Cross section for the mutual neutralization reaction $H_2^+ + H^-$, calculated in a multiple-crossing Landau-Zener approximation

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A multiple-crossing Landau-Zener model is applied to calculate mutual neutralization cross sections for the reactions $H^+ + H^-$ and $H_2^+ + H^-$ as a function of the principal quantum number n of the resulting H atom. For low-energy collisions ($E \leq 10$ eV), the total cross section for $H_2^+ + H^-$ is a factor of 8 larger than the one for $H^+ + H^-$. The cross section for the process including H_2^+, in which the H atom is excited to the quantum state n ($2 \leq n \leq 8$), has a nonmonotonic behavior as a function of the atomic quantum state. Comparison of the calculated results with newly received experimental data is made.

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I. INTRODUCTION

The reaction of mutual neutralization of positive and negative ions $A^+ + B^- \rightarrow A + B + \Delta E$ occurs in any ionized gas in which negative ions are formed. Practical interest in ion-ion mutual neutralization originates from its importance in the removal of charge of the Earth's ionosphere, in high energy physics, in fusion plasmas, and in plasma chemistry. Theoretically, for this type of reaction the cross section calculations based on curve-crossing models are relatively straightforward.

Many of the published theoretical studies have been based on some form of a Landau-Zener curve-crossing concept [1,2]. It is, of course, an approximate method and the limitations to its accuracy have been pointed out, especially for the high energy collision range ($E \geq 10$ eV), where the pure Landau-Zener approximation is not valid [3–5]. For the high energy range an agreement between the experimental data and various approximate curve-crossing theories as well as more sophisticated theories, based on a quantum mechanical approach, remained elusive even for the simplest (H^+-H^-) system until revised measurements [6–8] agreed with detailed close-coupling quantum mechanical calculations [9,10], two-electron calculations [11], and two molecular orbital calculations [12].

Most of the experiments and calculations have been performed for the simplest reaction of neutralization between H^+ and H^- since it provides the obvious starting point from which both experiment and theory can be developed. Some experiments and simple calculations have been done for more complex situations, such as atomic ion-ion reactions without the participation of hydrogen and reactions including molecular ions. The latter case, including molecular ions, is a more complicated problem from a theoretical point of view since additionally one has to take into account the molecular internal degrees of freedom. Systems with rotational and vibrational degrees of freedom have to be treated in a multiple curve-crossing approximation.

The calculations presented in this paper were stimulated by experiment where an inversion of the atomic hydrogen excited level populations in a magnetized expanding recombining hydrogen plasma has been observed [13]. We have attempted to explain the experimental data with an atomic collisional-radiative model. It was illustrated that these models cannot explain the large population densities for high excited states [13]. A possible explanation for the large densities are the mutual neutralization reactions [3,14]

$$H^+ + H^- \rightarrow H + H_n^*, \quad n = 2,3,\ldots \tag{1}$$

and

$$H_2^{+(v,J)} + H^- \rightarrow H_2^{v',J'} + H_n^*, \quad n = 2,3,\ldots \tag{2}$$

with the predominant selective excitation of some atomic quantum states.

A single-crossing Landau-Zener model for mutual recombination reactions was applied to reaction Eq. (1) by Bates and Lewis [3] and Olson, Peterson, and Moseley [14]. The result were in good agreement with experimental data, including the low-energy region. However, for reaction (2) neither calculations nor any experimental data exist for the low-energy range. In this paper, a multiple-crossing Landau-Zener model is used to calculate cross sections for these reactions as a function of the principal quantum number n.

