

Molecular treatment of the ion-pair formation reaction in  $H(1s) + H(1s)$  collisions

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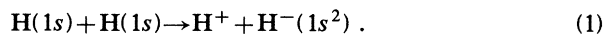
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(Received 14 July 1986)

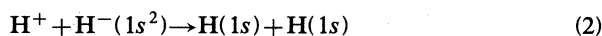
All the available theoretical calculations of the cross section for the ion-pair formation reaction  $H(1s) + H(1s) \rightarrow H^+ + H^-(1s^2)$  have been performed using methods that are only valid at high collision energies. They get good agreement with the experiments for impact energies greater than 25 keV, but fail completely at smaller energies. In this work we report the cross section for this reaction at impact energies less than 10 keV, calculated in the framework of the impact-parameter approximation and using the molecular method with a common translation factor.

## I. INTRODUCTION

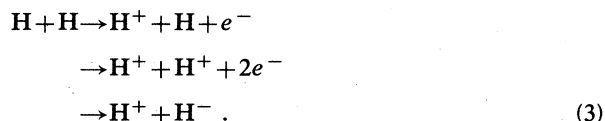
Among the most simple conceivable reactions are those which involve neutral hydrogen atoms and their ions. These reactions are quite common because hydrogen is the most abundant element in the universe; for example, they take place at high collision energies in the (relatively) cold surface of the stars which are in an advanced stage of their evolution,<sup>1</sup> and they are also very frequent in the very cold interstellar medium at much lower energies. One of the processes that occurs in such collision is the ion-pair formation reaction



The cross section of this reaction was determined experimentally by McClure in 1968 (Ref. 2) for collision energies ranging from 3.15 to 63 keV. From the theoretical point of view the inverse (neutralization) reaction



has been studied by Janev and Salin in 1971,<sup>3</sup> and by Moore and Banyard in 1978 (Ref. 4) using the continuum-distorted-wave (CDW) method; these two calculations differ in the description of the  $H^-$  target. In 1979 Becker and McKellar<sup>5</sup> carried out a four-body classical-trajectory Monte Carlo study of the projectile electron-loss process which includes the reactions



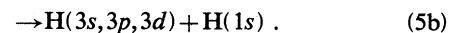
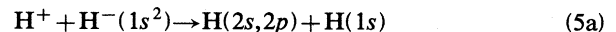
Finally, in 1980, Banyard and Shirtcliffe<sup>6</sup> calculated the cross section for reaction (1) using the method of continuum intermediate states (CIS), closely related to the CDW approximation.

All of these theoretical calculations employed methods that are only suitable for collision energies greater than the energy at which the maximum in the cross section appears. Then, as one could expect, they agree fairly well with the experimental results of McClure for impact energies greater than  $\sim 25$  keV. However, at smaller energies,

these theoretical predictions overestimate the cross section by an order of magnitude; clearly, a calculation valid in this region is missing. In our opinion, such a calculation has not yet been done for several reasons; perhaps the most important one is the fact that the contribution of reaction (2) to the cross section of the total neutralization process



is negligible at the collision energies at which this reaction has been studied ( $\sim 0.05$ – $10$  keV). In fact, the reactions which dominate the neutralization process in this range of energies are



The single charge exchange involved in these two reactions takes place at large internuclear distances, approximately 12 and 36 a.u., respectively, through the interaction of states that correlate with  $H^+ + H^-$  and  $H(nl) + H(1s)$  ( $n=2,3$ ) as  $R \rightarrow \infty$ . Some authors have calculated the corresponding cross sections taking advantage of this fact, either by using asymptotic or semiempirical methods to locate the region of interaction and to calculate its magnitude,<sup>7</sup> or by using a model potential in which only the outer (active) electron is considered explicitly.<sup>8</sup> The neutralization cross sections of (5a) and (5b) have also been extensively studied in our laboratory<sup>9</sup> using a molecular expansion, and calculating the corresponding energies and couplings with the configuration-interaction (CI) method. On the contrary, the electronic transitions responsible for process (1) take place at very short internuclear distances and that prevents the use of simple methods like those mentioned above<sup>7,8</sup> to study this reaction. Finally, we should mention that reaction (1) presents the additional complication that the entrance channel is coupled at infinity with other states of the system; this renders the use of translation factors unavoidable in the collisional treatment.

