu_c - t_{cc}]^{-1}t_{oc}.$$

Equation (3) and (4) can also be written in the following form:[57]

$$\mathbf{T}' = \mathbf{t} - i\mathbf{t}\sum_q^{N_o} |q^o\rangle\langle q^o|\mathbf{T}',$$

$$\mathbf{T} = \mathbf{T}' + \mathbf{T}'\sum_q^{N_c} |q^c\rangle\langle q^c|\cot\pi\nu_c\mathbf{T}.$$

Thus, we obtain the relationship between the required **T**-matrix and the T'_{oo} (of the $N_o \times N_o$ rank), T'_{cc} (of the $N_c \times N_c$ rank), and T'_{oc} (of the $N_o \times N_c$ rank) submatrices:

$$T_{oo} = T'_{oo} + T'_{oc}[\tan\pi\nu_c - T'_{cc}]^{-1}T'_{co}, \qquad (7)$$

where $T'_{cc} = t_{cc} - it_{co}T'_{oc}$. This relationship follows from the equation constructed on the basis of physically open channels. Expression (7) is apparently the most compact way of writing the formally general matrix relationships in the MQD theory. In addition, the resonance structure of the transition amplitudes can be more clearly followed here. At the same time, expression (7) is also more general, since it takes into account the reactive channels and interacting quasi-steady states of arbitrary type; for example, this equation makes it possible to describe processes occurring in the presence of an external field, periodic in time.[57]

Note also that in the complete basis set of rotational and vibrational states, other forms of Eq. (3) also exist. In the system of coordinates connected with the axis of the molecule, which we consider here for the sake of simplicity, the basis set of the channel functions is represented by the vibrational states $|v\rangle$ and is complete, *i.e.*, the condition $\Sigma|v\rangle\langle v| = \delta(R - R')$ is fulfilled, where R is the interatomic distance. In this case, the **t**-matrix, in conformity with the foregoing, is represented by the function $-\tan\pi\hat{\mu}(R)$. If we formally introduce the matrix $\tilde{\mathbf{T}} = \mathbf{T}\sin^{-1}\pi\hat{\nu}$ (here $\hat{\nu} = \hat{n} - \hat{\mu}$) and multiply the left- and right-hand sides of Eq. (3) by the matrix $\cos\pi\hat{\mu}$, then for the problem of the eigenvalues of the energy of the $e^- + XY^+$ system (with a fixed rotation axis), we obtain the following operator equation:

$$\sum_v [\sin\pi\hat{\mu}\cos\pi\nu_v + \cos\pi\hat{\mu}\sin\pi\nu_v]|v\rangle\langle v| = 0,$$

which is wholly equivalent to the set of algebraic equations obtained in the MQD method[46—48,58] for the vibronic spectrum of a Rydberg molecule.

In the determination of the scattering T- or S-matrices and of the wave functions of a continuous spectrum, substantial methodological differences arise. In previous studies,[46—48] the set of homogeneous equations for the fundamental scattering phases has been solved, and the results have been used to construct the complete S-matrix and the wave functions. In our approach this task is much simpler. The **T**-matrix and the discrete spectra are determined directly from Eqs. (3) and (4), and the wave functions of the continuous spectrum are constructed on the basis of simple (linear with respect to **T**) relationships. In a complete basis set, both approaches lead, naturally, to coinciding results.

Note also that the operator Eq. (3) involves an approach[59—61] in which the technique of continued fractions has been developed; this technique is used for the inversion of the Jacobian matrices arising during the description of the rovibronic interaction. This approach is

based on the use of the generalized adiabatic principle.[62] To pass to the expressions obtained previously,[59–61] it is sufficient to multiply the right- and left-hand sides of Eq. (3) by t^{-1} and to take into account the relation $t^{-1}T = \sum_v t^{-1}|v\rangle\langle v|T$ obeyed in the complete basis set. The possibility of the reverse transition has been noted in a study published previously.[61]

Thus, it can be claimed that all the above statements of the theory of MQD for the $e^- + XY^+$ system (in the complete basis set of the inner states of the XY^+ ion) are wholly equivalent and differ only in the method of parametrization. From our viewpoint, the integral variant of the MQD method[49–54] is the most universal: it is more complete than the Seaton method,[55] since, along with the S-matrix, it makes it possible to determine the wave functions and the Green function of a system, and is simpler than the Fano method[56] (in particular, because when the integral equations (3) and (4) are used, boundary conditions are automatically taken into account).

Thus, on the one hand, the integral variant of the MQD method (with allowance for the dissociative channel) used in the present study combines the merits of the two main approaches considered above [43,44;46–48] and, on the other hand, it is more general and more compact, since it:

— permits allowance for the direct coupling between discrete states (*cf.* Refs. 43, 44);

— uses the S-matrix (*cf.* Refs. 47, 48), which is unitary at any number of the channels taken into account, and requires no cumbersome procedure for the determination of the fundamental phases;

— takes into account, in the t-matrix (5), the $v \rightarrow v'$ step-by-step transitions through the dissociative continuum and the $d \rightarrow d$ transitions through the Rydberg state.

Dissociative recombination of electrons and molecular ions

Let us juxtapose quantitatively the approaches to the DR theory under consideration and compare the numerical results obtained using these approaches in relation to the reaction

$$H_2^+(v_i) + e^- \rightarrow H_2^{**}[^1\Sigma_g^+(2p\sigma_u)^2] \rightarrow \rightarrow H^*(2l) + H(1s), \quad (8)$$

where v_i is the initial vibrational state of the ion. We chose exactly this (the simplest) quantum-mechanical object since, for this species, all the necessary parameters of the theory are rather well known. Therefore, this comparison can serve as a sort of test for the reliability of the theory.

The H_2 molecule is known to possess one low-lying doubly excited state $^1\Sigma_g^+(2p\sigma_u)^2$, whose properties have been rather comprehensively discussed in the literature.[6,63] Its potential curve $U_\beta(R)$ intersects the ion term $U_i(R)$ in the vicinity of the $R_c^* = 2.65$ au point (Fig. 1), located between the right classical turning points of the ground and of the first excited vibrational states (near the $v = 1$ state). This means that the cross-section of reaction (8) should be small for $v_i = 0$ and should increase substantially with increase in v_i.