II. THEORY

For mutual neutralization reactions such as, for example, Eqs. (1) and (2), cross sections can be calculated using Landau-Zener theory [1,2,15]. These cross sections depend on single or multiple potential energy crossings. The probability of a transition when two curves cross is [14]

$$p = \exp\left[\frac{-2v_x}{v_l}\right], \tag{3}$$

where v_l, the radial velocity at the crossing point R_x, is given by

$$v_l = v\left[1 + (R_x E)^{-1} - \left[\frac{b}{R_x}\right]^2\right]^{1/2} \tag{4}$$

and

$$v_x = pR_x^2 H_{if}^2(R_x) , \tag{5}$$

with H_{if} the coupling matrix element. The cross section is obtained through

$$Q = 2\pi \int_0^{b_x} bP(b)db , \tag{6}$$

with b the impact parameter and P the total probability of a transition. The integral must be calculated up to b_x, where b_x is given by

$$b_x = R_x[1+(R_x E)^{-1}]^{1/2} . \tag{7}$$

In our model we have used an expression for the coupling matrix element derived by Smirnov [4]. This expression was derived for mutual recombination reactions such as Eq. (1), in which two atoms occur. It includes the wave functions of the electron in H^- and the excited electron in H_n*. As a first approximation we used this expression for the mutual recombination reaction Eq. (2) as well. Note that this is not straightforward since we assume that the intermediate H_3 complex can decay in channels in which, besides the transfer of an electron from H^- to H_2^+, the remaining H is excited. The expression given by Smirnov in atomic units is [16]

$$H_{if}^2 = \gamma\alpha^2 A^2 (2R_x^2)^{-1}(4/e)^{1/\gamma}(\alpha R_x)^{2/\alpha}(2l+1) \times \exp^{-(\alpha+\gamma)R_x} \Gamma^{-1}(1/\alpha+l+1)\Gamma^{-1}(1/\alpha-l) . \tag{8}$$

In this expression, $\gamma^2/2$ is the binding energy of the negative ion, $\alpha^2/2$ is the binding energy of the excited electron, and l is its angular momentum quantum number. $A^2 = -2.65$ for H^-.

Strictly speaking, the Landau-Zener approximation can only be applied to transitions involving zero angular momentum because it is an approximation to the equations describing only two coupled channels. In general, however, the angular momentum is nonzero and there will be a strong coupling between the magnetic sublevels. Nevertheless the aim of our calculations is to determine the integral cross section of reactions (1) and (2), i.e., only the cross sections as a function of the principal quantum number n, averaged over the various magnetic sublevels. Therefore, in practice, by using potential (8), we perform the calculations for each of the magnetic sublevels l of a particular quantum state n and average the cross sections over the various l. Since the strong coupling between the magnetic sublevels mainly leads to the redistribution of the populations among the various l, we assume that the procedure of averaging provides us with an accurate approximation for the integral cross section.

In the single-crossing case, the total probability of a transition is $P = 2p(1-p)$ [15], as the transition can take place at both passages of the crossing point. In the multiple-crossing case, the total probability changes on account of the influence of other crossings. The probability of a transition in the case of three crossings, leading to reaction product 1 (see Fig. 1), depends on b_x [3]:

$$p_{1a} = 2(1-p_a)p_a, \quad b_x^b < b < b_x^a \tag{9}$$

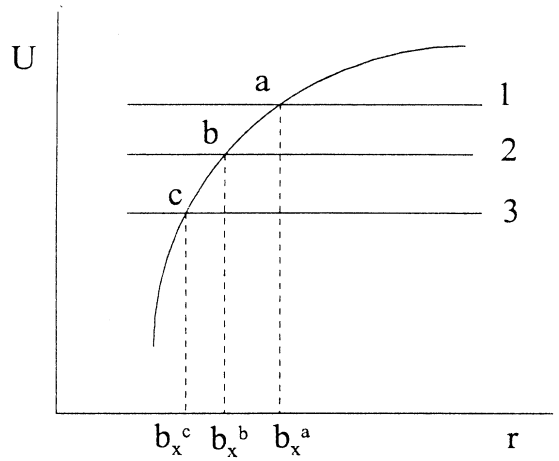

FIG. 1. Potential energy curve scheme for mutual neutralization reactions. The curved line is the potential energy curve of the reaction's input channel ($H^+ + H^-$ or $H_2^+ + H^-$). The straight lines are possible output channels, in which the resulting H atom is in different quantum states. Three crossings have been included.

