

Rotation in the dissociative–recombination reaction of electrons and ions of molecular hydrogen

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The influence of molecular rotation and non-adiabatic electronic–rotational coupling on the reaction $e^- + H_2^+(v_i=0, N_i) \rightarrow H^*(2l) + H(1s)$ is studied within the framework of the unitary theory of multichannel quantum defects. To simplify the calculations, we propose a procedure based on the possibility of using the adiabatic approximation (in the rotation of the nuclei) in the near-threshold region to account for the contributions of the vibrationally excited states of the Rydberg complex formed in the intermediate step of the reaction. It is shown that the partial rate constants (and the corresponding cross sections) are extremely critical for the initial rotational excitation. At the same time, the rotational motion has only a weak effect on the total rate constants under equilibrium conditions. © 1995 American Institute of Physics.

1. INTRODUCTION

Dissociative recombination reactions of electrons and molecular ions



have been studied intensively, both experimentally and theoretically. This fact is not hard to understand considering their important role in ionospheric and astrophysical phenomena, weakly ionized plasmas, and processes taking place in gas lasers.¹ Nevertheless, there are a number of questions that still remain unsettled. The dissociative recombination reaction (1), as is well known,² takes place in one step via direct transition to the dissociative continuum and through the stage of an intermediate Rydberg complex XY^{**} . The amplitudes corresponding to these processes interfere with each other, which leads to a complicated energy dependence of the dissociative recombination cross section.

The present paper is dedicated to a study of the role of molecular rotation and non-adiabatic electronic–rotational coupling in reactions of type (1), which were previously investigated without taking such phenomena into account.^{2–6} The difficulties that one meets here are due to the fact that the Rydberg complex XY^{**} formed in the intermediate stage of the process is characterized by a rich and extraordinarily complex rotational–vibrational structure of auto-ionization and predissociation states. Analysis of non-adiabatic effects associated with rotation of the nuclei is necessary, above all, to describe reactions in which hydrogen-bearing ions (of the type XH^+) participate, where the rotational constants $B \sim 10^{-4}$ a.u. and the first excitation threshold is reached at thermal electron energies.

Contemporary studies of electron–ion recombination, carried out using the technique of crossed beams,² lack sufficiently accurate methods of recording the initial states of the recombining system. Therefore the observed cross sections tend to be averaged over a spread of energy in the electron beams and the initial distribution of the ions over vibrational and rotational states, which hinders a direct comparison of experimental and theoretical results. This, in turn,

presents serious requirements on the existing theory and, in particular, on studies of processes in which simple diatomic ions XY^+ take part.

The theoretical investigation presented in this paper is based on the integral variant of the multichannel quantum defect theory proposed in Refs. 7–11, in which the equations are formed directly for the “observable” collision matrix (the T -matrix) and at each step of the calculation the unitarity of the S -matrix (the scattering matrix) is strictly monitored (i.e., conservation of the number of particles in the reaction). This is one of the most important criteria for validation of the theory. It should be noted that many approximate methods (e.g., the Born approximation, the momentum approximation, the adiabatic approximation, etc.) do not possess this property. Unitarity of the S -matrix is not preserved in the theory of dissociative recombination developed in Refs. 3, 5, and 6, either. In order to avoid the difficulties associated with including in the calculational scheme rotation–vibration coupling in all of the closed channels, we propose a two-step procedure that makes it possible to substantially simplify the calculations while preserving the main features associated with molecular rotation. As a specific application of the theory developed in this way, we consider the reaction $e^- + H_2^+$.

2. TWO-STEP METHOD FOR TAKING ACCOUNT OF NON-ADIABATIC COUPLING WITH ROTATION

In our exposition of the general theory we will follow the multichannel quantum defect method,^{9–11} which is the most convenient for the solution of this class of problems. We represent the Hamiltonian of the system under consideration in the form ($\hbar = m_e = e = 1$)

$$H = H_0 + V, \quad H_0 = -\frac{1}{2} \Delta_r - \frac{1}{r} + H_q, \quad (2)$$

where $-\frac{1}{2} \Delta_r$ is the kinetic energy operator of the electron, r is its radial coordinate, and H_q is the Hamiltonian of the molecular ion (q is the set of vibrational (v) and rotational (N) quantum numbers). The zeroth-order Hamiltonian H_0 is chosen in such a way that all interactions in the dissociative

(X+Y) configurations are taken exactly into account, and in the scattering channel ($e^- + XY^+$) only the Coulomb part of the interaction ($V_c = -\frac{1}{r}$) is taken into account. Thus, in the total Hamiltonian (2) the operator $V = V_{nc} + V^{CI}$ includes the non-Coulombic part of the interaction of the electron with the ionic core V_{nc} and the configurational interaction V^{CI} between the states $e^- + XY^+$ and X+Y, which we denote by the indices q and β . We write the corresponding wave functions as $|q\rangle$ and $|\beta\rangle$. In the open channels these functions are normalized by the energy:

$$\langle q_E | q_{E'} \rangle = \pi \delta(E - E'), \quad \langle \beta_E | \beta_{E'} \rangle = \pi \delta(E - E').$$

Note that at electron distances r of the order of atomic distances ($r \sim 1$), these functions describe the motion of a fast electron and a slow nuclear subsystem, and can be calculated in the Born–Oppenheimer approximation by the methods of quantum chemistry. Methods of writing down these functions in accordance with the rules for adding angular momenta and in accordance with Hund coupling are well known.