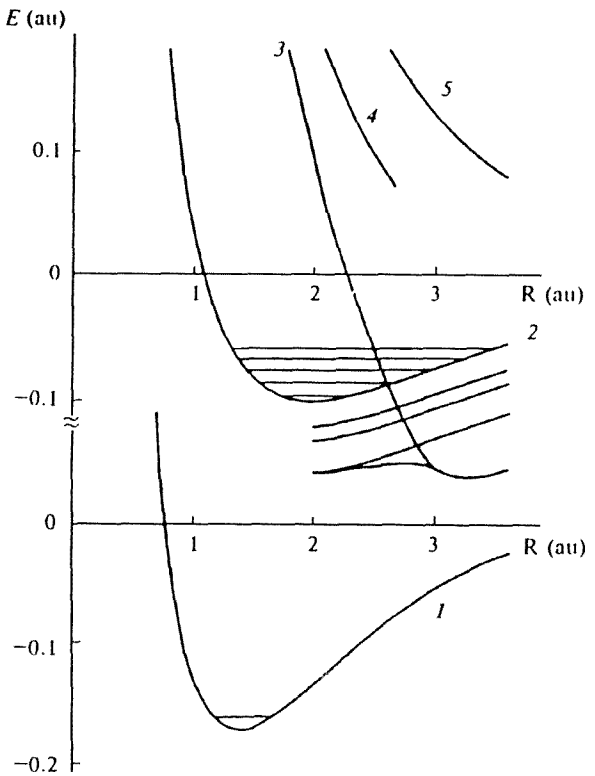

Fig. 1. Potential curves of the H_2 molecule near the ionization threshold[47]: H_2 ($X^1\Sigma_g$) (*1*); H_2^+ ($1s\sigma_g$) (*2*); H_2 ($^1\Sigma_g(2p\sigma_g)^2$) (*3*); H_2 ($^1\Sigma_g(2p\sigma_u 2s\sigma_g)$ (*4*); H_2^+ ($2p\sigma_u$) (*5*).

It is also known that in the Rydberg H_2^{**} complex, formed in an intermediate stage of the process, it is mostly the $nd\sigma_g(^1\Sigma_g^+)$ series, in which the angular momentum of the electron $l = 2$ is a "good" quantum number, that predissociates.[47] Since the previous calculations carried out for this reaction (see, for example, Refs. 29, 30, 40, 42–44, and 47) were based on the use of the adiabatic (with respect to the rotational motion) approximation, we shall initially pattern our behavior on this situation, *i.e.*, consider the molecular axis during the collision to be fixed and operate in the coordinate system linked to the molecule. Therefore, the main task of our study is to elucidate the role of the vibronic exchange through the dissociative continuum in the formation of the resonance structure of the cross-section of reaction (8).

Cross-section of the $e^- + H_2^+$ reaction. The complete cross-section of a DR reaction under the conditions considered is written in the following way:

$$\sigma^S_{\beta v_i}(\varepsilon) = \frac{2\pi}{\varepsilon} g^S \sum_{l\Lambda} \left| T^{(l\Lambda)}_{\beta v_i}(E) \right|^2, \qquad (9)$$

where ε is the energy of the electron (related to the total energy of the system $E = \varepsilon + E_v$), E_v is the energy of the vibrational excitation of the ion; g^S is the statistical weight of the initial state with the specified spin S, and $T^{(l\Lambda)}_{\beta v_i}$ is the partial reaction amplitude for the $l\Lambda$ wave of the incident electron, determined, in conformity with expression (3), from the following set of equations

$$\begin{aligned} T^{(l\Lambda)}_{\beta v} &= t^{(l\Lambda)}_{\beta v} + \sum_{v'} t^{(l\Lambda)}_{\beta v'} \cot\pi(\nu_{v'} + \mu^0_{l\Lambda}) T^{(l\Lambda)}_{v'v}, \\ T^{(l\Lambda)}_{v v'} &= t^{(l\Lambda)}_{v v'} + \sum_{v''} t^{(l\Lambda)}_{v v''} \cot\pi(\nu_{v''} + \mu^0_{l\Lambda}) T^{(l\Lambda)}_{v''v'} - \\ &\quad - i t^{(l\Lambda)}_{v\beta} T^{(l\Lambda)}_{\beta v'}, \end{aligned} \qquad (10)$$

in which, owing to the weakness of the configuration coupling,* the matrix elements have the following form (hereinafter, the indices $l\Lambda$ are omitted):

$$\begin{aligned} t_{vv'} &= t^{(o)}_{vv'} + \frac{1}{\pi} P\int \frac{V_{v\beta} V_{\beta v'}}{E - E_\beta} dE_\beta, \\ t_{v\beta} &= V_{v\beta} + \frac{1}{\pi} P\sum_{v'} \int \frac{t^{(o)}_{vv'} V_{\beta v'}}{E - E_{v'} - \varepsilon} d\varepsilon, \end{aligned} \qquad (11)$$

where

$$t^{(o)}_{vv'} = -\langle v | \tan[\pi(\mu_{l\Lambda} - \mu^0_{l\Lambda})] | v' \rangle.$$

The $T_{vv'}$ elements in Eq. (10) are symmetrical with respect to the indices and characterize the amplitudes of inelastic scattering of electrons. The diagonal $t_{\beta\beta}$ elements, which are quadratically small in this basis set with respect to the configuration coupling, are absent.

The $t_{vv'}$ elements in Eq. (11) are presented as sums of two addends, one of which is due to the interaction with the ion core, and the other describes mixing of the Rydberg series with the dissociative continuum. To determine its explicit form, it is convenient to use the quasi-classical approximation and to write $t_{vv'}$ as

$$t_{vv'} = t^{(o)}_{vv'} + \pi P\int \frac{V^2_\beta(R) \chi_v(R) \chi_{v'}(R)}{E - U_\beta(R)} dR, \qquad (12)$$

where $V_\beta(R)$ denotes the electronic part of the configuration interaction, and χ_v stands for the vibrational wave function of the ion. According to Eq. (12), the adiabatic quantum defect $\tilde{\mu}_{l\Lambda}$, far from the point of intersection R_c* of the Rydberg and dissociative terms, differs from the diabatic one $\mu_{l\Lambda}$ by the following value:

$$\Delta\mu_{l\Lambda} = \frac{1}{\pi} \arctan\pi\left[\frac{V^2_\beta(R)}{U_\beta(R)}\right], \qquad (13)$$

which leads to a downward shift of the position of the Rydberg term along the energy scale. The magnitude of this shift is $\sim\Delta\mu/n^3$; therefore, the allowance for the coupling with the dissociative continuum should be most clearly manifested for resonances with small principal quantum number, *i.e.*, for the series corresponding to the vibrationally excited states of the ion core.

The off-diagonal matrix elements $t_{vv'}$ in expression (12) describe the amplitudes of the $v \to v'$ transitions to the ionization continuum and the vibronic coupling in closed channels. Since the vibronic transitions are characterized by a small $\xi = a_0/R_c$ parameter, it can be shown that, to accuracy of the second derivative $\mu''_{l\Lambda}$ and to terms that are second degree with respect to V_β, the greatest contribution is made by single-quantum and two-quantum transitions. An important role is played by the second addend in expressions (11) and (12), caused by the interaction with the dissociative continuum. For example, for the first six vibronic Rydberg series, $d\sigma_g$ of the H_2 molecule ($v = 0$ to 5), the elements of the $t^{(o)}$-matrix calculated on the basis of the data reported previously[47,64] are equal to

$$\begin{aligned} t_{01}{}^{(o)} = -0.006,\ t_{12}{}^{(o)} = -0.008,\ t_{23}{}^{(o)} = -0.015, \\ t_{34}{}^{(o)} = -0.012,\ t_{45}{}^{(o)} = -0.013 \end{aligned} \qquad (14)$$

(the diagonal elements are small). The effect of the dissociative continuum is clearly demonstrated by Table 1, which presents the elements of the t-matrix for these series. It is seen that their absolute magnitudes increase with increase in the vibrational excitation, the diagonal elements $t_{vv'}$ being changed to the greatest degree.