$$p_{1b} = (1-p_a)p_a + (1-p_a)p_a p_b^2 + (1-p_a)p_a(1-p_b)^2 , \quad b_x^c < b < b_x^b \tag{10}$$

$$p_{1c} = (1-p_a)p_a + (1-p_a)p_a(1-p_b)^2 + (1-p_a)p_a p_b^2 p_c^2 + (1-p_a)p_a p_b^2(1-p_c)^2 , \quad 0 < b < b_x^c \tag{11}$$

with p_a the probability of an adiabatic transition, calculated from Eq. (3). The cross section is

$$Q = 2\pi \int_0^{b_x^c} bp_{1c}db + 2\pi \int_{b_x^c}^{b_x^b} bp_{1b}db + 2\pi \int_{b_x^b}^{b_x^a} bp_{1a}db , \tag{12}$$

in analogy with Eq. (6). Equations (3)–(12) have been used to calculated cross sections for the mutual neutralization reactions (1) and (2). Three ($n=2$–4) and seven ($n=2$–8) crossings have been used, respectively. The equations have been implemented in MAPLE V [17].

III. RESULTS AND DISCUSSION

A. $H^+ + H^-$

Applying the discussed model to the mutual recombination reaction Eq. (1) ($H^+ + H^-$) leads to the values for the total cross sections, presented in Fig. 2. Only the atomic excited state with $n=3$ is populated with a large cross section (see also [3,14]). For $n=2$ and 4, the cross sections are negligibly small. In these calculations the coupling matrix elements were averaged over all angular momentum quantum numbers. According to experiments by Moseley, Aberth, and Peterson [18] (see Fig. 2), the total cross section for mutual recombination of Eq. (1) is $\simeq 10^{-17}$ m^2. The calculated values agrees within a factor of 2 with these experiments. Agreement with calculations of Bates and Lewis [3] and Olson, Peterson, and Moseley [14] is much better.

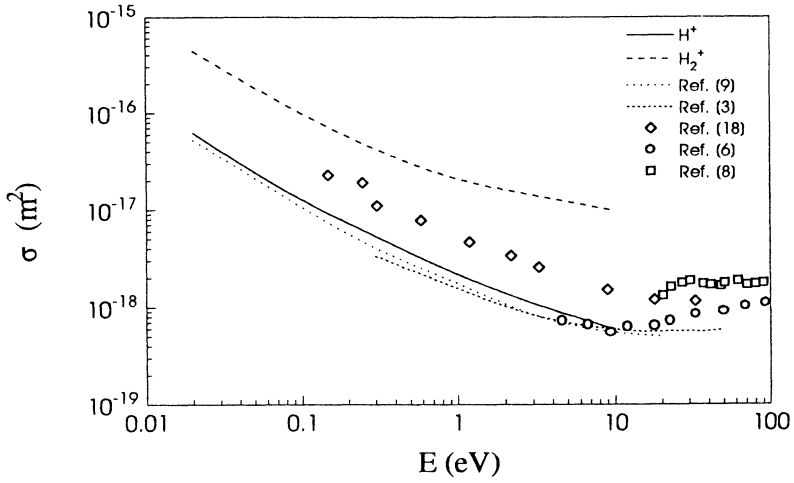

FIG. 2. Total cross sections for the mutual neutralization reactions $H_2^+ + H^-$ (upper dashed line) and $H^+ + H^-$ (other lines and points). Lines stand for theoretical calculations while the points are experimental data. The solid line and upper dashed line were calculated with Eqs. (3)–(12).

It is important to underline that our calculations of the atomic ions mutual neutralization reaction, based on a multiple-crossing Landau-Zener approximation, are actually in very good agreement with a more general quantum mechanical approach [9]. At low energies ($E \leq 5$ eV) the external interaction is more important than the internal movement of the electrons in the atoms or molecules. By realizing this, the agreement between the quantum mechanical approach and the Landau-Zener approximation can be understood [9]. This result gives us confidence in applying the same method to calculate the cross sections for low energy negative-ion–positive-molecular-ion mutual neutralization reactions.