In the solution of the problem of dissociative recombination, it is necessary to define the collision operator T (related to the S -matrix by the formula $S = 1 - 2iT$), which satisfies the system of readjusted Lippmann–Schwinger integral equations⁸

$$T = t + t(G - G_0)T, \quad (3)$$

$$t = V + VG_0t, \quad (4)$$

where $G = (E - H_0)^{-1}$ is the Green's function operation of the system with the interaction V turned off, and G_0 is the weakly energy-dependent Green's function operator, containing no poles of the Rydberg and dissociative configurations, i.e.,

$$G_0 = \frac{1}{\pi} \sum_q P \int \frac{|q\rangle \langle q|}{E - E_q - \varepsilon} d\varepsilon + \frac{1}{\pi} \sum_\beta P \int \frac{|\beta\rangle \langle \beta|}{E - E_\beta} dE_\beta \quad (5)$$

(P denotes the principal value, and the index q denotes summation over the set of vibrational (v) and rotational (N) quantum numbers, thus $q = \{v, N\}$) and also not taking the interaction V into account. Here E and E_q are the total energy of the system and the excitation energy, both reckoned from the ground state of the ion XY^+ . In this formulation the t -matrix is constructed from standing waves distorted by the presence of the Coulombic center. This corresponds to the definition of the K -matrix (the matrix of electron scattering from the ionic core). It should be stressed that equations (3)–(4) take into account contributions from the resonant interaction mechanism as well as the direct interaction mechanism. In addition, it formally describes all types of non-adiabatic couplings in the Rydberg states of the intermediate complex XY^{**} .

The basis wave functions of the Rydberg channels $e^- + XY^+$, which take account of the vibrational and rotational motion of the nuclei, are

$$|q\rangle = |lNv, JM\rangle = \pi^{1/2} \varphi_{l\varepsilon_q} \chi_v \Phi_{lN}^{JM}, \quad (6)$$

where $\varphi_{l\varepsilon_q}$ is the electronic radial wave function with orbital angular momentum l in the Coulomb field, which for

$r \ll |\varepsilon_q|^{2/3}$ does not depend on the electron energy ($\varepsilon_q = E - E_q$), and for discrete values of $\varepsilon_q = -1/2n_q^2$ coincides with the eigenfunctions of the hydrogen atom (n_q is the principal quantum number), χ_v is the vibrational wave function of the ion XY^+ . The angular function Φ_{lN}^{JM} is defined in the representation with total angular momentum J , projection M , and angular momentum of the rotational motion of the nuclei N and has the form

$$\Phi_{lN}^{JM}(\hat{r}, \hat{R}) = \sum_m Y_{lm}(\hat{r}) Y_{N, M-m}(\hat{R}) (lN, mM - m | JM) \quad (7)$$

(\hat{r} and \hat{R} are the corresponding spherical coordinates of the electron and nucleus, Y_{lm} is the l, m -th spherical harmonic, $(lN, mM - m | JM)$ are the coefficients of the vector sum, written in the notation of Ref. 12. The functions in (6) are defined in the laboratory reference frame, i.e., the coordinate system in which the direction of the beam of incident electrons is given. For subsequent calculations it is also necessary to introduce an adiabatic basis, i.e., one in which the electron wave function is written in a coordinate system bound to the axis of the molecule. The transformation to this basis is realized via the unitary rotation matrix U ,

$$|lNv, JM\rangle = \sum_\Lambda U_{\Lambda N}^J |l\Lambda v, JM\rangle, \quad (8)$$

whose elements are equal, Eq. (13)

$$U_{\Lambda N}^J = (-1)^{J+\Lambda} (lJ - \Lambda\Lambda | N0) (2 - \delta_{\Lambda 0})^{1/2}. \quad (9)$$

Motion in the adiabatic basis obeys the Born–Oppenheimer principle, according to which the wave function of the diatomic molecule is given by

$$|l\Lambda v, JM\rangle = \pi^{1/2} \varphi_{l\varepsilon_q} \chi_v Y_{l\Lambda}(\hat{r}') D_{M\Lambda}^J(\hat{R}') \left(\frac{2J+1}{4\pi} \right)^{1/2}. \quad (10)$$

Here $\varphi_{l\varepsilon_q}$ is defined as in expression (6), $D_{M\Lambda}^J$ is the generalized spherical harmonic (\hat{r}' and \hat{R}' denote, respectively, the position of the incident electron in the coordinate system bound to the molecule and the direction of the molecular axis).

