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Ion-ion recombination and ion-pair formation processes in alkali-hydrogen diatomic systems

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The mutual neutralization and ion-pair-formation reactions in alkali-hydrogen diatomic systems are investigated in the low-energy region. The ionic-covalent exchange interaction in these systems at the diabatic curve crossings is calculated by the Landau-Herring method. The cross sections and reaction-rate coefficients of these reactions are calculated using the Landau-Zener theory, modified to include the underbarrier transitions and the effects of the variation of coupling interaction within the transition zone. For Cs-H system, the calculated recombination and ion-pair-formation cross sections are compared with the existing theoretical calculations and experimental data.

I. INTRODUCTION

The mutual neutralization reactions between alkali positive and hydrogen negative atomic ions are of considerable importance in low-temperature alkali-plasma and gas-laser physics. This is a consequence of the fact that at low energies these recombination reactions are characterized by very large cross sections (10^{-12}–10^{-13} cm^2) and by selective population of some excited alkali-atom final states.[1,2] On the other hand, the development of the netural injection method for heating the thermonuclear-fusion plasma in tokamaks has stimulated considerable interest for investigation of ion-pair formation reactions between alkali and hydrogen atoms.[3,4] Despite the recognized importance of the ionic-pair reactions in alkali-hydrogen systems for the above mentioned research fields, little information on their cross sections and reaction rate constants is presently available. Exceptions are the theoretical studies of Bates and Boyd[5] and Olson *et al.*,[6] and experimental investigations of Schlachter *et al.*,[7] Spiess *et al.*,[8] Alvarez *et al.*,[3] and Cisneros *et al.*[9] In Refs. 6–9 only the reactions in Cs-H(D) system were studied, whereas Bates and Boyd[5] calculated the recombination rate constants in Li-, Na-, and K-hydrogen ionic systems.

The aim of this article is to present systematic cross-section and reaction-rate-coefficient data for ion-ion recombination and ion-pair formation reactions in alkali-hydrogen systems in a relatively wide energy range. Since the reaction dynamics in these systems is controlled by the long-range configuration interaction between the ionic and covalent molecular states, it is of crucial importance for the cross-section calculations to determine this interaction in the region of strong nonadiabatic coupling as exactly as possible. In this work (Sec. II) the ionic-covalent-coupling interaction is calculated using the Landau-Herring method,[10,11] which provides asymptotically correct results.

Another characteristic feature of alkali-hydrogen diatomic systems is that the ionic state [$M^+(^1S_0)$ + $H^-(^1S_0)$; M denotes the alkali atom] interacts with several covalent configurations [$M(^2L_j)$ + $H(^2S_{1/2})$] so that a multi-curve-crossing collisional problem arises. Consequently, in the case of the ion-ion recombination, several open channels are available for the reaction and one has to solve a multichannel problem. Fortunately, the curve-crossing regions in alkali-hydrogen systems are well separated from one another and the interference effects can be neglected. Thus, the probability for a particular reaction can be determined by using the standard procedure of accumulation of single-crossing probabilities.[11,12]

A final introductory remark concerns the method adopted in the present paper for calculating the reaction cross sections (Sec. III). We have used an extended Landau-Zener-type theory, parametrized to include the effects of both the peripheral (underbarrier) transitions and the exponential variation with the internuclear distance of the configuration (exchange) interaction within the region of strong nonadiabatic coupling.[13] Using such a method the ionic recombination and the ion-pair formation cross-section calculations (Sec. IV) are performed in the energy range of 10^{-2} eV to 1–10 keV.

Atomic units will be used in this work, unless otherwise indicated.