In this paper we present a calculation of the cross section for the ion-pair reaction (1) using the molecular

method which is valid at moderately low collision energies. In Sec. II we briefly discuss the theory of the molecular expansion used in our study. In Sec. III we present the calculated energies and couplings with and without the corrections due to the inclusion of a common translation factor in the formalism. And finally, in Sec. IV, we discuss the mechanism involved in process (1) and present the corresponding calculated cross sections. Atomic units will be used throughout unless otherwise stated.

## II. METHOD

The cross section of reaction (1) can be obtained by solving the time-dependent Schrödinger equation

$$i\frac{\partial}{\partial t}\Psi(\mathbf{r},t)=H_{el}\Psi(\mathbf{r},t), \quad (6)$$

where  $H_{el}$  is the electronic Born-Oppenheimer Hamiltonian of the colliding system and  $\Psi(\mathbf{r},t)$  is the corresponding electronic wave function. In the range of collision energies considered in this paper a molecular expansion of  $\Psi(\mathbf{r},t)$  is useful,

$$\begin{aligned} \Psi(\mathbf{r}_1,\mathbf{r}_2,t) &= e^{i[U(\mathbf{r}_1,t)+U(\mathbf{r}_2,t)]} \\ &\times \sum_j a_j(t)\chi_j(\mathbf{r}_1,\mathbf{r}_2;R) \\ &\times \exp\left[-i\int_0^t E_j dt'\right], \end{aligned} \quad (7)$$

$$M_{jk} = \left\langle \chi_j \left| -i\frac{\partial}{\partial t} \right| \chi_k \right\rangle + \sum_l \left\langle \chi_j \left| -i(\nabla_l U) \cdot \nabla_l - \frac{i}{2}(\nabla_l^2 U) + \frac{1}{2}(\nabla_l U)^2 + \frac{\partial U(\mathbf{r}_l,t)}{\partial t} \right| \chi_k \right\rangle. \quad (11)$$

The first term of this expression is the usual dynamical coupling of the PSS method, and the second contains the corrections to the energies and couplings introduced by the CTF.

The dynamical couplings between the modified molecular wave functions

$$\Phi_j(\mathbf{r}_1,\mathbf{r}_2,t) = e^{i[U(\mathbf{r}_1,t)+U(\mathbf{r}_2,t)]}\chi_j(\mathbf{r}_1,\mathbf{r}_2,t) \quad (12)$$

are independent of the choice of the origin of the electronic coordinates, i.e., independent of the value of  $p$ .

Integration of the differential equations system (10) gives the transition probability to each of the channels included in the expansion

$$P_j(b) = \lim_{t \rightarrow \infty} |a_j(t)|^2, \quad (13)$$

which, after integration over all impact parameters, yields the corresponding cross sections

$$\sigma_j = 2\pi \int_0^\infty b P_j(b) db. \quad (14)$$

Finally, we shall remark that  $U$ , as chosen in Eqs. (8) and (9), depends parametrically on  $\beta$  and  $p_0$ . The parameter  $\beta$  defines the extent of a cutoff factor in the switching function  $f(\mathbf{r},t)$ , and  $p_0$  defines the position of the so-called "privileged origin" (see discussion in Ref. 11). A practical

where  $\chi_j$  are the eigenfunctions of  $H_{el}$ ,  $E_j$  their energies, and  $\exp\{i[U(\mathbf{r}_1,t)+U(\mathbf{r}_2,t)]\}$  is the common translation factor (CTF) introduced by Schneiderman and Russek<sup>10</sup> in order to avoid the problems of a simple perturbed-stationary-states (PSS) approach. In this paper we have chosen for  $U(\mathbf{r},t)$  the form proposed by Errea *et al.*,<sup>11</sup>

$$U(\mathbf{r}_j,t) = f(\mathbf{r}_j,R)\mathbf{v} \cdot \mathbf{r}_j - \frac{1}{2}f^2(\mathbf{r}_j,R)v^2t \quad (8)$$

with

$$f(\mathbf{r}_j,R) = \frac{R^2}{R^3 + \beta^3} [\mathbf{r}_j \cdot \mathbf{R} + (p - p_0)R] - (p - p_0), \quad (9)$$

where the origin of the electronic coordinates is placed at a distance  $pR$  from the nucleus  $A$ .

