Asymmetry Effect in the Neutralization Reaction $H^+ + H^-$

F. Borondo, A. Macias, and A. Riera
Departamento de Química Física y Química Cuántica, Centro Coordinado CSIC-UAM,
Universidad Autónoma de Madrid, Canto Blanco, Madrid 34, Spain

(Received 23 September 1980)

The transition between the ionic state of H_2 correlated with $H^+ + H^-$, and the covalent states correlated with $H(1s) + H(nl)$ is studied. The processes whereby the diffuse electron of H^- is carried off by the proton dominate the neutralization cross section. This asymmetry effect is used to explain an (apparent) disagreement between experimental results of neutralization cross sections at high impact energies.

PACS numbers: 34.70.+e

Following the early work of Bates and Lewis,[1] the reactions

$$H^+ + H^- \rightarrow H(1s) + H(n), \quad n = 2, 3, 4,$$

are usually presented[2] as standard examples of neutralization processes which occur via ionic-covalent transitions, and of the applicability of Landau-Zener theory. In a recent work[3] we have found that the Landau-Zener model cannot be applied to study these reactions for two reasons: (1) strong nonorthogonality between the covalent and ionic states, at least for $n = 2$, and (2) the exponential behavior of the electrostatic interaction between the diabatic states in the crossing region. The detailed analysis of these features and, in particular, the necessity of replacing Landau-Zener theory by Nikitin's exponential-linear model[4] has been presented elsewhere.[3]

In this Letter we point out a different feature of these reactions, which has its origin in the open-shell structure of the negative ion H^-, and which has hitherto passed unnoticed in the literature. We shall then use this feature in order to explain an (apparent) disagreement between experimental results for neutralization cross sections at high impact energies, which has been the object of discussion in the recent literature.[5,6] Like Bates and Lewis,[1] for the energy range considered ($E > 500$ eV), we shall employ a semiclassical approach with straight-line trajectories. The system is initially described by a wave function

$$\psi = \psi_g + \psi_u \underset{t \to -\infty}{\sim} (\sqrt{2})^{-1}[\chi_g(H^-) - \chi_u(H^-)]\exp[-iE(H^-)t].$$

For each g, u subsystem, the H_2 quasimolecule evolves adiabatically, except in the vicinity of the avoided crossings between the molecular states which correlate with $H^+ + H^-$ and $H(1s) + H(nl)$. As is well known,[7] a consequence of this is that the states $H(n = 4, 3, 2)$ are *selectively* populated as the nuclear relative velocity increases, because for each avoided crossing the transitions will not be effective if the system behaves adiabatically (low velocities) or diabatically (high velocities) in this region; this gives rise to characteristic peaks of the neutralization cross section for the intermediate velocities.[8]

Our main point is that to calculate, however roughly, the neutralization cross sections, one should consider transition amplitudes, and not transition probabilities, in the avoided crossing regions, as is always done.[2] This is so because the interference (or coherence) effects between the g and u channels are very important; this coherence is due to the fact that for large internuclear distances the molecular energies and couplings for the g, u subsystems involved in the neutralization processes are practically identical, and so will be the g, u transition amplitudes, provided the cross sections are dominated by trajectories with large impact parameters.

To show this in more detail, let us consider a particular velocity range for which the transitions to $H(1s) + H(nl)$ are favored. We can then use a $(n+1)$-state molecular expansion to describe the evolution of each g, u subsystem:

$$\begin{aligned}\psi_{g,u} &= \sum_{j=1}^{n} a_{g,u}{}^{j}\varphi_{g,u}{}^{j}\exp\left(-i\int^{t}E_{g,u}{}^{j}dt'\right) + a_{g,u}{}^{n+1}\varphi_{g,u}{}^{n+1}\exp\left(-i\int^{t}E_{g,u}{}^{n+1}dt'\right)\\ &\underset{t\to\infty}{\sim} \sum_{j=1}^{n} a_{g,u}{}^{j}\chi_{g,u}{}^{j}\exp\left(-i\int^{\infty}E_{g,u}{}^{j}dt\right) + a_{g,u}{}^{n+1}\chi_{g,u}(H^-)\exp\left(-i\int^{\infty}E_{g,u}{}^{n+1}dt\right),\end{aligned}$$