It is convenient to write the wave function of the dissociative channel, which describes the relative motion of the nuclei with direction of the wave vector n_β (characterized by azimuthal and polar angles φ_β and θ_β) fixed at infinity, in the form

$$\Psi_{X+Y} = \sum_{JM\Lambda} i^J \left(\frac{2J+1}{4\pi} \right)^{1/2} D_{M-\Lambda, \beta}^J(\varphi_\beta, \theta_\beta, 0) |\beta\Lambda, JM\rangle, \quad (11)$$

where Λ_β is the projection of the electronic angular momentum in the direction of n_β , $|\beta\rangle = |\beta\Lambda, JM\rangle$ are the basis functions of the dissociative configuration, introduced in analogy with (10).

In Refs. 7 and 8 it was shown that for Rydberg systems, the structure of Eqs. (3)–(4) allows one to use an algebraic approach to construct the unitary S -matrix (the scattering matrix). The equations for the T -matrix (the collision matrix)

were formulated in Refs. 9–11 with the dissociative channels taken into account. These equations are formally exact, and describe all types of non-adiabatic coupling in the Rydberg states of the complex XY^{**} . In this case, however, the calculations, which include a large number of vibrational–rotational channels, turn out to be quite lengthy.

As a consequence of the specifics of the molecular objects, the contributions of channels with $v=0$ and $v \geq 1$ in the propagator $G-G_0$ of Eq. (3) can be considered in various approximations. For states with $v=0$, below the rotational excitation threshold of the XY^+ ion, $Bn_0^3 > 1$ (for molecules of H_2^{**} $B \cong 1.3 \cdot 10^{-4}$ and $n_0 > 30$). Thus here we run up against a highly nonadiabatic situation. In contrast, for $v \geq 1$ at low energies, with $Bn_v^3 \ll 1$ (and $n_v \leq 8$), the conditions of the adiabatic approximation are easily met. Therefore, the calculation can be divided into two steps: in the first (taking the contribution of the states with $v \geq 1$ into account), we consider the traditional adiabatic formulation of the problem (without allowance for coupling with rotation), and in the second, we include rotational motion. On the basis of this approach, we obtain two operator equations (for fixed quantum numbers J and M):

$$T = T^{(1)} + T^{(1)} \sum_{IN} |lN0\rangle \langle lN0| \cot \pi \nu_{N0} T, \quad (12)$$

$$T^{(1)} = t + t \sum_{v \geq 1} |l\Lambda v\rangle \langle l\Lambda v| \cot \pi \nu_v T^{(1)} - it \sum_{\beta} |\beta\rangle \langle \beta| T^{(1)}. \quad (13)$$

According to Eq. (12), taking rotational motion into account in the $v=0$ channel requires us first to determine the adiabatic submatrix, which, however, is not the true adiabatic scattering matrix T^{ad} , since in Eq. (13) there is no term corresponding to the open entrance channel. Note that Eq. (12) transforms into the equation for T^{ad} in the above-threshold region (with regard to rotations in the $v=0$ channel), where $\cot \pi \nu_{N0} = -i$ for all N . Therefore, there exists a simple connection between $T^{(1)}$ and T^{ad} , which follows from the operator relation

$$T^{\text{ad}} = T^{(1)} - iT^{(1)} \sum_{l\Lambda} |l\Lambda 0\rangle \langle l\Lambda 0| T^{\text{ad}}. \quad (14)$$

The matrices $T^{(1)}$ and T^{ad} are defined in the coordinate system attached to the axis of the molecule. Transformation of the matrix elements to the laboratory frame is accomplished with the help of the unitary matrix U .¹³

On the basis of Eq. (12), we obtain a system of algebraic equations for the unknown matrix $T_{N0,\beta}$ that takes rotation of the ion into account. This system has the form

$$T_{N0,\beta} = A_{N0,\beta}(E) + \sum_{N'} B_{N0,N'0}(E) \cot \pi \nu_{N'0} T_{N'0,\beta}, \quad (15)$$

where we have introduced the following notation (the indices J and M have been dropped):

$$A_{N0,\beta} = \langle l\Lambda_{\beta} 0 | T^{(1)} | \beta \Lambda_{\beta} \rangle U_{N\Lambda_{\beta}}, \quad (16)$$

$$B_{N0,N'0} = \sum_{\Lambda} \langle l\Lambda 0 | T^{(1)} | l\Lambda 0 \rangle U_{N\Lambda} U_{\Lambda N'}.$$

These expressions have a transparent physical meaning. Indeed, the quantity $A_{N0,\beta}$ describes a purely adiabatic process in which the projection of the electronic angular momentum Λ onto the molecular axis is conserved, i.e., $\Lambda = \Lambda_{\beta}$. States with differing Λ are mixed as a result of non-adiabatic coupling with rotation (which is due to the second term in (15)), whereby scattering channels with different symmetry ($\Lambda \neq \Lambda_{\beta}$), which under adiabatic conditions of motion ($Bn^3 \ll 1$) are not predissociative, take part in the reaction. Their contribution to the process is determined by the elements of the rotation matrix U and depends strongly on J and N .