II. EXCHANGE INTERACTION BETWEEN IONIC AND COVALENT STATES IN ALKALI-HYDROGEN DIATOMIC SYSTEMS

The ionic-covalent configuration-coupling interaction in molecular systems has attracted recently much theoretical interest[10,14-19] in connection with the dominant role that this interaction plays in many nonadiabatic energy-transfer processes, collision-dynamics problems, etc.[11] The configuration-coupling (or exchange) interaction $\Delta(R)$, associated with a pseudocrossing of two diabatic potentials, is directly related to the adiabatic energy splitting $\Delta U(R)$ at the diabatic crossing point $R=R_x$ by[14-16]

$$\Delta U(R_x)=\frac{\Delta(R_x)}{1-S^2}\,,\quad \Delta(R)=2\left|H_{12}-SH_{11}\right|\,, \tag{1}$$

where $H_{kj}(k,j=1,2)$ are the matrix elements of the electronic Hamiltonian in the diabatic molecular basis and S is the overlap integral. It should be admitted that for not too distant pseudocrossings (S not too small), the energy splitting $\Delta U(R_x)$ may be appreciably larger than $\Delta(R_x)$. In alkali-hydrogen diatomic systems such a situation is met for the crossings of the ionic potential with the covalent ones, corresponding to the ground and first-excited alkali-atom states.[16] Moreover, the relation, Eq. (1), between $\Delta(R)$ and $\Delta U(R)$ holds strictly at the diabatic crossing point R_x. Since for $R\neq R_x$ the functions $\Delta(R)$ and $\Delta U(R)$ behave quite differently, the use of relation, Eq. (1), to determine $\Delta(R_x)$ from other data on $\Delta U(R)$ in the pseudocrossing region crucially depends on the proper determination of R_x.

Some controversy has recently appeared in the literature (cf. Refs. 18 and 19) concerning the role of the ion-induced dipole forces in the ionic diabatic states, and consequently, the determination of diabatic crossing point R_x. The two customary approximations of the diabatic ion potentials $V_{\text{ion}}(R)$

$$V_{\text{ion}}^{c}(R)=\Delta\epsilon-1/R \tag{2a}$$

and

$$V_{\text{ion}}^{c,p}(R)=\Delta\epsilon-1/R-\frac{1}{2}\,\frac{(\alpha_{+}+\alpha_{-})}{R^4}\,, \tag{2b}$$

(with $\Delta\epsilon$ being the difference between the electron binding energies in the atomic and negative ion states, and $\alpha_{\pm}$ being the positive and negative ion polarizabilities) give considerably different values for the lower crossing points R_x, as determined from the equation

$$V_{\text{ion}}(R_x)=V_{\text{cov}}(R_x)\,, \tag{3}$$

where $V_{\text{cov}}(R)$ is the diabatic potential of the corresponding covalent state.

Adelman and Herschbach[19] have pointed out that for H(1s)+H(2s,2p), and H(1s)+Li(2s,2p) systems, the approximation Eq. (2a) gives a much better agreement of $V_{\text{ion}}(R)$ with the extensive variational adiabatic energy calculations[20,21] at distances far from the pseudocrossing region, than the approximation Eq. (2b). However, the value of $\Delta U(R_x^c)$ for H-Li(2s,2p) system, taken as difference of the corresponding adiabatic energies[21] at $R_x=R_x^c$ [R_x^c calculated from Eqs. (2a)–(3)], is considerably larger than the value $\Delta U(R_x^{c,p})$. On its turn, $\Delta U(R_x^{c,p})$ is very close to the minimum value of $\Delta U(R)$. Similar is the situation in H-Na and H-K systems.[17,18] Since the configurational mixing is expected to be most pronounced at the minimum of $\Delta U(R)$, it follows that for purposes of nonadiabatic transition-probability calculations the choice of $R_x^{c,p}$ is most appropriate as a distance where the electron-exchange effects are strongest. For higher covalent states, of course, there is no such uncertainty in the choice of R_x, since the polarization term in Eq. (2b) is negligibly small. Moreover, for these states, the overlap integral S with the ionic state is also small and the quantities $\Delta(R_x)$ and $\Delta U(R_x)$ are essentially equal. (In what follows, by R_x we shall mean $R_x^{c,p}$.)