When the expansion (7) is substituted in (6) one gets the following system of coupled linear differential equations for the expansion coefficients:

$$i\frac{da_j}{dt} = \sum_{k(\neq j)} M_{jk} a_k \exp\left[-i\int_0^t (E_k - E_j) dt'\right], \quad (10)$$

where the coupling matrix elements are given by

criterion for the determination of the optimal values of these parameters was given by Riera.<sup>12</sup> This method uses the generalized Euclidean norm to gauge the closure of the manifold spanned by the basis set of the modified molecular expansion (7). However, when the calculated cross sections are (approximately) independent of the values of  $\beta$  and  $p_0$  for a wide variation of these parameters, their optimization can be avoided. As we shall see in Sec. III this is the case for process (1).

## III. ADIABATIC ENERGIES AND RADIAL COUPLINGS

According to the symmetry of the entrance and exit channels, we have calculated the energies of the  $1\Sigma_g^+$  states of the  $H_2$  molecule and their corresponding radial couplings. To approximate the wave functions of the adiabatic states we have used the CI method with a basis set of Gaussian-type orbitals (GTO's) centered on each nucleus. In practice, we found it convenient to use two different atomic basis sets, one in the range of internuclear distances  $0.3 < R < 5.0$  a.u., and the other for  $R > 5.0$  a.u. The exponents of these two sets have been approximately optimized and are presented in Table I. We have included in our calculation all the configurations of  $1\Sigma_g^+$  symmetry that can be formed from those sets of atomic orbitals.

TABLE I. Exponents of the Gaussian orbitals used in the molecular calculations of  $1\Sigma_g^+$  states for (a)  $0.3 < R < 5.0$  a.u. and (b)  $R > 5.0$  a.u.

(a)	
$\alpha_{1s}$	$\alpha_{2p_z}$
0.01	0.005
0.06	0.02
0.3	0.1
1.5	0.5
8.0	
(b)	
$\alpha_{1s}$	$\alpha_{2p_z}$
0.003	0.02
0.018	0.1
0.09	0.5
0.45	
2.0	
8.0	

The calculated total energies for the four lowest states are presented in Fig. 1.

The corresponding radial couplings between these states have been analytically calculated using the method of Macías and Riera,<sup>13</sup> and are presented in Fig. 2. The origin of the electronic coordinates has been placed in the middle of the internuclear axis.

The electronic states presented in Fig. 1 correlate in the united-atom (UA) and separated-atoms (SA) limits as follows:

$$\begin{aligned}
 1s^2 &\sim 1^1\Sigma_g^+ \sim H(1s) + H(1s), \\
 1s2s &\sim 2^1\Sigma_g^+ \sim H(1s) + H(2s), \\
 1s3s &\sim 3^1\Sigma_g^+ \sim H(1s) + H(2p), \\
 1s3d &\sim 4^1\Sigma_g^+ \sim H^+ + H^-(1s^2), \\
 \text{UA: } R \rightarrow 0, \text{ SA: } R \rightarrow \infty.
 \end{aligned}
 \tag{15}$$

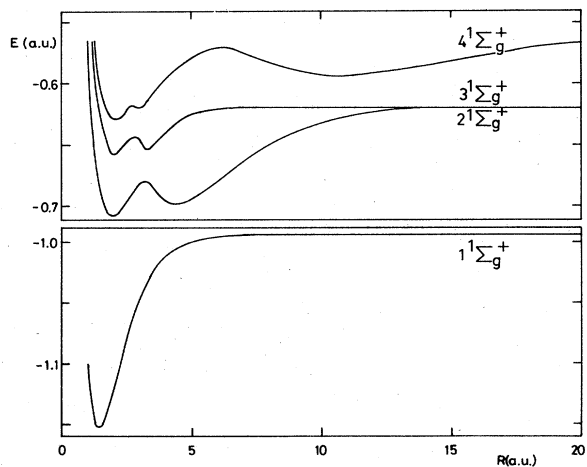


FIG. 1. Potential energy curves for the first four  $1\Sigma_g^+$  states of the  $H_2$  molecule.