3. CROSS SECTION OF THE DISSOCIATIVE RECOMBINATION REACTION

The total cross section of the dissociative recombination reaction (1) with formation of atomic fragments in a given channel $|\beta\Lambda\rangle$, averaged over the initial rotational states of the XY^+ ion, has the form

$$\sigma_{\beta} = \sum_{N,s} A(T_i) \exp\left\{-\frac{BN(N+1)}{T_i}\right\} \sigma_{\beta N}^s(E_e), \quad (17)$$

where the partial cross section $\sigma_{\beta N}^s$ depends on the electron energy E_e , the total spin of the system s , and the initial rotational state N . The averaging is carried out over the Boltzmann distribution with rotational temperature of the ions T_i (B is the rotational constant). The normalization constant A is equal to $1/Z_{\text{curl}}^s(T_i)$ where $Z_{\text{curl}}^s(T_i)$ is rotation statistical summation (14) which depends on T_i temperature. In the present article we examine the case of low temperatures $T_i \ll \omega$ (where ω is the vibrational frequency of the ion XY^+ , so the only open channel in the vibrational basis $\{\chi_v\}$ is the state with $v=0$).

The partial cross section of the dissociative recombination reaction for the initial state of the XY^+ ion ($v=0, N$) can be expressed in terms of the elements of the T -matrix of multichannel scattering:

$$\sigma_{\beta N}^s = \frac{2\pi}{E_e} g^s \sum_{Jl} (2J+1) |T_{lN0,\beta\Lambda}(E)|^2 \quad (18)$$

(g^s is the spin degeneracy factor, J is the total angular momentum of the system, consisting of the orbital angular momentum l of the electron and the rotational angular momentum N of the nuclei of the XY^+ ion, and $E = E_e + BN(N+1)$ is the total energy of the system). To determine the amplitudes $T_{lN0,\beta\Lambda}$, we must, according to Eqs. (15)–(16), first find the elements $T_{l\Lambda 0,\beta\Lambda}^{\text{ad}}$ and $T_{l\Lambda 0,l\Lambda v'}^{\text{ad}}$, of the adiabatic scattering matrix. Equations (13)–(14), which describe them, contains the elements of the t -matrix of the reaction (4), which, taking account of the smallness of the configurational coupling, can be written as follows (the indices l and Λ are dropped from here on):

$$t_{0v} = t_{0v}^{(0)} + \frac{1}{\pi} \sum_{\beta} P \int \frac{V_{0\beta} V_{\beta v}}{E - E_{\beta}} dE_{\beta}, \quad (19)$$

$$t_{0\beta} = V_{0\beta} + \frac{1}{\pi} \sum_v P \int \frac{t_{0v}^{(0)} V_{v\beta}}{E - E_v - \varepsilon} d\varepsilon,$$

where the elements of the t_0 -matrix are equal to

$$t_{0v}^{(0)} = -\langle 0 | \tan \pi \mu_{l\Lambda} | v \rangle. \quad (20)$$

Note that in this system the diagonal element $t_{\beta\beta}$, which is quadratic in the configurational coupling, vanishes. The elements of the vibronic coupling t_{0v} in Eqs. (19) can be represented as a sum of two terms. The first is due to the interaction with the ionic core, and the second describes the mixing of the Rydberg series with the dissociative continuum. To evaluate it in explicit form, it is convenient to make use of the quasiclassical approximation,¹⁵ and also the fact that for a sharp enough term $U_\beta(R)$ in the vicinity of the classical turning point $R_c[E=U_\beta(R_c)]$ for the nuclear wave function $\chi_\beta(R)$ for $a_0 U'_\beta \gg \omega$ the Winans–Stueckelberg approximation is valid.¹⁶ As a result, we have

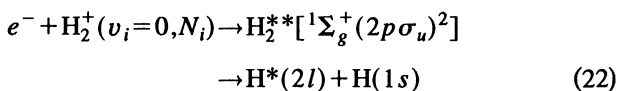
$$t_{vv'} = t_{vv'}^{(0)} + \pi P \int \frac{V_\beta^2(R) \chi_v(R) \chi_{v'}(R)}{E - U_\beta(R)} dR \quad (21)$$

($V_\beta(R)$ is the electronic part of the configurational interaction associated with the large splitting of the Rydberg term $l\Lambda$ and the dissociative term β by the relation $\Delta = 2V_\beta / (\pi n^3)^{1/2}$).

The off-diagonal matrix elements $t_{vv'}$ [Eq. (21)] describe the amplitudes of the $v'-v$ transitions to the ionization continuum and the vibronic coupling in the closed channels. Since the vibronic transitions are characterized by the small physical parameter $\xi = a_0 R_{eq}^{-1}$ (where a_0 is the amplitude of the zero-point oscillations and R_{eq} is the equilibrium interatomic distance), it can be shown that up to terms in the second derivative $\mu''_{i\Lambda}$ and quadratic terms in V_β , the main contribution to the overall scheme comes from one-quantum and two-quantum transitions. In this case the second term in Eq. (21), the term due to the interaction with the dissociative continuum, plays an important role, as will be shown below in the example of the Rydberg complex H_2^{**} .