Most of the recent calculations concerning ionic-covalent configuration interaction in alkali-hydrogen systems were performed for $\Delta U(R_x)$[5,16-19] using the LCAO method. For Li-H, Na-H, and Cs-H systems, the adiabatic energies of low-lying molecular states have been calculated, respectively, by Docken and Hinze,[21] Sachs *et al.*,[22] and Olson *et al.*,[6] using the variational method. From these calculations one can estimate the value of the adiabatic energy splitting $\Delta U(R_x)$. However, as the above discussion illustrates, direct derivation of the exchange interaction $\Delta(R_x)$ from these data is not possible. [Note that only $\Delta(R_x)\simeq 2H_{12}$ is the quantity relevant for nonadiabatic transition probability calculations.] Moreover, as argued in Refs. 10 and 11, the LCAO and variational methods suffer from some substantial drawbacks in determining the exchange interaction at large internuclear distances. Therefore, in calculating the exchange interaction between ionic and covalent states in alkali-hydrogen systems it is more appropriate to apply the method developed in Refs. 10, 11, 14, and 15. This nonperturbative method, inspired by the work of Landau and Herring (for details see Ref. 11), involves an integration of the electron-exchange current over a surface separating the influence of atomic-core potentials. General expressions for the ionic-covalent exchange interaction at the crossing point R_x obtained by this method are given elsewhere.[10,11]

For the case of alkali-hydrogen diatomic systems the expression for $\Delta(R_x)$ is given by the following formula:

$$\Delta(R_x)=N_2\left(\frac{(2l+1)(l+m)!}{(l-m)!}\right)^{1/2}\varphi_{\text{at}}(R_x)\,. \tag{4}$$

Here N_2 is a "normalization" constant in the asymptotic radial wave function of the hydrogen negative ion, $\varphi_{\rm at}$ is the radial wave function of the electron bound on the alkali atom in a state characterized by a binding energy $-\frac{1}{2}\gamma^2$, angular momentum l, and its projection m on the internuclear axis. The value of N_2 is determined[22] by matching the electron-density distribution obtained by the asymptotic radial wave function

$$\varphi^{(-)}(r)=N_2 r^{-1}e^{-\beta r}, \quad \tfrac{1}{2}\beta^2=EA(X) , \qquad (5)$$

with that calculated using the three-parameter variational wave function of Chandrasekhar. The obtained value for N_2 is $N_2=1.1532$. Since the crossing points for alkali-hydrogen systems are at large enough distances, one can use for $\varphi_{\rm at}(r)$ its asymptotic form

$$\varphi_{\rm at}(r)=N_1 r^{1/\gamma\,-1}e^{-\gamma r} , \qquad (6)$$

where the constant N_1 has analogous meaning as N_2. For the ground-state alkali atoms N_1 has the following values[23]: 0.765(Li), 0.751(Na), 0.533(K), 0.491(Rb), and 0.416(Cs). For the excited alkali-atom states one can use for N_1 its Coulomb value

$$N_1^{\rm Coul}=\gamma(2\gamma)^{1/\gamma}\left[\Gamma\left(\frac{1}{\gamma}+l+1\right)\Gamma\left(\frac{1}{\gamma}-l\right)\right]^{-1/2} . \qquad (7)$$

We note that in the work of Grice and Herschbach[16] and Adelman and Herschbach[19] essentially the same asymptotic forms for $\varphi^-(r)$ and $\varphi_{\rm at}(r)$ were used [as in expressions (5) and (6)], except for other choices of the constants N_1 and N_2.

The results of our calculations on $\Delta(R_x)$ for alkali-hydrides are given in Table I. The crossing points R_x are determined with inclusion of the polarization term in the ionic potential. In order to make a closer comparison with the results of other theoretical calculations on configuration interaction in alkali hydrides, we have calculated the overlap integral S with the above asymptotic functions and then used relation (1) to obtain $\Delta U(R_x)$. These results are also given in Table I. The comparison of the obtained values for $\Delta U(R_x)$ is made with the corresponding data due to Bates and Boyd[5] (BB), Numrich and Truhlar[17,18] (NT) (the values in parentheses in the NT column of Table I are taken from Ref. 18), Adelman and Herschbach[19] (AH), and Grice and Herschbach[16] (GH). In Table I are also listed the values of $\Delta U(R_x)$ estimated from the variational adiabatic energy calculations, where available[6,21,22] (the

TABLE I. Curve-crossing parameters for alkali-hydrogen systems. BB, AH, NT, and GH are the results of Refs. 5, 19, 17 (and 18), and 16, respectively. The results in MCSCF column are taken from Refs. 21 (DH), 22 (SHS), and 6 (OSB).