where φ^j are the molecular wave functions, with energies E^j, and χ^j are their asymptotic forms for infinite internuclear distance. For $j=1,\ldots,n$ the functions χ^j are the covalent states correlated with H(1s) + H(n), and χ^{n+1} is the ionic state.

An important property of the covalent states, but one which is not essential to the point raised in this paper, is that the exponentially decreasing electric field due to the H(1s) atom mixes the n spherical states of the H(n) atom, yielding n Stark, or hybrid, atomic orbitals. This Stark mixing has a negligible contribution (exponentially decreasing terms) to the asymptotic form of the covalent energies, which are dominated for large R by the Coulomb (R^{-3}) dipole-dipole resonant interaction. Hence, the asymptotic form of the covalent wave functions is

$$\chi_{\mathrm{g,u}}{}^j=\tfrac{1}{2}[(1s_A)(n\xi_B{}^j)\pm(1s_B)(n\xi_A{}^{n-j+1})+(n\xi_B{}^j)(1s_A)\pm(n\xi_A{}^{n-j+1})(1s_B)].$$

For example, for the $n=2$ manifold, we have

$$2\xi^1=(2s+2p)/\sqrt{2},\quad 2\xi^2=(2s-2p)/\sqrt{2}.$$

The expression for the total probability amplitude for the reactions

$$\mathrm{H}^+ + \mathrm{H}^- \rightarrow \mathrm{H}(nl)+\mathrm{H}(1s),\quad l=0,1,\ldots,n-1, \tag{1}$$

is

$$A=\lim_{t\to\infty}\sum_{j=1}^{n}\langle(\sqrt{2})^{-1}(\chi_{\mathrm{g}}{}^j+\chi_{\mathrm{u}}{}^j)\exp(-iE^jt)|\psi_{\mathrm{g}}+\psi_{\mathrm{u}}\rangle=(\sqrt{2})^{-1}\sum_{j=1}^{n}(a_{\mathrm{g}}{}^j+a_{\mathrm{u}}{}^j),$$

and for the complementary reactions

$$\mathrm{H}^+ + \mathrm{H}^- \rightarrow \mathrm{H}(1s)+\mathrm{H}(nl),\quad l=0,\ 1,\ldots,n-1, \tag{2}$$

is

$$B=\lim_{t\to\infty}\sum_{j=1}^{n}\langle(\sqrt{2})^{-1}(\chi_{\mathrm{g}}{}^j-\chi_{\mathrm{u}}{}^j)\exp(-iE^jt)|\psi_{\mathrm{g}}+\psi_{\mathrm{u}}\rangle=(\sqrt{2})^{-1}\sum_{j=1}^{n}(a_{\mathrm{g}}{}^j-a_{\mathrm{u}}{}^j).$$

Now, under our basic assumption that transitions take place only for large internuclear distances, $a_{\mathrm{g}}{}^j\simeq a_{\mathrm{u}}{}^j$, and hence $|A|\gg|B|$.

This result is not surprising when one considers that the H$^-$ ion is described by an open-shell wave function with an electron occupying a contracted orbital and the other occupying a very diffuse one. In the collision with a proton at large distances, it seems more likely that the outer electron of H$^-$ will make a transition to a diffuse H(n = 2, 3, 4) orbital.