Table 1. Matrix elements $t_{vv'}$ for the $d\sigma_g$-series of the H_2 molecule calculated from formula (11)*

v′	v					
	0	1	2	3	4	5
0	−0.169	−0.089	−0.045	—	—	—
1	−0.089	−0.233	−0.125	−0.078	—	—
2	−0.045	−0.125	−0.472	−0.230	−0.110	—
3	—	−0.078	−0.230	−0.414	−0.177	−0.143
4	—	—	−0.110	−0.177	−0.424	−0.198
5	—	—	—	−0.143	−0.198	−0.488

Note. Data from Refs. 47 and 64 and $\varepsilon = 0.02$ eV were used.
* The dashes mean that the values are small with respect to 10^{-3}.

* The magnitude of the configuration coupling is determined by the particular features of the electronic structures of molecules. Examples of thoroughly studied $e^- + XY^+$ systems ($XY^+ = H_2^+, N_2^+, NO^+, O_2^+$, *etc.*) indicate that it is actually small (*i.e.*, the $V^2_{v\beta}$ values are small compared to unity).[17]

Let us proceed now to the calculation of the cross-section of reaction (8) and compare the existing numerical data with one another. Since the electronic part of the configuration interaction V_β depends only slightly on the interatomic distance R, the matrix elements $V_{v\beta}$ (describing the coupling of the states of the H_2^{**} Rydberg complex with the dissociative continuum) can be represented as $V_{v\beta} = V_\beta(R_c)\alpha_{v\beta}$, where $\alpha_{v\beta}^2 = \langle v|\beta\rangle^2$ are the Franck—Condon factors depending on the energy E, which have been calculated in the quasi-classical approximation. The Morse potential with the previously reported[64] parameters was used for the vibrational wave functions of the H_2^+ ion, and the data obtained by Nakashima *et al.*[47] were used for the dissociative term.

A comparison of the results of calculations carried out previously[43,44,47] with experimental results[23] and with the dependences obtained by us using Eqs. (9)—(12) is presented in Fig. 2 (see *a*—*c*). It follows from Fig. 2 that with increase in the initial vibrational excitation (v_i = 0 to 2), the cross-section actually markedly increases. The continuous thick line denotes the cross-section for the direct transition to the dissociative $^1\Sigma_g^+$ state, while the continuous thin line corresponds to the results of our calculations carried out in the seven-channel approximation (see Fig. 2, lines *1* and *2*, respectively). In Fig. 2, *d* (curve *6*), we present a comparison with the experimental dependence,[23] for which the distribution over the initial states for v_i = 0, 1, and 2 was specified as the 1 : 2 : 2 ratio. The results of the calculations were added according to this (in other studies,[43,47] an additional averaging over the energy of electrons was carried out). The same figure (curve *5*) shows the results obtained by Hickman with the use of the Bardsley formalism (Hickman[44] did not take into account the interaction of closed channels).

In the MQD theory,[43,47] this interaction is taken into account; however, the calculation of the $t_{vv'}$ elements in Eq. (11) does not take into account the contribution of the second term, responsible for these transitions. For this reason, the dependences shown in Fig. 2, *a*,*b* (curves *3* and *4*; see Refs. 43 and 47) have a clear-cut "antiresonance" character, which is consistent with the small values of the profile index q in Eq. (2). In the integral variant of the MQD theory used by us, the vibronic transitions through the dissociative continuum have been successively taken into account. Therefore, our results are closer to those obtained previously[43] in terms of the Bardsley formalism (which contain typical Fano—Feshbach maxima, along with dips).

Despite the fact that the results of the calculations discussed differ from one another, they all reflect the most typical feature of DR, namely, the presence of clear-cut resonance structure of the cross-sections. The resonances are so narrow that they have been virtually imperceptible in the experiment with combined beams.[23] The dependence obtained by Hus *et al.*[24] looks somewhat more graphic; however, they gave no clear information on the distribution function of the ion beam over the vibrational states with v_i = 0 and 1. The fact that the initial state of molecular ions in beams is difficult to detect results in the experimental pattern being more complex and in the specific features being smoothed.

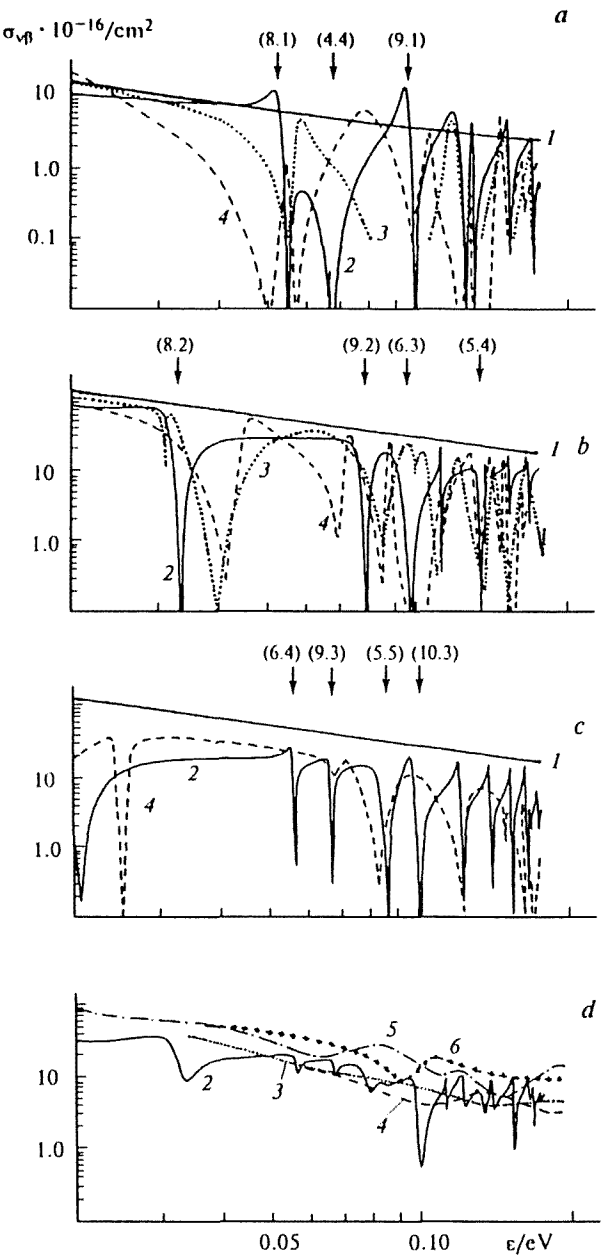

Fig. 2. Dependences of the cross-section of the $e^- + H_2^+(v_i) \rightarrow H^*(21) + H(1s)$ reaction on the energy of the electron ε: v_i = 0 (*a*); v_i = 1 (*b*); v_i = 2 (*c*); cross-section averaged in the 1 : 2 : 2 ratio for v_i = 0, 1, 2, respectively (*d*): cross-section of the direct transition to the dissociative state (*1*); calculation in terms of the integral variant of the MQD method (*2*); calculation in terms of the two-step MQD method[43] (*3*); the same[47] (*4*); calculation by the CI method[44] (*5*); experimental results[23] (*6*). The arrows denote the resonance *n*,v-states.