						$\Delta U(R_X)$ (eV)				
H-M^+	State of M^+	R_X (a_0)	$\Delta(R_x)$ (eV)	S	$\frac{\Delta(R_x)}{1-S^2}$	BB	AH	NT	MCSCF	GH
H-Li$^+$	2*s*	7.40	0.737	0.452	0.926	0.61	1.35		1.20(DH)	1.69
	2*p*	10.61	0.509	0.260	0.546	0.43	0.71			
	3*s*	21.52	5.41(−2)[a]	0.115	5.48(−2)	5.36(−2)	6.24(−2)			
	3*p*	33.8	7.70(−3)	0.1	7.70(−3)	9.14(−3)	1.02(−2)			
	3*d*	35.8	6.28(−3)	0.1	6.28(−3)	4.53(−3)	5.02(−3)			
H-Na$^+$	3*s*	7.66	0.760	0.475	0.982	0.59	1.36	0.57 (1.05)	1.22 (SHS)	1.54
	3*p*	12.6	0.397	0.239	0.421	0.32	0.46	0.29		
	4*s*	22.8	4.35(−2)	0.1	4.35(−2)	4.35(−2)	5.05(−2)	7.88(−2)		
	3*d*	35.4	3.35(−3)	0.1	3.35(−3)	4.86(−3)	5.40(−3)			
	4*p*	43.0	1.04(−3)	0.1	1.04(−3)	1.87(−3)	2.01(−3)			
H-K$^+$	4*s*	8.86	0.599	0.417	0.725	0.50	0.94	0.49 (0.66)		1.06
	4*p*	14.3	0.310	0.216	0.325	0.24	0.33	0.23 (0.24)		
	5*s*	27.8	1.85(−2)	0.1	1.85(−2)	1.90(−2)	2.15(−2)	3.12(−3)		
	5*p*	51.9	2.99(−4)	0.1	2.99(−4)	3.81(−4)	3.86(−4)			
H-Rb$^+$	5*s*	9.11	0.585	0.410	0.703		0.88			0.96
	5*p*	15.66	0.225	0.179	0.232		0.27			
	6*s*	29.4	1.39(−2)	0.1	1.39(−2)		1.66(−2)			
	6*p*	57.0	1.10(−4)	0.1	1.10(−4)		1.56(−4)			
H-Cs$^+$	6*s*	9.74	0.512	0.387	0.602		0.75		0.789(OSB)	0.80
	6*p*	16.2	0.219	0.179	0.226		0.23		0.305(OSB)	
	7*s*	32.3	8.30(−3)	0.1	8.30(−3)		9.93(−3)			
	7*p*	63.2	3.19(−5)	0.1	3.19(−5)		4.97(−5)			

[a] (−X) means 10^{-x}.

MCSCF column). The values of $\Delta U(R_x)$, calculated by the present asymptotic method, are smaller by about 20% with respect to MCSCF values. It is interesting to note that OSB (Ref. 6) value for $\Delta U(R_x)$ is closer to the GH value than to the AH value, assumed to be more accurate.[19] We have also calculated $\Delta U(R_x)$ for H-H$^+$ ($n=2$) with the asymptotic Landau-Herring method and obtained a value of 0.688 eV. The energy splitting of the adiabatic RKR potential curves at $R_x = 11.08$ is 0.69 eV, as estimated by Adelman and Herschbach.[19] The AH value for this case is 0.80 eV.[19]