4. CROSS SECTIONS AND RATE CONSTANTS OF THE $e^- + H_2^+$ REACTION

We turn now to an analysis of the role of non-adiabatic coupling with rotation in the reaction



(v_i and N_i are the initial vibrational and rotational states of the ion). The H_2 molecule, as is well known, possesses one low-lying doubly excited state ${}^1\Sigma_g^+(2p\sigma_u)^2$ (Ref. 5). Its potential energy curve $U_\beta(R)$ intersects the ionic term $U_i(R)$ in the vicinity of the point $R_c = 2.65$ a.u. (see Fig. 1), located between the right classical turning points of the ground state and the first vibrational-excitational state (closer to the $v=1$ state). In addition, in the Rydberg complex H_2^{**} , which is formed during the intermediate stage of the process, it is mainly the series $nd\sigma_g({}^1\Sigma_g^+)$, in which the angular momentum of the electron $l=2$ is a “good” quantum number, that predissociates.⁵ Note also that none of the calculations that have been carried out to date for this reaction (see, e.g., Ref.

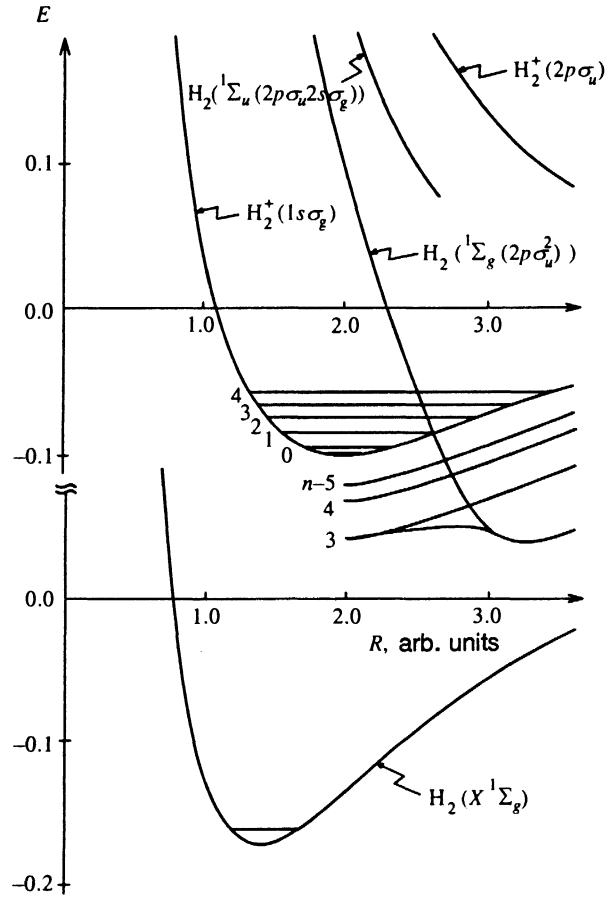


FIG. 1. Potential energy of the H_2 molecule near the ionization threshold.⁵

2) have taken account of rotation. In this regard, the most successful calculation of the cross section of reaction (22) is considered to be that of Nakashima *et al.*⁵ Therefore, availing ourselves for the diabatic quantum defect $\mu_{l\Lambda}$ and the dissociative ${}^1\Sigma_g^+$ -term of the results of this work, we carry out a numerical comparison of the results of Ref. 5 with the cross sections we have calculated (taking rotational coupling into account in the rotationally adiabatic approximation).

As a consequence of the weak dependence of the electronic part of the configurational interaction V_β on the interatomic distance R , the matrix elements $V_{v\beta}$ (describing the coupling of the states of the Rydberg complex H_2^{**} to the dissociative continuum) can be represented in the form

$$V_{v\beta} = V_\beta(R) \alpha_{vd},$$

where $\alpha_{vd}^2 = \langle \chi_v | \chi_d \rangle^2$ are the energy-dependent (E) Franck–Kondon factors, which we calculated in the semiclassical approximation. Here, to calculate the vibrational wave functions of the H_2^+ ion we used the Morse potential with the parameters from Ref. 17

Figure 2 shows the partial cross sections of reaction (22), calculated for $g^s = \frac{1}{4}$ using (15)–(16), (18)–(21) in the adiabatic approximation, i.e.,

$$\sigma_{\beta N_i}(E_e) = \frac{\pi}{2E_e} |\langle l\Lambda_\beta 0 | T^{\text{ad}}(E_e) | \beta\Lambda_\beta \rangle|^2, \quad N_i = 0 \quad (23)$$