Nevertheless, the dip in the experimental curve[23] (see Fig. 2, *d*) indicates that the (5,5), (6,3), and (10,3) antiresonances contribute to the formation of its structure.

The effect of the dissociative continuum. To elucidate the characteristic features of the effect of the vibronic mixing with the dissociative channel on the formation of the resonance structure, let us compare the partial cross-section $\sigma_{\beta 0}(\varepsilon)$ found previously[47] (we have used the results of this study) with the dependence calculated from Eqs. (9)—(12) without allowance for the second term in Eqs. (11)—(12) (when the elements given by (14) are taken as $t_{vv'}$). The results of this calculation are shown in Fig. 3, in which line *1* denotes the cross-section found without taking this coupling into account, line *2* corresponds to the results of our previous calculation (see Fig. 2, *a*), and line *3* represents the dependence taken from the literature.[47]

The greatest interest is aroused by the (4,4) resonance level, whose position is defined as

$$E_{n,v} = E_{n,v}^{(o)} + \frac{1}{\pi n^3} \arctan t_{vv}, \qquad (15)$$

where $E_{n,v}^{(o)}$ corresponds to the resonance Rydberg level, not perturbed by interaction with dissociative continuum, the energy of which is 0.1264 eV. Allowance for the configuration coupling gives $E_{4,4} = 0.0685$ eV. Thus, the presence of the dissociative continuum results in a displacement of the resonance level by 0.0579 eV. This interaction also has an effect on the shape of the contour of the resonance line, leading to its deformation caused by a variation of the resulting self-decay width. The total width may be both smaller or greater than the nonperturbed one, depending on the ratio of the parameters of a particular system.[17] In the case of an isolated resonance (for example, for the (4,4) level), the resulting width increases. According to Eq. (15), the magnitude of the shift of a level rapidly decreases with increase in n; therefore, the positions of the perturbed $E_{n,v}$ and nonperturbed $E_{n,v}^{(o)}$ resonances for the $(n,1)$ series (with the principal quantum number $n \geq 8$) differ only slightly from one another.

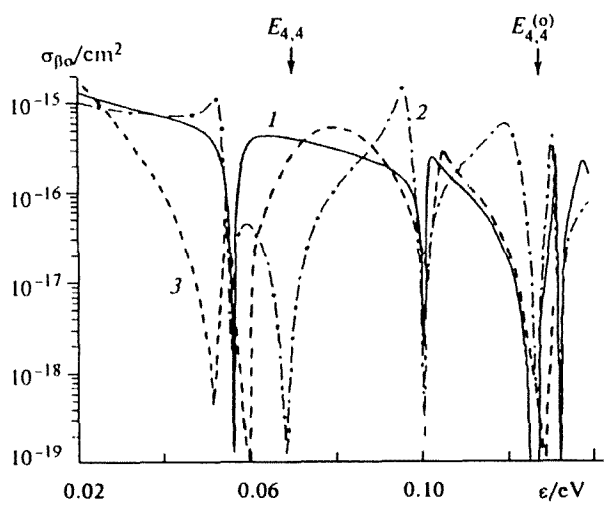

Fig. 3. Comparison of the cross-sections of the $e^- + H_2^+(v_i) \rightarrow H^*(2l) + H(1s)$ reaction calculated with (*1*) and without (*2*) allowance for the vibronic coupling with the dissociative continuum with the results obtained previously.[47]

The analysis carried out by us indicates that the theory of MQD (including its various modifications) is the most consistent procedure for the mathematical investigation of reaction (1). The main drawbacks of the two-step Guisti method[29,45—48] are due to the violation of the unitarity of the S-matrix in a limited basis set, which substantially hampers the investigation of the whole set of processes occurring in the $e^- + XY^+$ system in a unified concept. The integral variant of the theory of MQD,[49—54] which was formulated directly for the collision T-matrix and requires no additional cumbersome procedures for the construction of the scattering S-matrix is free of this drawback. The question of the unitarity of the matrix is crucial, because it is associated with the strict correspondence between the various reaction channels rather than with the inaccuracy of the theory. At the same time, in relation to reaction (8), none of the theories under consideration give a consistent description of the phenomenon, since they do not take into account the rotational motion of the H_2^+ ions, which is rather significant for this reaction.

The role of nonadiabatic cooupling with rotation in the DR reaction (8)

Let us consider the nonadiabatic coupling between the electronic and rotational motions in the general Scheme (3)—(4) and its role in DR (8). We will take into account that the contributions of channels with $v = 0$ and $v \geq 1$ can be considered in various approximations. For states with $v = 0$ below the threshold of the rotational excitation of the ion, $Bn_0^3 > 1$, where B is the rotational constant (for H_2^+, $B \simeq 1.3 \cdot 10^{-4}$ and $n_0 \geq 30$). Here we come across an essentially nonadiabatic situation. Conversely, for $v \geq 1$ at low energies, $Bn_v^3 \ll 1$, *i.e.*, the adiabatic approximation is properly fulfilled.

Therefore, the calculation can be divided into two stages: in the first stage (when states with $v \geq 1$ are taken into account) we shall consider the traditionally adiabatic statement of the problem (with no allowance for the coupling with rotation), and in the second stage, we shall include the rotational motion. Based on this approach we obtain

$$\mathbf{T} = \mathbf{T}^{(1)} + \mathbf{T}^{(1)} \sum_N |No\rangle\langle No| \cot \pi\nu_{No} \mathbf{T}, \qquad (16)$$

$$\mathbf{T}^{(1)} = \mathbf{t} + \mathbf{t} \sum_{v \geq 1} |\Lambda v\rangle\langle \Lambda v| \cot \pi\nu_v \mathbf{T}^{(1)} - i\mathbf{t} \sum_\beta |\beta\rangle\langle\beta| \mathbf{T}^{(1)}. \qquad (17)$$

According to Eq. (16), the allowance for the rotation (N is the rotational quantum number) in the channel with v = 0 requires the preliminary determination of the adiabatic submatrix; however, the latter is not a true adiabatic scattering $\mathbf{T}^{ad}$ matrix, because Eq. (17) contains no term corresponding to the input open channel. Note that Eq. (16) is transformed into an equation for $\mathbf{T}^{ad}$ in the above-threshold region (regarding the rotations in the channel with v = 0), in which the relationship $\cot\pi\nu_{No} = -i$ holds for all N. Therefore, a simple correlation exists between $\mathbf{T}^{(1)}$ and $\mathbf{T}^{ad}$ expressed by the operator relationship:

$$\mathbf{T}^{ad} = \mathbf{T}^{(1)} - i\,\mathbf{T}^{(1)}|\Lambda o\rangle\langle\Lambda o|\mathbf{T}^{ad}.$$

The $\mathbf{T}^{(1)}$ and $\mathbf{T}^{ad}$ matrices are determined in the system linked to the axis of the molecule. The transition of the matrix elements to a laboratory system of coordinates is carried out using the unitary matrix **U** (see Refs. 56, 58).