III. METHOD FOR CALCULATING THE CROSS SECTIONS

In calculating the reaction cross sections for ion-ion recombination and ion-pair formation in alkali-hydrogen systems we shall utilize an improved Landau-Zener (LZ) theory, based on the work by Ovchinnikova.[13] The conventional formulas for cross-section calculations in the LZ approximation are[11,24]

$$Q_{\mathrm{LZ}} = 4\pi g R_x^2 (1 + \Delta\epsilon/E) F_3(\lambda) \ , \tag{8}$$

$$F_3(\lambda) = \int_1^\infty e^{-\lambda x}(1 - e^{-\lambda x}) x^{-3} dx \ , \tag{9}$$

$$\lambda = \tfrac{1}{2}\pi(\tfrac{1}{2}\mu)^{1/2}[R_x \Delta(R_x)]^2/(E + \Delta\epsilon)^{1/2} \ , \tag{10}$$

where $\Delta\epsilon$ ($\simeq R_x^{-1}$) is the reaction exothermicity, $E = \frac{1}{2}\mu v^2$ is the relative collision energy, and g is a statistical factor.[12]

It is presently well recognized that the major deficiencies of the LZ approximation come from the small width of the transition zone (the region of strong nonadiabatic coupling) and the lack of variation of the coupling interaction with internuclear distance within the transition zone. These aspects of the collision dynamics are not included in the LZ model. In a recent paper, Ovchinnikova[13] has systematically investigated the influence of the above mentioned dynamical parameters on the magnitude and energy dependence of the reaction cross section. Assuming an exponential variation of the nonadiabatic coupling $\Delta(R) = \Delta(R_x)\exp(-\gamma|R - R_x|)$ (for the ionic-covalent case this is a correct representation) and introducing two parameters

$$A = (2/\pi)(R_x/\delta R_x)^{1/2} \tag{11}$$

and

$$\nu = 2\gamma\delta R_x \ . \tag{12}$$

Ovchinnikova solved numerically the two-state coupled equations for a set of A and ν values. In Eqs. (11) and (12), δR_x is the half width of the transition zone and for a distant ionic-covalent curve crossing is $\delta R_x \simeq \frac{1}{2}R_x^2 \Delta(R_x)$. It was shown that the parameter A significantly affects the cross-section maximum (with very little influence on its position), whereas the parameter ν introduces a shift of the cross section towards the lower energies. For $A \to \infty$ ($\delta R_x \to 0$) and $\nu = 0$ [$\Delta(R) = \mathrm{const}$] the LZ model result is obtained. The effect of the parameter A on the cross section maximum can be parametrized as

$$Q^{\max} = (1 + 0.924 A^{-2})^2 Q_{\mathrm{LZ}}^{\max} \ . \tag{13}$$

In the adiabatic energy region ($v \ll 1$), the parameter ν can be incorporated in the function $F_3(\lambda)$ of Eq. (8) replacing λ by λ_1, where[13]

$$\lambda_1 = \lambda e^{-0.77\nu} \ . \tag{14}$$

It is important to note that parameter ν affects directly the nonadiabatic transition probability per unit passage of the transition zone $p = e^{-\lambda_1/v}$. Therefore, in a multi-curve-crossing situation the effects of parameters ν_i, defined for each curve-crossing i, are separable. The reaction channel probability P_j can be constructed by the mentioned accumulation procedure of single-crossing probabilities p_i in the usual way.[11,12] On the other hand, since in calculating a given reaction channel cross section Q_j the integration of P_j over the impart parameters ρ is carried out up to the corresponding curve-crossing distance R_{xj}, it is obvious that only the peripheral collisions with $\rho \sim R_{xj}$ contribute significantly to the underbarrier (tunneling) transitions, involved in that particular reaction channel. This means that in calculating a cross section Q_j for a given channel, only the corresponding parameter A_j is involved. The inclusion of the effects of parameter A_j on the cross section Q_j (for a given value of the collision velocity) can be achieved by applying an interpolation procedure to the numerically computed cross sections[13] for a set of A values. This procedure allows one to obtain Q_j with an accuracy of about 10%. The total cross section can be obtained by summing the cross sections Q_j.