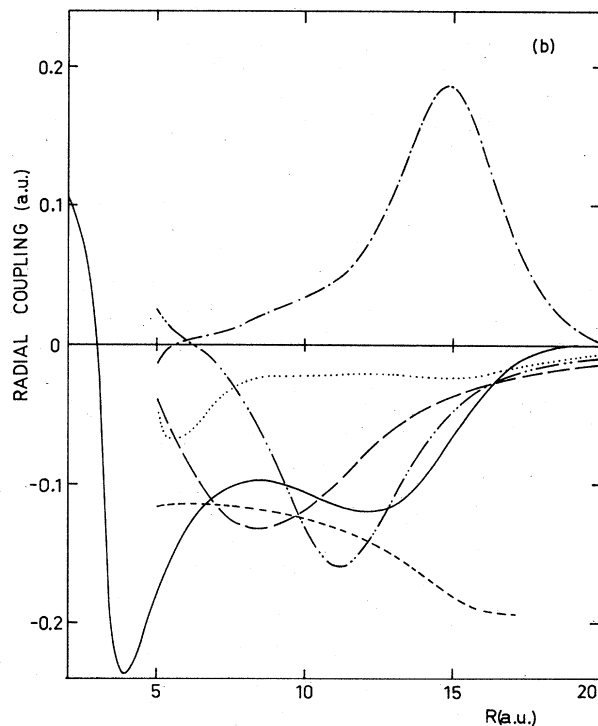
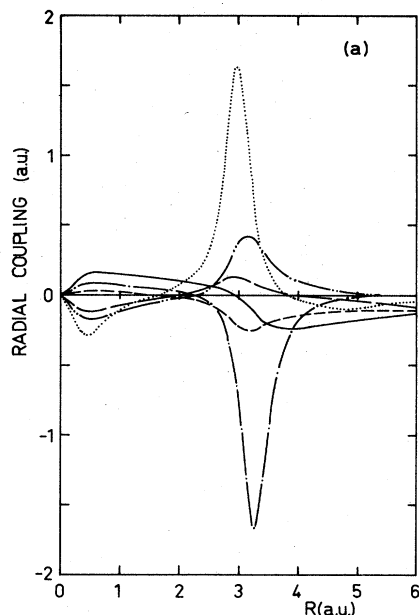


FIG. 2. Radial couplings between the first four  $1\Sigma_g^+$  states of the  $H_2$  molecule without CTF and with the origin of electronic coordinates placed in the middle of the internuclear axis for (a) short distances ( $R < 5.0$  a.u.) (b) long distances ( $R > 5.0$  a.u.). The 1,2 radial coupling has been extended to shorter distances in order to show its shape more clearly than in (a). —, 1,2; ----, 1,3; - - - -, 1,4; - · - · - ·, 2,3; · - · - ·, 2,4; · · ·, 3,4. [Notice the different scale in (a) and (b).]