The set of algebraic equations based on Eq. (16) for the required $\mathbf{T}_{q\beta}$ matrix with allowance for the molecular rotation has the following form:

$$T_{No,\beta} = A_{No,\beta} + \sum_{N'} B_{No,No'} \cot \pi\nu_{No} T_{No',\beta}, \qquad (18)$$

in which the following designations have been introduced:

$$A_{No,\beta} = \langle\Lambda_\beta o|T^{(1)}|\beta\rangle\, U_{N\Lambda_\beta},$$
$$B_{No,No'} = \sum_{\Lambda}\langle\Lambda o|T^{(1)}|\Lambda o\rangle\, U_{N\Lambda}U_{\Lambda N'}.$$

Here Λ_β is the projection of the angular momentum of the electrons in the β-channel.

Expressions (18) have a clear physical sense. In fact, the value $A_{q\beta}$ describes a purely adiabatic process in which the projection of the electron angular momentum Λ onto the molecular axis is retained, *i.e.*, $\Lambda = \Lambda_\beta$. Mixing of states with different Λ occurs as a result of nonadiabatic coupling with rotation (which is due to the second term in Eq. (18) with coefficients $B_{qq'}$), when scattering channels with a different symmetry ($\Lambda \neq \Lambda_\beta$), which are not predissociative under the adiabatic motion conditions, are involved in the reaction. Their contribution to the process is determined, according to Eq. (18), by the elements of the rotation matrix **U** and depends substantially on the total angular momentum J and on N.

The complete cross-section of reaction (1) giving atomic fragments in a specified channel $|\beta\rangle$, averaged over the initial rotational states of the XY^+ ion, can be written as

$$\sigma_\beta = \sum_{N_i S} 0(T_i) \exp\left[-\frac{BN_i(N_i+1)}{T_i}\right]\sigma^S_{\beta,\nu_i N_i}(\varepsilon), \qquad (19)$$

where the partial cross-section $\sigma^S_{\beta,\nu_i,N_i}$ depends on the energy of the electron ε, on the total spin of the system S, and on the initial vibrational ν_i and rotational N_i states. The averaging is carried out in terms of the Boltzmann distribution at the rotational temperature T_i (B is the rotational constant). The normalization constant $0 = 1/Z^S_{rot}(T_i)$, where $Z^S_{rot}(T_i)$ is the rotational statistic sum,[65] depending on the temperature of the ions T_i. We studied the case of low temperatures $T_i \ll \omega$ (ω is the frequency of vibrations of the XY^+ ion); therefore, the state with v = 0 is the only open channel in the $\{\chi_v\}$ vibrational basis set.

The partial cross-section of the DR reaction for the initial state of the XY^+ ion ($\nu_i = 0$, N_i) is expressed in terms of the elements of the **T**-matrix of multichannel scattering:

$$\sigma^S_{\beta,oN_i} = \frac{2\pi}{\varepsilon} g^S \sum_{Jl}(2J+1)\left|T^{(Jl)}_{oN_i,\beta}(E)\right|^2. \qquad (20)$$

Here J is the full angular momentum of the system comprising the orbital momentum of the electron l and the rotational angular momentum of the nuclei N in the XY^+ ion, and $E = [\varepsilon + BN(N+1)]$ is the total energy of the system.

Figure 4 presents the partial cross-sections for reaction (8), calculated using the data[47] on the diabatic quantum defect $\mu_{l\Lambda}$ and the dissociative $^1\Sigma_g^+$-term according to Scheme (18) and Eq. (20), as well as in the adiabatic approximation with respect to rotation. The calculation was carried out in the six-channel approximation taking into account five vibronic (v = 0 to 4)

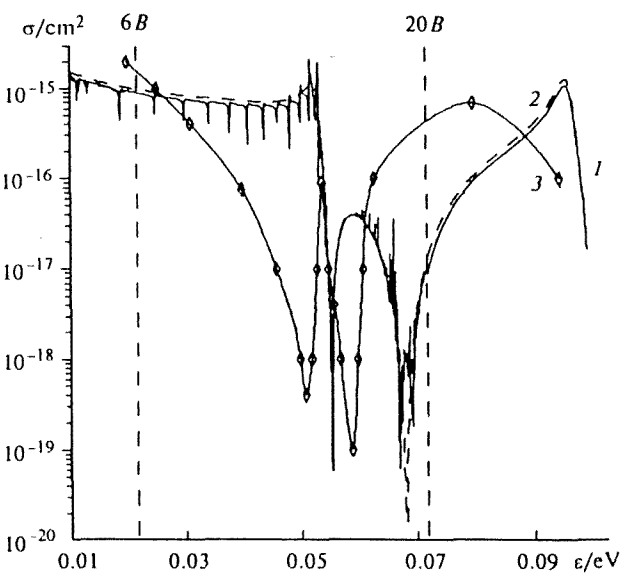

Fig. 4. Dependence of the partial cross-sections of reaction (8) on the electron energy ε: calculation taking into account the rotation for the initial state ($N_i = 0$) (*1*); adiabatic approximation (*2*); published results[47] (*1*). The vertical dashed lines mark the excitation thresholds for the rotational states with $N = 2$ and 4.

and one dissociative channel. In addition, rotation in the channel with v = 0 was taken into accout. Thus, seven channels with $N_i = 0$, eight channels with $N_i = 2$, and ten channels with $N_i = 4$ were included in scheme (18). It follows from Fig. 4 that the cross-sections calculated both taking and not taking into account the molecular rotation are close to each other, although their resonance structures are dissimilar. The cross-section found with allowance for the nonadiabatic coupling with the rotation is characterized by the presence of additional Fano-Feshbach resonances converging to the excitation thresholds for the rotational states with $N = 2$ and 4 (*i.e.*, 6 *B* and 20 *B*, respectively). Figure 4 (curve *3*) also shows the cross-section calculated in the ten-channel approximation[47] (neglecting the inelastic vibronic transition through the dissociative continuum). Furthermore, the Guisti formalism,[43] in which the condition of unitarity of the S-matrix is violated in a limited basis set, was used in this study.

The effect of the initial vibrational excitation is shown in Figs. 5 and 6, which present the temperature dependences of the partial cross-sections and the corresponding rate constants

$$k_\beta(T_e, N_i) = \left(\frac{2}{\pi T_e^3}\right)^{1/2} \int_0^\infty \varepsilon \sigma_{\beta,0N_i}(\varepsilon) \exp\left(-\frac{\varepsilon}{T_e}\right) d\varepsilon, \qquad (21)$$

T_e is the temperature of electrons for three rotational quantum numbers $N_i = 0$, 2, and 4. As N_i increases, the dependences shift to the left along the electron energy scale by the value of the threshold of the vibrational excitation $BN(N + 1)$. In addition, for $N_i = 2$, the cross-section and the rate constant increase by an order of magnitude compared to those for the nonexcited state. It is also noteworthy that for $N_i = 4$ at $T_e \sim 10^2$ K, in the region of energies making the main contribution to Eq. (21), where the cross-section $\sigma_{\beta,04}(\varepsilon)$ increases (see Fig. 5), the partial rate constant follows a temperature dependence which differs appreciably from the law $\sim T_e^{-1/2}$.