IV. IONIC RECOMBINATION AND ION-PAIR FORMATION CROSS-SECTION CALCULATIONS FOR ALKALI-HYDROGEN SYSTEMS

The ion-ion recombination and ion-pair formation reaction in alkali-hydrogen systems are not properly time-reversed processes, due to the fact that ionic recombination in these systems is a multichannel reaction. We shall, therefore, consider these two classes of reactions separately.

A. Ionic recombination

The reaction channels in ion-ion recombination

$$M^+ + H^- \to M(i) + H \ , \tag{15}$$

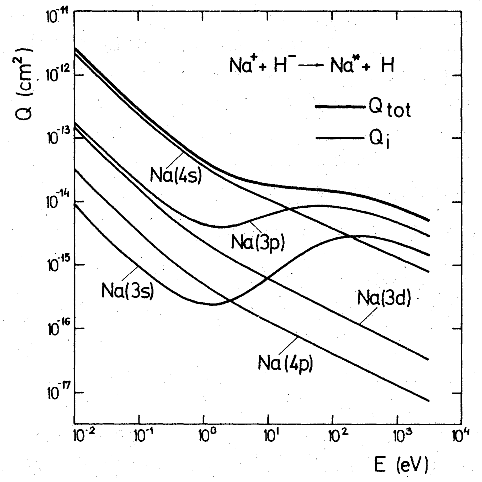

FIG. 1. Total and partial reaction channel cross sections for Na^+-H^- recombination.

which significantly contribute to the total cross section in the energy region from 10^{-2} eV to a few keV, are those which lead to formation of the alkali product atom in the states listed in Table I. Thus, for the Li^+, Na^+-H^- ionic pairs we have five significant reaction channels, whereas for each of the other ionic pairs we have four such channels. For each of these channels we have constructed the corresponding channel probability P_j and the reaction channel cross section Q_j have been calculated by the method described in Sec. IV. Considerable A and ν corrections in the cross sections are found only in the first two (low-lying product state) channels for each reaction. It is found that the total recombination cross sections for all reactions have a broad maximum around 100 eV and that dominant contribution to the cross section in this energy range gives the reaction channel leading to formation of the product alkali atom in its first (np) excited state. At energies below 1 eV, dominant contribution in the total cross sections comes from the reaction channel producing alkali atoms in the $(n+1)s$ excited state, where n is the principal quantum number of the alkali atom ground state. The situation is illustrated in Figs. 1 and 2, where the partial and total cross sections for Na^+-H^- and Cs^+-H^- recombination reactions are given. The dashed curve in Fig. 2 represents the total Cs^+-H^- recombination cross section, calculated by Olson *et al.*[6] by numerical integration of the corresponding semiclassical coupled equations. Only the Cs(6s)-H and Cs(6p)-H covalent states were included in these calculations, for which *ab initio* potential-energy curves and coupling matrix elements (both radial and rotational) were generated. As seen from Fig. 2, this approximation of the many-channel problem is justified in the energy region investigated by Olson *et al.*,[6] but not for energies below ~ 100 eV.

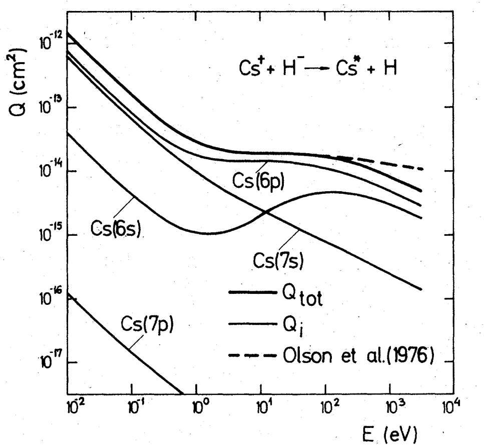

FIG. 2. Total and partial reaction channel cross sections for Cs^+-H^- recombination. Dashed curve represents the results of Olson *et al.* (Ref. 6).