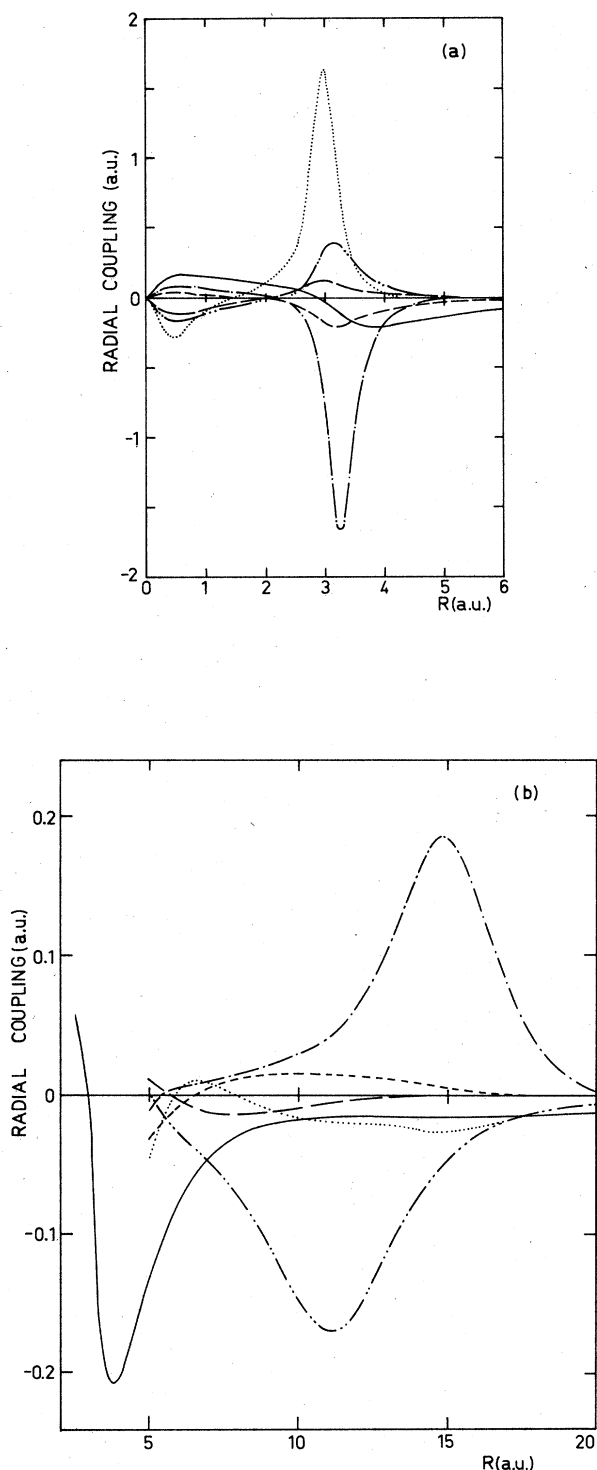


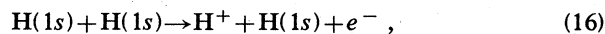
FIG. 3. Radial couplings between the first four  $1\Sigma_g^+$  states of the  $H_2$  molecule with the CTF of Eqs. (7)–(9) with  $\beta=6.0$  and  $p_0=0.5$  for (a) short distances ( $R < 5.0$  a.u.) and (b) long distances ( $R > 5.0$  a.u.). The 1,2 radial coupling has been extended to shorter distances in order to show its shape more clearly than in (a). —, 1,2; ----, 1,3; - · - ·, 1,4; ·····, 2,3; - - - -, 2,4; ···, 3,4. [Notice the different scale in (a) and (b).]

The entrance and exit channels for the reaction considered in this paper (1) are represented, respectively, by the first and the fourth states. We should note that in Eqs. (15) we have written down the diabatic correlation SA limit of the fourth state, since at  $R \approx 36.5$  and 262 a.u. this ionic diabatic state crosses the covalent states which correlate as  $R \rightarrow \infty$  to the  $H(n=3) + H(1s)$  and  $H(n=4) + H(1s)$  manifolds.<sup>9</sup> However, as we shall discuss in Sec. IV, the transitions to these covalent states are completely negligible at the collision energies considered in this paper, and then they have not been included in our treatment.

We see in Fig. 2 that there exists a radial coupling which is constant at infinity between the third state and the entrance channel. As is well known this implies that when a simple PSS method is used, the calculated transition probabilities oscillate with the starting point of the integration of the coupled equations; this problem disappears when the translation factor of Eqs. (7)–(9) is included in the molecular expansion. As we mentioned in Sec. II the modified dynamical couplings [Eq. (11)], and then the cross sections, depend on the value chosen for the parameter  $\beta$ . In our calculations we have found that the cross section for reaction (1) is practically independent of the value of  $\beta$  when this parameter is in the range  $4 < \beta < 8$ . The modified radial couplings corresponding to a value of  $\beta=6.0$  are shown in Fig. 3. We see that the CTF eliminates the constant couplings  $\langle 1^1\Sigma_g^+ | d/dR | 3^1\Sigma_g^+ \rangle$  at infinity, and also reduces the value of the couplings  $\langle 1^1\Sigma_g^+ | d/dR | 2^1\Sigma_g^+ \rangle$  and  $\langle 1^1\Sigma_g^+ | d/dR | 4^1\Sigma_g^+ \rangle$  at  $R > 7$  a.u., leaving the others practically unchanged.