In Fig. 7, the overall cross-sections of reaction (8), averaged over the initial rotational states with the Boltzmann equilibrium distribution (19), are compared with those measured previously.[24] This comparison is presented as an illustration and reflects the main characteristic feature of the cross-section of this reaction, namely, the presence of resonance structure, since in the study cited,[24] no sufficiently clear selection over the initial vibrational states of the ion beam (containing a mixture of states with v = 0 and 1) or checking of the impurity with v = 1 was carried out. For a more detailed comparison, information on the real distribution function over the initial vibrational states, found in the previous paper,[24] is required and the initial vibrational state (v_i = 1) needs to be included in the calculation scheme.

The dependences of the overall rate constant for reaction (8) on the ion T_i and electron T_e temperatures

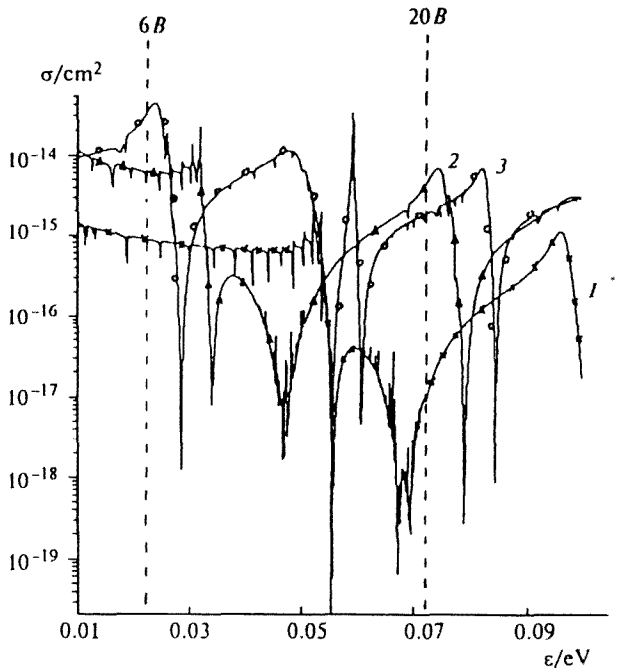

Fig. 5. Partial cross-sections of reaction (8) for $N_i = 0$ (*1*), 2 (*2*), 4 (*3*). The vertical dashed have the same meaning as those in Fig. 4.

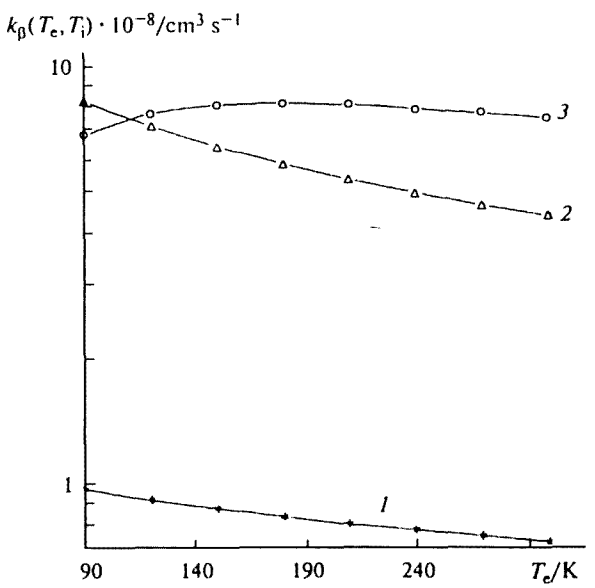

Fig. 6. Temperature dependences for the partial rate constants (k_β (T_e, T_i) of reaction (8) calculated from formula (21) for $N_i = 0$ (*1*), 2 (*2*), 4 (*3*).

are presented in Fig. 8, which indicates that the higher the temperature of the electrons, the less pronounced the dependence of the rate constant on T_i and that the initial rotational excitation has only a slight effect on the

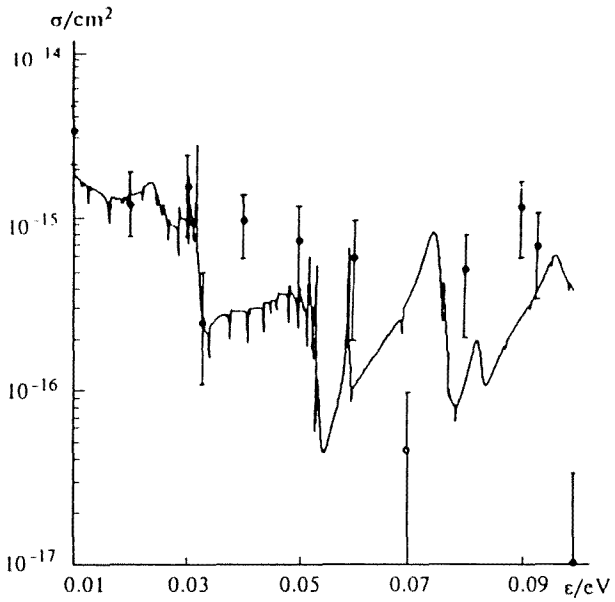

Fig. 7. Dependences of the overall cross-sections of reaction (8) on the electron energy (ε). The continuous line corresponds to averaging over the initial rotational states with the Boltzmann distribution (19); the dots show experimental results.[24] The vertical lines denote the errors of the measurement.

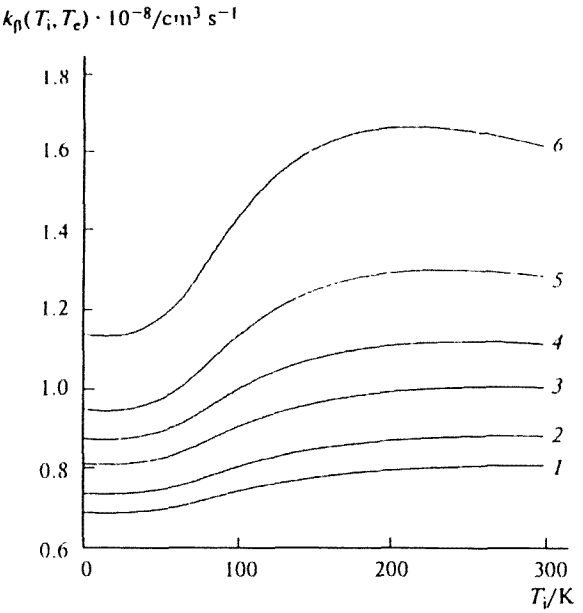

Fig. 8. Two-temperature dependences $k(T_e, T_i)$ of the overall rate constant of reaction (8) calculated from the formula $k_\beta(T_e, T_i) = \left(\frac{2}{\pi T_e^3}\right)^{1/2} \int_0^\infty \sigma_\beta(T_i, \varepsilon) \exp\left(-\frac{\varepsilon}{T_e}\right) \varepsilon d\varepsilon$ with the averaged cross-section (19) and for the initial data taken from the literature[47] at T_e/K = 300 (*1*); 250 (*2*); 200 (*3*); 150 (*4*); 100 (*5*); 50 (*6*).

profile of the curve. The maxima of these curves lie at $T_i \simeq 200$ K. After that, smooth decay is observed, which is due to a specific feature of the behavior of the rotational statistic sum in Eq. (19):

$$Z_{rot}(T_i) = \sum_{N=0,2,\ldots} (2N + 1) \exp\left[-\frac{BN(N+1)}{T_i}\right],$$

which is proportional to T_i starting from ~10^2 K for the para-modification of the molecular hydrogen ions.[65]