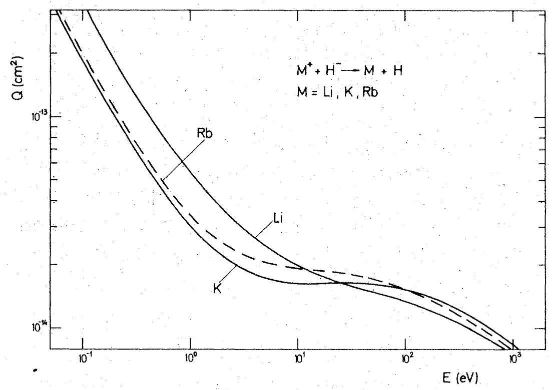

FIG. 3. Total cross sections for Li^-, K^-, and Rb^+-H^- recombination.

For Li^+, K^+, Rb^+-H^- pairs, the reaction channel cross sections Q_j have similar behavior as in

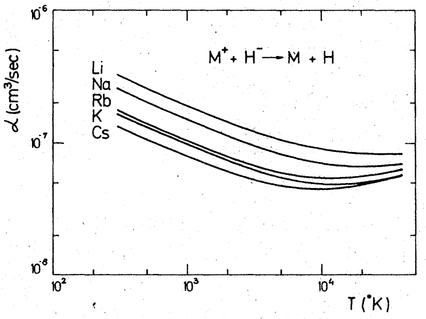

FIG. 4. Reaction-rate coefficient for alkali-hydrogen ionic recombination.

the Na^+-H^- or Cs^+-H^- case. The total recombination cross sections for these pairs are given in Fig. 3.

We have also calculated the total recombination rate coefficients $\alpha = \langle vQ \rangle$ for all alkali-hydrogen ionic pairs in the temperature range from 300 to 5×10^4 °K. The results are presented in Fig. 4. As expected, the ion-ion recombination rate coefficients are fairly large, having an order of magnitude of $\sim 10^{-7}$ cm^3/sec in the entire temperature region investigated.

B. Ion-pair formation

When the interacting atoms are initially in their ground states, the ion-pair formation reactions have only one exit channel. In hydrogen–alkali-atom systems a number of alkali-atom excitation channels are open due to the existence of several ionic-covalent curve crossings, when the collision energy is higher than the ion-pair formation threshold $(E_{\mathrm{th}} = \Delta\epsilon_0' \simeq R_{x_0}^{-1})$. The effect of these channels on the ion-pair formation cross section is to lower its magnitude with respect to the case when no intermediate excitation channels exist. Within the corrected LZ method, the presence of the intermediate curve crossings has a significant influence on the ion-pair formation cross section through the dynamical parameters ν_i $(i=0,1,\ldots)$ and A_0 ("0" designates the ionic ground-state covalent curve crossing). Since the ion-pair formation threshold in alkali-hydrogen systems is of about a few eV's, only the first three curve crossing have a considerable ν-correction effect to the cross section.

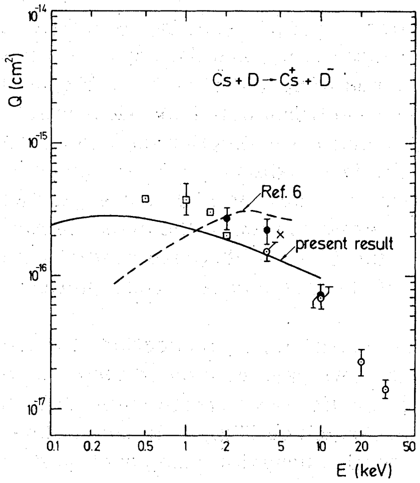

FIG. 6. Ion-pair formation in Cs + D: □ from Ref. 9; ● and ○ from Ref. 7; × from Ref. 8. Theory: full curve—present calculations; dashed curve—Olson *et al.* (Ref. 6).