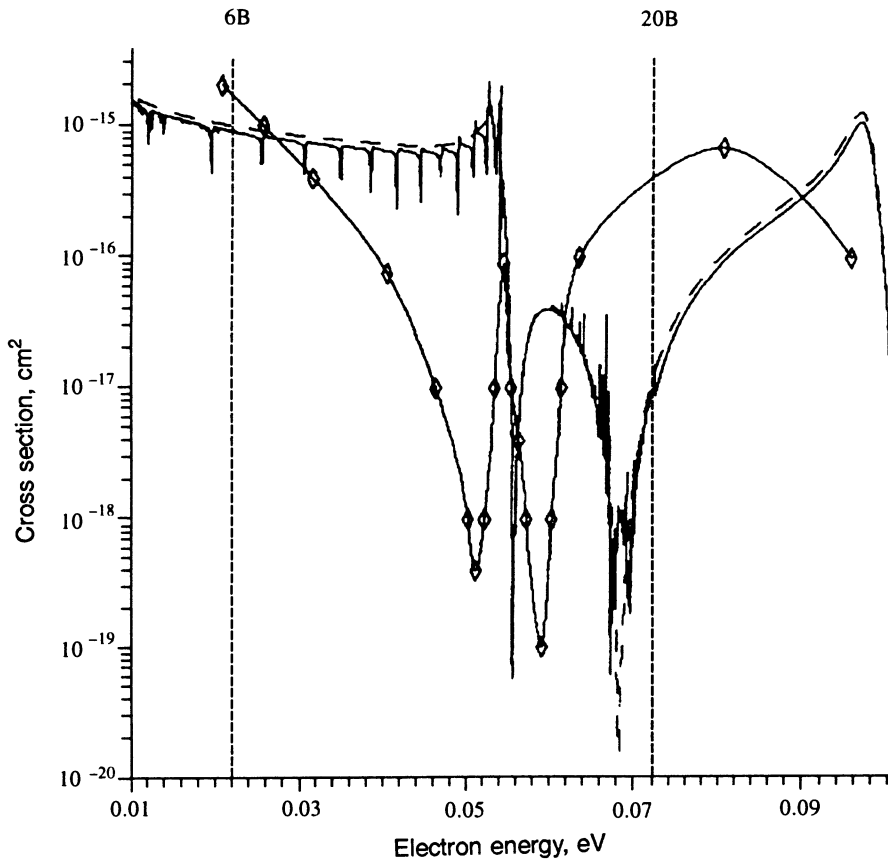


FIG. 2. Partial cross section of reaction (22) as a function of the electron energy E_e . The solid line corresponds to the calculation taking account of rotation for the initial state $N_i=0$, the dashed line corresponds to the adiabatic approximation (23), and the diamond symbols, to the numerical calculation in Ref. 5. The vertical dashed lines correspond to the excitation threshold of rotational states with $N=2$ and $N=4$.

(the summation over J in this case is implemented in analytic form). Cross section (23) was calculated in the 6-channel approximation (five vibronic $v=0-4$ and one dissociative β -channel). As follows from Fig. 2, the two cross sections are close in magnitude, but they have a different resonance structure. The cross section found taking non-adiabatic coupling with rotation in the $v=0$ channel into account is characterized by the presence of additional Fano-Feshbach resonances, converging to the excitation thresholds of the rotational states with $N=2$ and 4 (i.e. 6B and 20B, respectively). Additional distortions also take place in the vicinity of the poles of the elastic scattering amplitude $T_{00}^{\text{ad}}(E)$. This same figure depicts the cross section from Ref. 5, calculated in the 11-channel adiabatic approximation ($v=0-9$) without allowance for the second term in (19)—in other words, neglecting inelastic vibronic transitions via the dissociative continuum. For this reason, the cross section from Ref. 5 depicted in Fig. 2 by diamond symbols, has the character of an “antiresonance,” which agrees with the small value of the profile index. In this regard, in the formalism used by Nakashima *et al.*, namely that of Giusti-Suzor *et al.*³ (with the limited basis of the vibronic states that have been taken into account), the unitarity of the S -matrix is violated.

In the integral variant of the multichannel quantum effect theory which we propose, the vibronic transitions via the dissociative continuum are correctly taken into account. The existence of this coupling leads to a shift in the resonance level toward lower electron energies E_e (for the level $n=4$, $v=4$, for example, this shift is equal to approximately 0.06 eV).

The influence of the initial rotational excitation is graphically demonstrated in the following two figures (Figs. 3 and 4), which depicts the partial cross sections and the corresponding rate constants $k_{\beta}(T_e, N_i)$, averaged over the Maxwell distribution with prescribed electron temperature T_e for three values of the rotational quantum numbers $N_i=0, 2$, and 4, which are denoted, respectively, by asterisks, triangles, and circles. It can be seen that as N_i increases, the cross sections shift along the energy scale E_e to the left by the distance of the rotational excitation threshold $BN_i(N_i+1)$. In addition, for $N_i=2$ the partial cross section and the rate constant turn out to be approximately an order of magnitude larger than for $N_i=0$. It should also be noted that for $N_i=4$ at $T_e=10^2$ K in the energy region where the cross section $\sigma_{\beta 4}(E_e)$ grows (see Fig. 3), the temperature dependence of the partial rate constant $k_{\beta}(T_e, N_i)$ differs markedly from a $T_e^{-1/2}$ law.