Let us consider the dependences presented in Fig. 6 in terms of the generally accepted views, approximating the partial rate constants of recombination (21) in a finite temperature range T_e (as is usually done[66,67]) by an exponential function:

$$k_\beta(T_e, N_i) = \alpha_{N_i} \left(\frac{T_e}{300\ \text{K}}\right)^{-x(N_i)}, \qquad (22)$$

and use this function to carry out numerical estimates for particular types of transitions. The values of the coefficient α and the exponents x for N_i = 0, 2, and 4, together with the T_e ranges in which approximation (22) is applicable, are listed in Table 2. It is seen that with increase in N_i the partial constants $k_\beta(T_e, N_i)$ markedly increase. The exponent x for the overall constant k_β (averaged over N_i) is close to the experimental value, although the α value calculated by us is ~3-fold smaller than the observed one, which is explained by the presence of vibrationally excited states with v_i = 1 and 2 in ion beams used in the previous paper.[23] Therefore, the parameters given in Table 2 make it possible to carry out kinetic calculations, using expression (22) as a working formula.

Table 2. Coefficients α_{N_i} and exponents $x(N_i)$ incorporated in expression (22) for the $H_2^+(o, N_i) + e^- \rightarrow H^*(21) + H(1s)$ reaction

N_i	$\alpha \cdot 10^{-7}$/cm³ s⁻¹	x	T_e/K
0	0.07	0.28	100—300
2	0.44	0.50	100—300
4	0.76	−0.11	100—150
4	0.76	0.04	150—300
*	0.80	0.44	100—300

* The values for the overall recombination constant averaged over the initial rotational distribution (19) at T_i = 210 K.

Conclusion

The process of formation of neutral fragments in the interaction of electrons and molecular ions (DR (1)) is in some sense an analog of a chemical reaction, since it

is accompanied by reorganization of species. The process involves intermediate formation of a Rydberg XY** complex characterized by an extremely complex and rich structure of self-ionization and predissociation states. The diversity of forms of the nonadiabatic coupling and of the interference structure in various physical manifestations of the Rydberg states of the XY** complexes makes them especially significant. For this reason, DR is not only of interest in itself but is also a tool that can be used for testing modern methods of the quantum theory of scattering and of chemical reactions.

The critical analysis of the existing calculation methods and the comparison of the results obtained by various methods carried out in this study indicate that the method of MQD, in which equations are formulated directly for the "observed" collision T-matrix and the unitarity of the scattering S-matrix is checked at each step of the calculations, is the most consistent and efficient technique for the investigation of DR and of the whole set of processes giving Rydberg complexes. The unitarity (as the constancy of the number of species before and after scattering) is one of the most important criteria of the reliability of the theory. Many approximations (for example, Born, pulse, adiabatic, *etc.*) do not possess this property. The unitarity of the S-matrix has also not been ensured in the previously developed theory of DR.[43]

Within the framework of the unitary theory of MQD we studied for the first time the effects of rotation and of the nonadiabatic electron-rotational coupling on reaction (8); we suggested a procedure that makes it possible to simplify substantially the calculations, while maintaining the main specific features due to the molecular rotation. The partial rate constants (and also the corresponding cross-sections) were found to be fairly sensitive to the initial excitation. At the same time, the time-averaged rate constants are affected only slightly by the rotational motion under equilibrium conditions.

The next stage of the development of the theory is the need to study high ionic temperatures at which more highly excited rotational states are involved in the process and the Coriolis interaction with the dissociative configurations begins to be manifested. One more stage due to the current state of the theory is also necessary; this is the allowance for the effect of the medium on the Rydberg complexes and on the processes involving them. The Rydberg molecules are characterized by large sizes ($R \sim 100$ Å at $n \sim 10$); therefore, their interaction with their own gas or a buffer gas is manifested even under conditions of high rarefaction.

This work was carried out with the financial support of the Russian Foundation for Basic Research (Project No. 93-03-4700).

References

1. Y. N. Bardsley and M. A. Biondi, *Adv. At. Mol. Phys.*, Eds. D. R. Bates and I. Isterman, Academic Press, New York, 1970, **6**, 1.
2. M. A. Biondi, *Plazma v lazerakh* [*Plasma in Lasers*], Energoatomizdat, Moscow, 1982, 145 (in Russian).
3. A. V. Eletskii, and B. M. Smirnov, *Usp. Fiz. Nauk*, **136**, 25 [*Sov. Phys. Uspekhi*, 1982, **136** (Engl. Transl.)].
4. H. S. W. Massey, *Applied Atomic Collision Physics*, Eds. H. S. W. Massey, E. V. McDaniel, and B. Bederson, Academic Press, New York, 1982, **1**, 21.
5. J. Wm. McGowan and J. B. A. Mitchell, in *Electron-Molecule Interactions and Their Appications*, Ed. L. G. Christophorou, Academic Press, New York, 1984, **2**, 65.
6. S. L. Guberman, in *Fizika ion-ionnykh i elektron-ionnykh stolknovenii* [*Physics of Ion-Ion and Electron-Ion Collisions*], Ed. F. Brouillard, D. McGouen, Mir, Moscow, 1986, 110 (Russ. Transl.).
7. J. B. A. Mitchell and J. Wm. McGowan, in *Fizika ion-ionnykh i elektron-ionnykh stolknovenii* [*Physics of Ion-Ion and Electron-Ion Collisions*], Ed. F. Brouillard, D. McGouen, Mir, Moscow, 1986, 219 (Russ. Transl.).
8. J. B. A. Mitchell, in *Atomic Processes in Electron-Ion and Ion-Ion Collisions*, Ed. F. Brouillard, Plenum, New York, 1986, 185.
9. S. L. Guberman, in *Thermophysical Aspects of Re-entry Flows*, Eds. J. N. Moss and C. D. Scott, New York, 1986, 223.
10. A. Guisti-Suzor, in *Atomic Processes in Electron-Ion and Ion-Ion Collisions*, Ed. F. Bruillard, Plenum, New York, 1986, 223.
11. A. Kh. Mnatsakanyan and G. V. Naidis, *Khimiya plazmy* [*Plasma Chemistry*], Ed. B. M. Smirnov, Energoizdat, Moscow, 1987, **14**, 227 (in Russian).
12. A. P. Hickman, in *Dissociative Recombination: Theory, Experiment and Applications*, Eds. J. B. A. Mitchell and S. L. Guberman, World Scientific, Singapore, 1989, 35.
13. S. L. Guberman, in *Dissociative Recombination: Theory, Experiment and Applications*, Eds. J. B. A. Mitchell and S. L. Guberman, World Scientific, Singapore, 1989, 45.
14. H. Nakamura, H. Takagi, and K. Nakashima, in *Dissociative Recombination: Theory, Experiment and Applications*, Eds. J. B. A. Mitchell and S. L. Guberman, World Scientific, Singapore, 1989, 73.
15. J. B. A. Mitchell and S. L. Guberman, in *Dissociative Recombination: Theory, Experiment and Applications*, Eds. J. B. A. Mitchell and S. L. Guberman, World Scientific, Singapore, 1989, 91.
16. J. B. A. Mitchell, *Phys. Rep.*, **186**, 215.
17. G. V. Golubkov and G. K. Ivanov, *Itogi nauki i tekhniki, Kinetika i kataliz*, **24** [*Results in Science and Engineering. Kinetics and Catalysis*], VINITI, Moscow, 1991, 82 (in Russian).
18. V. A. Ivanov, *Usp. Fiz. Nauk*, 1992, **162**, 227 [*Sov. Phys. Uspekhi*, 1992, **162** (Engl. Transl.)].
19. B. Peart and K. T. Dolder, *J. Phys.*, 1974, **B7**, 236, 1948.
20. M. Volger and G. H. Dunn, *Bull. Am. Phys. Soc.*, 1970, **15**, 417; *Phys. Rev.*, 1975, **A11**, 1983.
21. R. A. Phaneuf, D. H. Crandall, and G. H. Dunn, *Phys. Rev.*, 1975, **A11**, 528.
22. D. Mathur, S. U. Khan, and J. B. Hasted, *J. Phys.*, 1978, **B11**, 3615.
23. D. Auerbach, R. Cacak, R. Caudano, T. D. Gaily, C. J. Keyser, J. Wm. McGowan, J. B. A. Mitchell, and S. F. J. Wilk, *J. Phys.*, 1977, **B10**, 3797.
24. H. Hus, F. B. Yousif, C. Noren, A. Sen, and J. B. A. Mitchell, *Phys. Rev. Lett.*, 1988, **60**, 1008.
25. J. Wm. McGowan, R. Caudano, and J. Keyser, *Phys. Rev. Lett.*, 1976, **36**, 1447.