#### IV. CROSS SECTION

The cross section for reaction (1) has been calculated using the program PAMPA,<sup>14</sup> conveniently modified to include the “corrected” energies and couplings [see Eq. (11)] reported in Sec. III. We present our calculated cross sections in Table II and in Fig. 4 along with the experimental measurements of McClure<sup>2</sup> and the available theoretical calculations.<sup>3,4,6</sup> As we mentioned in the Introduction, all the studies reported in the literature make use of methods which are only valid at high impact energies. Consequently, they yield results in fairly good agreement with the experimental measurements for impact energies above  $\approx 25$  keV, whereas at smaller energies the agreement is quite poor, and the calculated cross sections are one order of magnitude greater than the experimental ones for  $E \leq 10$  keV. However, in this energy range, our calculation (see Fig. 4) reproduces much better both the magnitude and the slope of the experimental data than the theoretical calculations mentioned above. However, our calculated cross sections are still slightly greater than the experimental values and this difference increases with the impact energy. This discrepancy can be accounted for by the ionization process



which competes at these impact energies with the charge-exchange reaction (1) [see Ref. (2)]. To estimate the influ-

TABLE II. Calculated cross section for reaction (1) with the molecular wave functions calculated with the basis of Table I and the CTF of Eqs. (7)–(9) with  $\beta=6.0$ .

Nuclear velocity (a.u.)	H impact energy (keV)	Cross section ( $10^{-17} \text{ cm}^2$ )
0.10	0.25	0.0018
0.12	0.36	0.0043
0.14	0.49	0.0097
0.16	0.64	0.0186
0.18	0.81	0.0364
0.20	1.00	0.0534
0.25	1.56	0.1534
0.30	2.25	0.4149
0.40	4.00	1.1444
0.50	6.25	2.0613
0.60	9.00	3.1412

ence of this ionization process we can use the following approximate argument:<sup>15</sup> assuming that the ionization process takes place for all internuclear distances, we can consider processes (1) and (16) as roughly independent and obtain a more accurate upper bound for the former by subtracting from our results the ionization cross section. This cross section can be evaluated from the experimental data reported in Ref. 2, and making the assumption that roughly  $\frac{1}{4}$  of the ionization comes from the singlet channels and  $\frac{3}{4}$  from the triplets. The corrected results are also presented, by a dashed line, in Fig. 4. Given the approximate character of our reasoning, the agreement be-

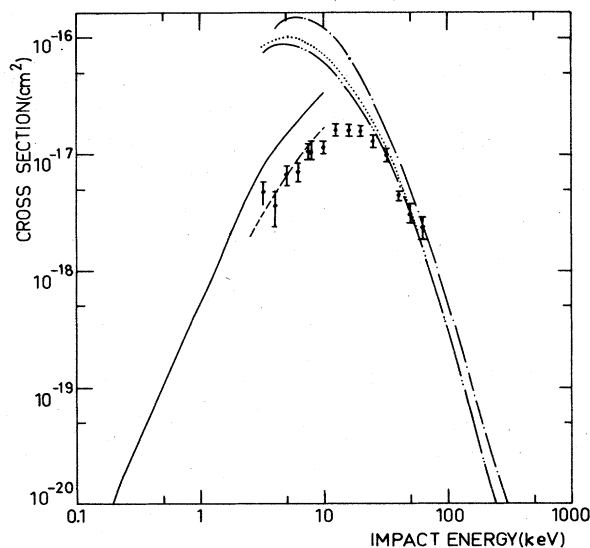


FIG. 4. Cross section for reaction (1). —, same results as in Table II using the CTF of Eqs. (7)–(9) with  $\beta=6.0$ . ···, theoretical results of Janev and Salin (Ref. 3). —·—·, theoretical results of Moore and Banyard (Ref. 4). — — —, theoretical results of Banyard and Shirtcliffe (Ref. 6). - - - -, results of Table II corrected with the experimental cross section for the ionization process (16).  $\updownarrow$ , experimental results of McClure (Ref. 2).

tween these results and the experimental data is excellent and clearly indicates that our explanation of the mechanism involved in reaction (1) is basically correct.