This result can explain the apparent disagreement between the experimental results obtained for the reactions

$$\mathrm{H}(2s)+\mathrm{H}(1s)\rightarrow\mathrm{H}^-+\mathrm{H}^+, \tag{3}$$

$$\mathrm{H}^+ + \mathrm{H}^- \rightarrow \mathrm{H}+\mathrm{H}. \tag{4}$$

In the impact energy range of 40 eV to 25 keV, the total cross section for the first reaction is $O(10^{-17}\ \mathrm{cm}^2)$,[5,6] while for the second reaction, the total cross section is greater than 10^{-15} cm^2.[8] Assuming (correctly, as we shall see) that the cross section for H(2p) + H(1s) → H$^-$ + H$^+$ is of the same order as that of reaction (3), and taking into account that the initial states of the system in (3) were not spin polarized,[8] one obtains[9] a factor of $\frac{1}{16}$ between the total cross sections for (3) and (4); to explain the remaining difference it has been suggested that higher states have an important role.[5,6] This explanation, though obviously correct for relatively low energies, is unlikely to hold for the whole range of nuclear velocities used in Ref. 8, and another reasoning is needed for the high energies considered in Ref. 5. We shall now show that a likely cause of discrepancy is that Hill, Geddes, and Gilbody[5] have measured the cross section for reactions of type (2) while the experiments of Peart, Grey, and Dolder[8] included the much larger cross sections for reactions of type (1).

We show, in Fig. 1, the energies of the H$_2$ molecular states correlated with H(1s) + H(2s, 2p) and (diabatically) with H$^+$ + H$^-$ in the avoided crossing region. These energies were calculated with use of a configuration interaction method with the basis set described in Ref. 3. These values are slightly above (< 0.01 a.u.) and almost parallel to the accurate results of Ref. 10. The radial couplings between our approximate wave functions were calculated exactly[11] and are presented in Fig. 2. The (small) radial coupling $\langle\varphi_{\mathrm{g,u}}{}^2|d/dR|\varphi_{\mathrm{g,u}}{}^1\rangle$ has been integrated out (see Ref. 3).

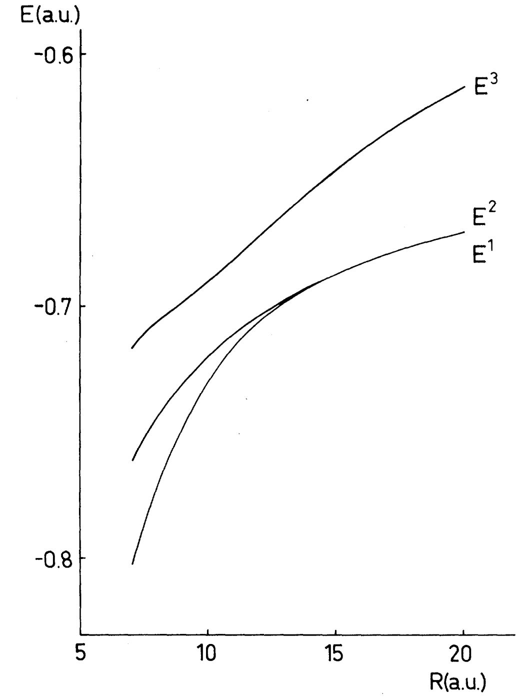

FIG. 1. Electronic energies (without nuclear repulsion), in atomic units, for the molecular states correlated with H(1s) + H(2s, 2p) and (diabatically) with $H^+ + H^-$. E^1, E^2, and E^3 are the energies of $(E, F\,{}^1\Sigma_g{}^+;\ B\,{}^1\Sigma_u{}^+)$, $(G, K\,{}^1\Sigma_g{}^+;\ B'\,{}^1\Sigma_u{}^+)$, and $(H, \bar{H}\,{}^1\Sigma_g{}^+;\ B'', \bar{B}\,{}^1\Sigma_u{}^+)$, respectively. Results for g, u subsystems are indistinguishable in the scale of the figure.

Angular and radial couplings to other states are unimportant in this internuclear range and have, therefore, been neglected.