Figure 5 plots the total cross section of reaction (22), as averaged over the initial rotational states with the Boltzmann equilibrium distribution (17), and as measured by Hus *et al.*¹⁸ Unfortunately, Hus *et al.* did not make a fine enough selection of the ion beams for the initial vibrational states and did not monitor the magnitude of the admixture of $v=1$ states. Therefore, the comparison is for illustrative purposes only and illustrates the main feature of the reaction cross section, namely, the presence of a resonance structure, which previously went unobserved. For a more detailed comparison of these dependences it is necessary to know the actual distribution function over the initial vibrational states in the

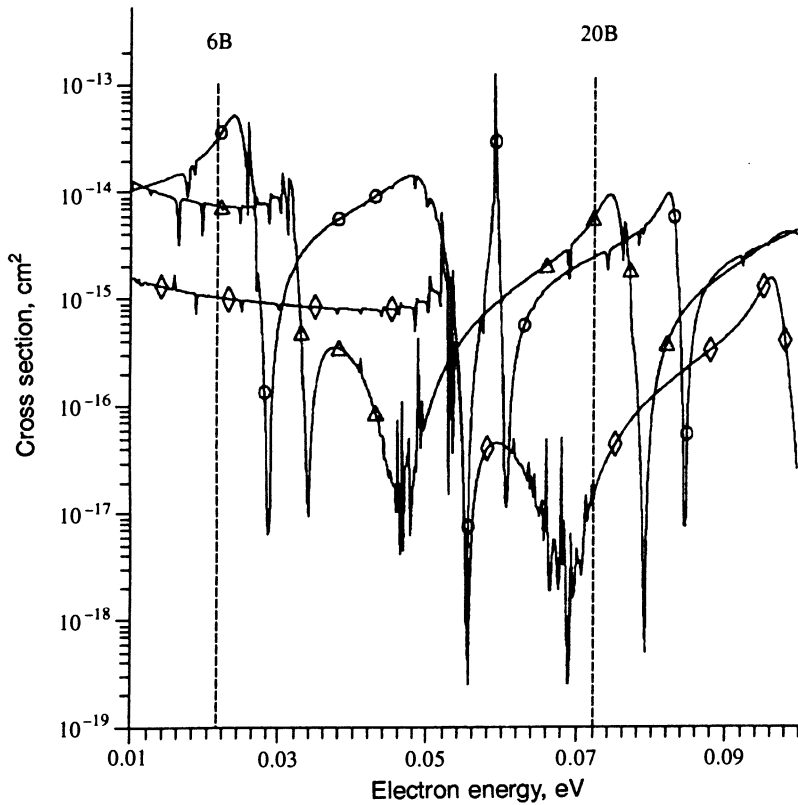


FIG. 3. Partial cross section of reaction (22) for $N_i=0$ (diamonds), 2 (triangles), and 4 (circles).

experiment¹⁸ and to include the initial vibrational state ($v=1$) in the overall scheme.

Figure 6 shows the dependence of the total rate constant of reaction (22) on the ion (T_i) and electron (T_e) temperatures, from which it follows that with increasing electron temperature, there is a smoothing out of the dependence of the rate constant on the ion temperature T_i , i.e., the initial rotational excitation has little effect on the profile of the curve. The maximum of these curves is attained at $T_i \cong 200$ K, after which there is a smooth decay, which is explained by the a feature of the behavior of the rotational partition function for the *para* form of the molecular hydrogen ions in Eq. (17), which, starting at $T_i \cong 100$ K, is proportional to T_i .¹⁴

5. CONCLUSION

In the present paper we have proposed a procedure for calculating the cross sections and rate constants of dissociative recombination reactions, which, on the one hand, takes account of the main features associated with rotational motion of molecular ions and, on the other, allows one to avoid the difficulties of direct formal solution of the multichannel equations (3)–(4). For example, in the calculation of four closed vibronic channels for the initial rotational state $N_i=4$, this requires the solution of a 26-channel problem, while using the approximate equations (12)–(14) reduces the number of channels needed to 10. The efficiency of the procedure is further enhanced by the fact that it simplifies subsequent refinements of the calculations. Indeed, if it is necessary to allow for rotational–vibrational coupling in the two vibrational channels $v=0$ and 1, Eqs. (12)–(14) should be rewritten so as to allow for channels with $v \geq 2$ in the rotationally

adiabatic approximation for $T^{(1)}$ and to include the rotational–vibrational states with $v=1$ in Eq. (12). In this case, the total number of channels taken into account will again be substantially less than necessary in an accurate calculation.