As we pointed out in Sec. III we have not included in our treatment the electronic states which dissociate as  $R \rightarrow \infty$  in  $\text{H}(n=3) + \text{H}(1s)$  and  $\text{H}(n=4) + \text{H}(1s)$ . The couplings between our exit channel and these states have been extensively studied by Borondo, Macías, and Riera.<sup>9</sup> They concluded that in the region where those states pseudocross, the interaction is well described by the Landau-Zener model and they gave values for the corresponding interaction parameters. Using these data we have concluded that the inclusion of those states in our calculation would reduce the cross section less than 1%.

To elucidate the mechanism for the charge-exchange process involved in reaction (1) we present in Fig. 5 the value of the transition probability  $P_{4^1\Sigma_g^+}(b)$  of Eq. (13) times the impact parameter  $b$  as a function of  $b$  [see Eq. (14)] for a collision energy of 6.25 keV. The maximum of the electronic transition is localized near the internuclear distance  $R=3.25$  a.u. where the matrix element  $\langle 1^1\Sigma_g^+ | d/dR | 2^1\Sigma_g^+ \rangle$  presents a peak (see Fig. 2). This pattern does not change significantly for other values of the collision energies.

The "history" of the collision process is displayed more clearly in Fig. 6, where we plot the values of the transition probabilities  $|a_{2^1\Sigma_g^+}|^2$ ,  $|a_{3^1\Sigma_g^+}|^2$ , and  $|a_{4^1\Sigma_g^+}|^2$  of Eq. (7), as functions of the collision path  $z = vt = [R(t)^2 - b^2]^{1/2}$  for a trajectory with  $b=3.5$  a.u. and  $E=6.25$  keV. This figure shows that at  $z \sim -4$  a.u. ( $R \sim 5$  a.u.) the  $2^1\Sigma_g^+$  state begins to be populated due to

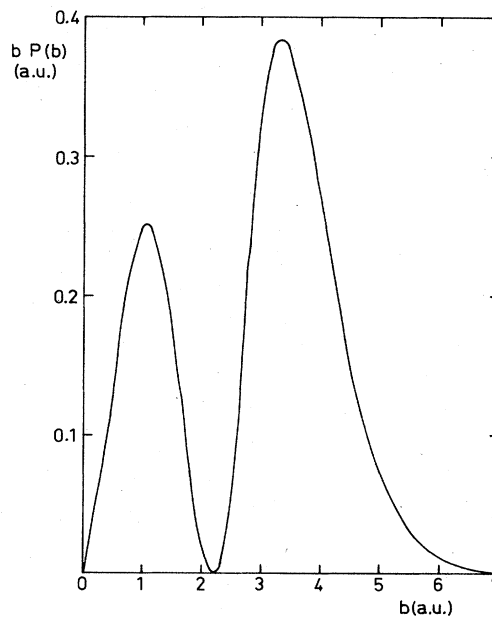


FIG. 5. Plot of  $bP(b)$  vs  $b$  for  $E=6.25$  keV. Notice that the probability  $P(b)$  used in this figure is normalized, as usual, to 1. To calculate the cross section for process (1) a further factor of  $\frac{1}{8}$  should be used to account for the spin statistic and the lack of  $g-u$  symmetry in the experiment.

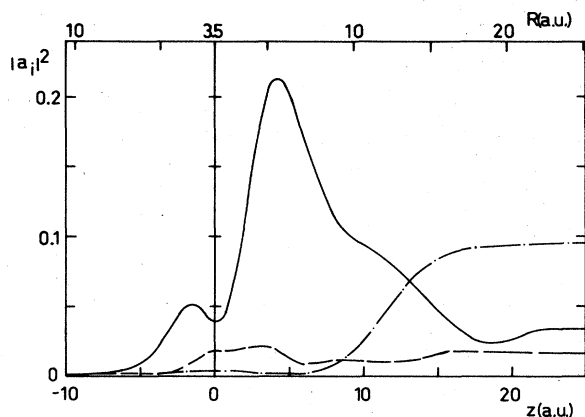


FIG. 6. Plot of the values of the transition probabilities  $|a_j(t)|^2$  to the exit channels  $j=2^1\Sigma_g^+, 3^1\Sigma_g^+, 4^1\Sigma_g^+$ , of reaction (1) included in the molecular expansion (7). —,  $|a_{2^1\Sigma_g^+}|^2$ ; ---,  $|a_{3^1\Sigma_g^+}|^2$ ; - · - · - ·,  $|a_{4^1\Sigma_g^+}|^2$ , for  $E=6.25$  keV and  $b=3.5$  a.u. (See comment in caption to Fig. 5.)