The cross-section calculations are performed by the modified LZ method of Sec. III and the results are given in Fig. 5. The results are presented on a deuterium energy scale. For all reactions the cross-section maxima are fairly broad and lie within the interval between 100 and 1000 eV. The largest among them is the cross section for Cs^+-D^- ion-pair formation. For this reaction experimental cross-section data also exist.[7-9] Figure 6 gives a comparison of our theoretical calculations for Cs^+-D^- ion-pair formation (the full curve) with the experimental data and the close-coupled calculations of Olson *et al.*[6] (the dashed curve). The results of Olson *et al.*[6] have been reduced by a statistical weigh factor of $\frac{1}{4}$ to incorporate the fact that only the singlet molecular channel can lead to $\mathrm{H}^-(^1S) + M^+(^1S)$ products. The squares in Fig. 6 represent the data of Cisneras *et al.*,[9] the solid and open circles are the

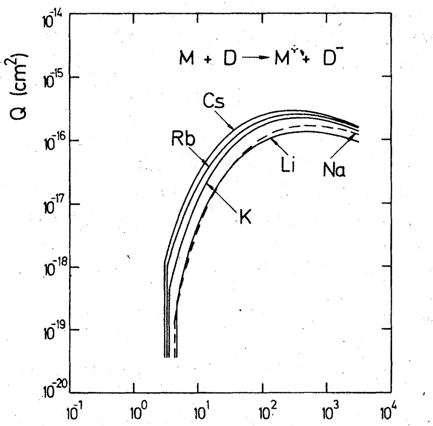

FIG. 5. Ion-pair formation cross sections in alkali-deuterium collisions.

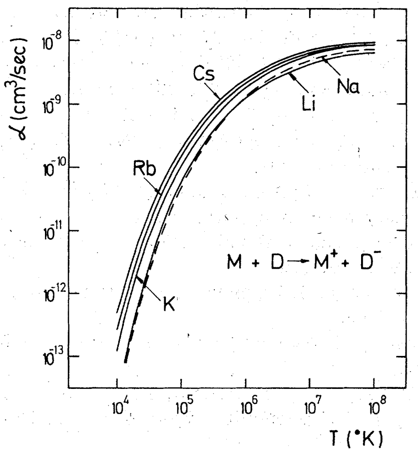

FIG. 7. Reaction-rate coefficient for ion-pair formation in alkali-deuterium systems.

data of Schlachter *et al.*[7] (for Cs + H and Cs + D systems, respectively) and the cross is a measured value due to Spiess *et al.*[8] As Fig. 6 shows, the agreement between our theoretical results and the experimental cross-section data can be considered as quite satisfactory. The extrapolation of the theoretical curve to higher energies would lead to an overestimation of the cross section, because all the LZ-type theories predict an incorrect $E^{-1/2}$ behavior of the cross section at high energies.

Using the theoretical cross sections for ion-pair formation we have calculated also the corresponding reaction-rate coefficients. The results are presented on Fig. 7. In accordance with the cross-section behavior, the reaction rate coefficients increase with temperature in the whole temperature range investigated.

V. CONCLUDING REMARKS

In the present paper we have considered theoretically the ion-ion recombination and ion-pair formation reactions in alkali-hydrogen systems. The method which has been applied for calculating the exchange interaction at the crossing points of diabatic ionic and covalent potentials assures accurate results for this quantity. The method for calculating the reaction cross sections, however, is not so accurate since it involves an interpolation procedure (to include the effects of parameter A), and for energies appreciably beyond the cross-section maximum the effects of the parameters ν_i are not properly included. The high-energy behavior of the inelastic cross section cannot, however, be correctly described in any LZ-type approach.

A final remark should be added concerning the role of rotational coupling on the processes investigated in the present paper. Since in the ion-ion recombination the main contribution to the total cross section for energies below the cross-section peak comes from the $(n+1)s$ covalent channel, one concludes that in this energy region the radial Σ-Σ coupling is the dominant transition mechanism. For energies above the cross-section peak important contribution to the total ion-ion recombination, gives also the np covalent channel. The partial recombination cross section Q_{np} of this channel might be significantly affected by rotationally induced transitions. However, one can expect that their contribution to Q_{np} is not larger than the uncertainty introduced by the nonproper account of the ν corrections in this energy region.

The ion-pair formation total cross sections is mainly determined by the radial coupling of the ionic and ground-state covalent states in the whole energy region investigated. Therefore it is not expected that rotational transitions, that might populate the intermediate p-covalent states, will change considerably the total ion-pair formation cross section.

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