Our analysis demonstrates that in the region of low ion temperatures T_i rotational motion under equilibrium conditions does not have an appreciable effect on the temperature dependence of the rate constants of reaction (22). The partial rate constants (like the corresponding cross sections) are extremely critical for the initial rotational excitation. With increasing ion temperature T_i (beyond the limits of the tem-

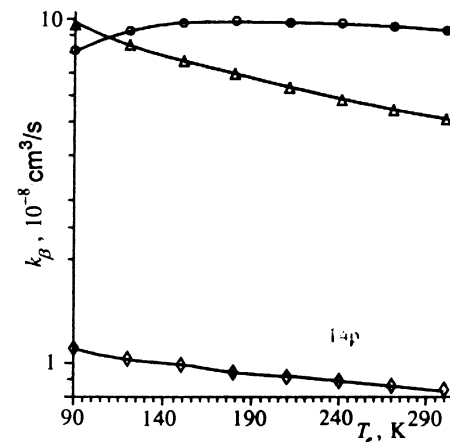


FIG. 4. Temperature dependence of the partial rate constant $k_\beta(T_e, N_i)$ of reaction (22) for $N_i=0$ (diamonds), 2 (triangles), and 4 (circles).

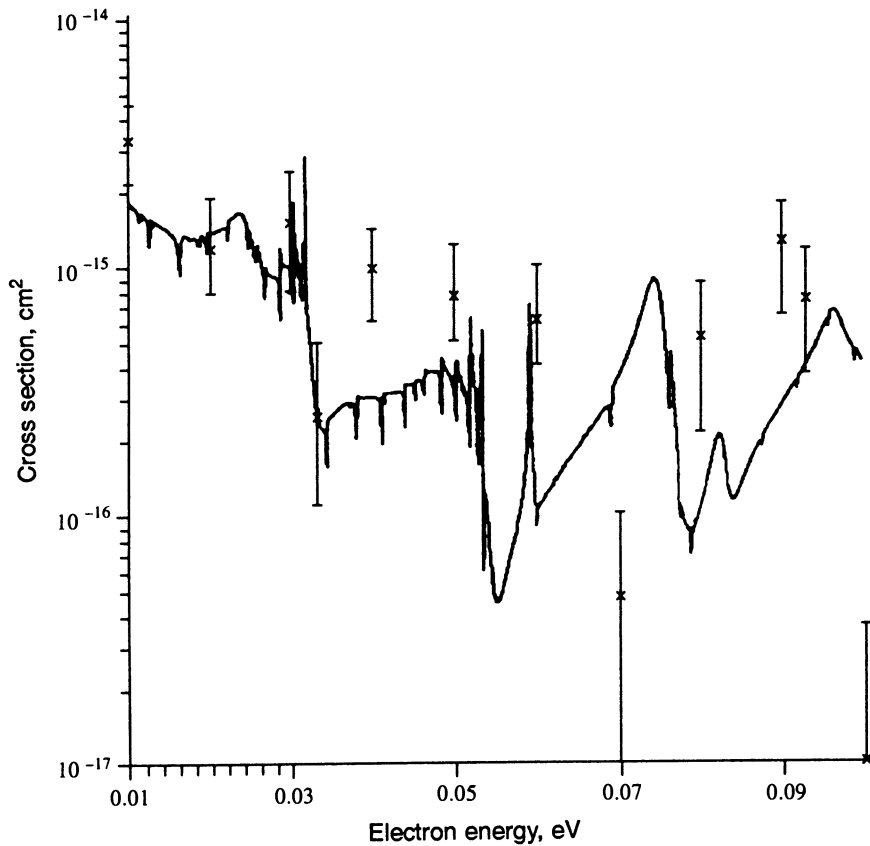


FIG. 5. Dependence of the total cross section of reaction (22) on electron energy E_e . The solid line represents the cross section averaged over initial rotational states with the Boltzmann distribution (17), asterisks represent the results of experiment.¹⁸ The vertical bars denote corresponding measurement errors.

perature interval considered here), they should grow substantially as a consequence of including additional channels in the process due to the Coriolis interaction with the dissociative configuration, in which, along with d -harmonics of the incident electrons, the p -harmonics also make an appreciable contribution. The latter is particularly important for strongly nonequilibrium conditions (e.g., behind a shock front, for intense irradiation of the system, etc.). Of course, taking them into account would require some embellishment of the calculation scheme, but such a complication is com-

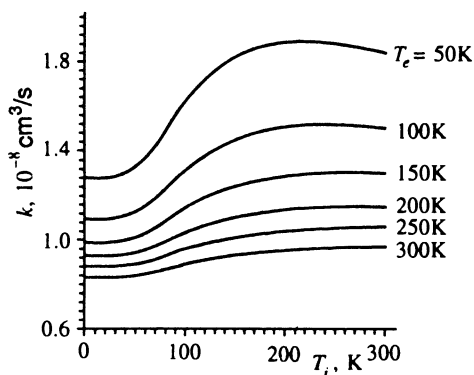


FIG. 6. Two-temperature dependence of the total rate constant of reaction (22), calculated according to the formula $k_{\beta}(T_e, T_i) = (2/\pi T_e^3)^{1/2} \times \int_0^{\infty} \sigma_{\beta}(T_i, \epsilon) \exp(-\epsilon/T_e) d\epsilon$ where σ_{β} is the averaged cross section (17) calculated on the basis of the initial data of Ref. 5.

pletely realizable within the framework of the proposed procedure.

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