the  $\langle 1^1\Sigma_g^+ | d/dR | 2^1\Sigma_g^+ \rangle$  coupling (see Fig. 2) and this is the most effective interaction in the region  $-4 < z < 4$  a.u. Afterwards, for  $z > 9$  a.u. ( $R > 10$  a.u.) the radial coupling between  $2^1\Sigma_g^+$  and  $4^1\Sigma_g^+$  states (see Fig. 2) populates the latter state yielding the final transition probability of the exit channel of reaction (1). We should remark that the  $\langle 2^1\Sigma_g^+ | d/dR | 3^1\Sigma_g^+ \rangle$  coupling is practically ineffective in this collision because it acts in a region

where the  $2^1\Sigma_g^+$  is almost depopulated due to the  $2^1\Sigma_g^+ - 4^1\Sigma_g^+$  transition indicated above.

## V. CONCLUSIONS

In this paper we have extended previous calculations made in our laboratory,<sup>9</sup> to the evaluation of the energies of the molecular states involved in the ion-pair-formation reaction  $H(1s) + H(1s) \rightarrow H^+ + H^-(1s^2)$  using a CI method. The corresponding radial couplings, as well as the corrections to the energies and couplings which appear when the CTF of Eqs. (7)–(9) is introduced in the molecular expansion, have been calculated analytically. The corresponding cross sections were calculated for impact energies between 0.1–10 keV. The agreement with the experimental results when we correct our theoretical outcomes to take into account the competing ionization process is excellent, showing that the explanation proposed for the mechanism involved in the ion-pair formation (1) is correct.

## ACKNOWLEDGMENTS

Useful discussions with Dr. A. Salin are acknowledged. All calculations were performed at the Centro Coordinado Universidad Autónoma de Madrid-IBM (Madrid). This work was supported in part by the Comisión Asesora de Investigación Científica y Tecnológica (Spain), Project No. 890/84.

<sup>1</sup>D. D. Clayton, *Principles of Stellar Evolution and Nucleosynthesis* (University of Chicago Press, London, 1983).

<sup>2</sup>G. W. McClure, *Phys. Rev.* **166**, 22 (1968).

<sup>3</sup>R. K. Janev and A. Salin, *J. Phys. B* **4**, L127 (1971); *Fizika* **4**, 165 (1972).

<sup>4</sup>J. C. Moore and K. E. Banyard, *J. Phys. B* **11**, 1613 (1978).

<sup>5</sup>R. L. Becker and A. D. McKellar, *J. Phys. B* **12**, L345 (1979).

<sup>6</sup>K. E. Banyard and G. W. Shirtcliffe, *Phys. Rev. A* **22**, 1452 (1980).

<sup>7</sup>D. R. Bates and J. T. Lewis, *Proc. Phys. Soc. London, Sect. A* **68**, 177 (1955).

<sup>8</sup>V. Sidis, C. Kubach, and D. Fussen, *Phys. Rev. Lett.* **47**, 1280 (1981).

<sup>9</sup>F. Borondo, A. Macías, and A. Riera, *J. Chem. Phys.* **74**, 6126

(1981); *Chem. Phys. Lett.* **100**, 63 (1983); *Chem. Phys.* **81**, 303 (1983).

<sup>10</sup>S. B. Schneiderman and A. Russek, *Phys. Rev.* **181**, 311 (1969).

<sup>11</sup>L. F. Errea, L. Méndez, and A. Riera, *J. Phys. B* **15**, 101 (1982).

<sup>12</sup>A. Riera, *Phys. Rev. A* **30**, 2304 (1984).

<sup>13</sup>A. Macías and A. Riera, *J. Phys. B* **10**, 861 (1977); **11**, 1077 (1978).

<sup>14</sup>C. Gaussorgues, R. D. Piacentini, and A. Salin, *Comput. Phys. Commun.* **10**, 223 (1975).

<sup>15</sup>F. Borondo, A. Macías, and A. Riera, *Phys. Rev. Lett.* **46**, 420 (1981).