26. J. N. Bardsley, *J. Phys.*, 1968, **B1**, 365.
27. J. C. Y. Chen and M. A. Mittleman, *Intern. Conf. Phys. Elect. Atom. Collisions*, Leningrad, Abstracts of Papers, 1967, p. 329.
28. M. I. Chibisov and S. I. Yakovlenko, *Zh. Eksp. Teor. Fiz.*, [*J. Exp. Theor. Phys.*] 1977, **73**, 43 (in Russian).
29. A. Guisti, *J. Phys.*, 1980, **B13**, 3867.
30. C. Derkits, J. N. Bardsley, and J. M. Wadehra, *J. Phys.*, 1979, **B12**, L529.
31. E. P. Wigner, *Phys. Rev.*, 1948, **73**, 1002.
32. A. I. Baz', *Zh. Eksp. Teor. Fiz.* [*J. Exp. Theor. Phys.*], 1957, **36**, 1762 (in Russian).
33. L. Fonda and R. G. Newton, *Ann. Phys.*, 1959, **7**, 133.
34. M. K. Gailitis, *Zh. Eksp. Teor. Fiz.* [*J. Exp. Theor. Phys.*], 1963, **44**, 1974 (in Russian).
35. M. J. Seaton, *Proc. Phys. Soc.*, 1966, **88**, 801; *J. Phys.*, 1969, **B2**, 5.
36. J. Wm. McGowan, P. M. Mul, V. S. D'Angelo, J. B. A. Mitchell, P. Defrance, and H. R. Froelich, *Phys. Rev. Lett.*, 1979, **42**, 373.
37. T. F. O'Malley, *J. Phys.*, 1981, **B14**, 1229.
38. D. R. Bates, *Phys. Rev.*, 1950, **78**, 492.
39. U. Fano, *Phys. Rev.*, 1961, **B1**, 1866.
40. J. N. Bardsley, *J. Phys.*, 1968, **B1**, 349.
41. F. Fiquet-Fayard, *J. Phys.*, 1975, **B8**, 2880.
42. C. Bottcher, *Proc. R. Soc. London Ser.*, 1974, **A340**, 301.
43. A. Guisti-Suzor, J. N. Bardsley, and C. Derkits, *Phys. Rev.*, 1983, **A28**, 682.
44. A. P. Hickman, *J. Phys.*, 1987, **B20**, 2091.
45. C. M. Lee and H. Nakamura, *J. Chem. Phys.*, 1986, **84**, 2431.
46. H. Takagi and H. Nakamura, *J. Chem. Phys.*, 1986, **84**, 2431.
47. K. Nakashima, H. Takagi, and H. Nakamura, *J. Chem. Phys.*, 1987, **86**, 726.
48. S. L. Guberman and A. Guisti-Suzor, *J. Chem. Phys.*, 1991, **95**, 2602.
49. G. V. Golubkov and G. K. Ivanov, *Zh. Eksp. Teor. Fiz.* [*J. Exp. Theor. Phys.*], 1981, **80**, 1321; *Khim. Fiz.* [*Chem. Phys.*], 1982, **6**, 729 (in Russian).
50. G. V. Golubkov and G. K. Ivanov, *Chem. Phys. Lett.*, 1981, **81**, 110; *J. Phys.*, 1984, **B17**, 747.
51. G. K. Ivanov and G. V. Golubkov, *Chem. Phys. Lett.*, 1984, **107**, 261.
52. G. K. Ivanov and G. V. Golubkov, *J. Phys.*, 1986, **D1**, 199.
53. G. V. Golubkov and G. K. Ivanov, *J. Phys.*, 1988, **B21**, 2049.
54. G. V. Golubkov and G. K. Ivanov, *IL Nuovo Cimento*, 1990, **12D**, 1.
55. M. J. Seaton, *Rep. Prog. Phys.*, 1983, **46**, 167.
56. U. Fano, *Phys. Rev.*, 1970, **A2**, 353; *J. Opt. Soc. Am.*, 1975, **65**, 979.
57. G. V. Golubkov and G. K. Ivanov, *Zh. Eksp. Teor. Fiz.* [*J. Exp. Theor. Phys.*], 1993, **104**, 3334 (in Russian).
58. Ch. Greene and Ch. Jungen, *Adv. At. Mol. Phys.*, 1985, **21**, 51.
59. F. I. Dalidchik, *Chem. Phys. Lett.*, 1985, **119**, 71.
60. A. E. Bodrov and F. I. Dalidchik, *Chem. Phys. Lett.*, 1986, **130**, 531.
61. A. E. Bodrov and F. I. Dalidchik, *Khim. Fiz.* [*Chem. Phys.*], 1987, **6**, 153; 1988, **7**, 1199; 1989, **8**, 876 (in Russian).
62. R. K. Nesbet, *Phys. Rev.*, 1979, **A19**, 551.
63. A. U. Hazi, C. Derkits, and J. N. Bardsley, *Phys. Rev.*, 1983, **A27**, 1751.
64. A. A. Radtsig and B. M. Smirnov, *Spravochnik po atomnoi i molekulyarnoi fizike* [*Handbook of Atomic and Molecular Physics*], Atomizdat, Moscow, 1980, 240 pp. (in Russian).
65. L. D. Landau and E. M. Lifshits, *Statisticheskaya fizika* [*Statistical Physics*], Nauka, Moscow, 1976, 583 pp. (in Russian).
66. S. L. Guberman, *Nature*, 1987, **327**, 408.
67. S. L. Guberman, *Planet. Space Sci.*, 1988, **36**, 47.

Received February 9, 1995;
in revised form April 9, 1996