B. $H_2^+ + H^-$

The model has been applied to the mutual recombination reaction Eq. (2), in which electronically excited $H^*(n)$ atoms and rovibrationally excited $H_2^{(v',J')}$ molecules are produced. The cross sections depend on the energy deficit after the reaction. This energy deficit can be adjusted by manipulating the rotational and vibrational quantum numbers v' and J'. In this way maximum cross sections have been calculated for $n = 2$ up to 8. The results of the calculations of the total cross section are also presented in Fig. 2. As seen from Fig. 2, the experimental data of Moseley, Aberth, and Peterson [18] lie somewhere in the middle of the theoretical curves for the reactions Eqs. (1) and (2). A possible explanation for the discrepancy is that the real positive ion beam not only consists of H^+ (as is stated in [18]), but that it also contains a certain amount of H_2^+. Therefore the final detector's signal in the experiments of Moseley, Aberth, and Peterson could be influenced by both reactions of mutual neutralization Eqs. (1) and (2).

The calculated total cross section is rather large, reaching from $\simeq 10^{-17}$ m^2 at $E = 10$ eV to $\simeq 4.4 \times 10^{-16}$ m^2 at $E = 0.02$ eV. It has been shown [19] that total cross sections for both mutual recombination reactions Eqs. (1) and (2) are equally large for the high-energy range [19]. However, in our calculations total cross section for the low-energy interaction Eq. (2) is a factor of 8 larger than that for Eq. (1). This fact has never been discussed in the literature; however, it is very important for recombination kinetics in low temperature plasma.

In Fig. 3 the variation of the "partial" cross sections, i.e., cross sections for the reactions Eq. (2) as a function of atomic quantum state $H^*(n)$, is shown. From this

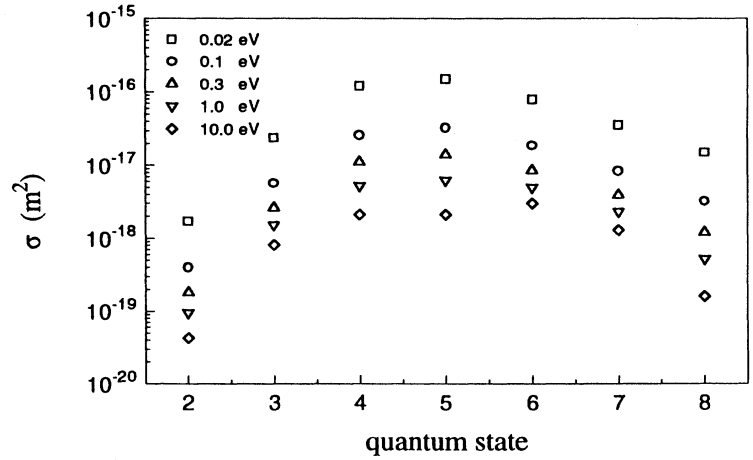

FIG. 3. Partial cross sections for the mutual neutralization reaction $H_2^{+(v,J)} + H^- \rightarrow H_2^{v',J'} + H_n^*$ as a function of the quantum state n and the center of mass energy E.

figure rather curious phenomena can be seen. There is a nonmonotonic behavior of partial cross section as a function of n, with the maximum efficiency of excitation for the quantum states with $n=5$ and 6. This suggests that if only the mutual neutralization Eq. (2) is responsible for the excitation of the levels $H^*(n)$, population inversion between various quantum states can occur and as a consequence, there might be a potential for a hydrogen laser.

It was mentioned already that the calculations of mutual neutralization cross sections have been stimulated by the experimental observation that inversion of the atomic hydrogen excited level populations occurs in an expanding recombining hydrogen plasma [13]. A possible explanation for the inversion and large absolute densities of atomic hydrogen is the reaction of molecular mutual recombination Eq. (2) with the predominant excitation of some atomic quantum levels. The detail of the kinetics of atomic hydrogen quantum levels in a magnetized expanding recombining plasma will be discussed in a subsequent paper.

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