The cross sections for the reactions (1) with $n = 2$ were calculated with the program PAMPA[12] and are presented in Fig. 3, while those for reactions (2), calculated in the same way by numerical integration of the impact-parameter–coupled equations, were found to be $O(10^{-17}\ \text{cm}^2)$ and are therefore not shown in the figure. Hence, for high energies the discrepancy between Refs. 5 and 8 can be explained without involving higher molecular states.

It should be pointed out, however, that in order to compare our results with the experimental data[8] one should also take the following into account.

(1) The ionization process $H^+ + H^- \rightarrow H^+ + H(1s) + e^-$, which becomes very important at high energies. We notice that the complementary reaction that yields $H(1s) + H^+ + e^-$ would be highly unlikely for the reasons presented above.

To estimate the influence of this ionization

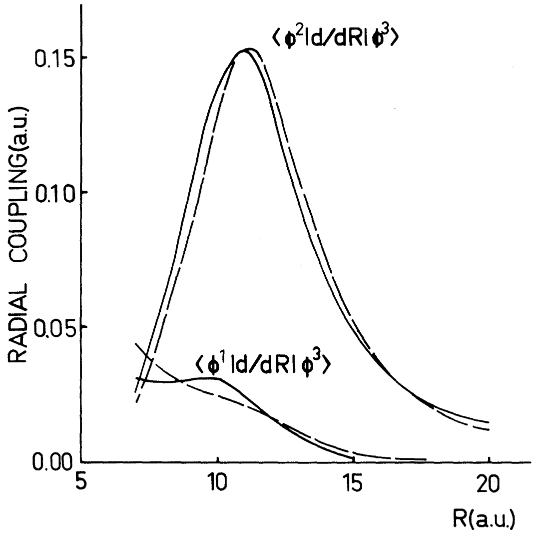

FIG. 2. Radial couplings, in atomic units, between the states of Fig. 1 (solid line, g; dashed line, u).

process we can use the following approximate argument. If transitions to H(2s, 2p) occur only in the avoided crossing region (Fig. 1) and ionization takes place for all internuclear distances, we can consider these processes as roughly independent and obtain a more accurate upper bound for the neutralization cross section by subtracting from our results the ionization cross section. As theoretical estimates of this cross section are not available yet, we have subtracted from our results the experimental ionization cross sec-

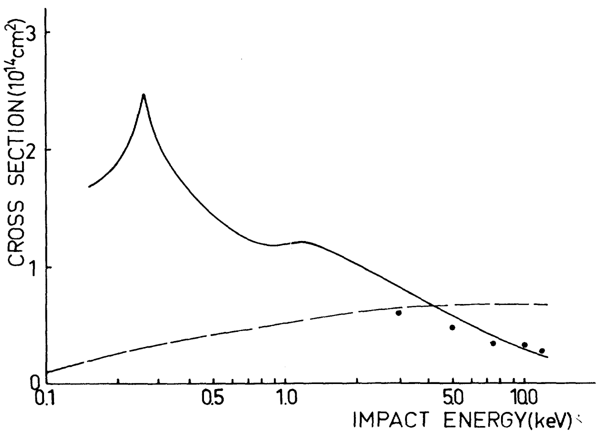

FIG. 3. Solid line, cross section measured by Peart, Grey, and Dolder for the reaction $H^+ + H^- \rightarrow H + H$. Dashed line, calculated cross section for the reaction $H^+ + H^- \rightarrow H(2s, 2p) + H(1s)$. Dotted line, same as dashed line "corrected" by subtracting the experimental ionization cross section for $H^+ + H^- \rightarrow H^+ + H(1s) + e^-$.

tion[13]; these "corrected" results are also presented in Fig. 3. Given the approximate character of our argument, the excellent agreement between these results and the experimental data is probably fortuitous. What these results show is that the flat maximum of the neutralization cross section corresponding to transitions to H($n = 2$) is not observed experimentally as it is canceled out by the ionization process.

(2) At high velocities the processes occurring for trajectories with small impact parameters become important. One should notice the logarithmic energy scale of Fig. 3 and realize that the last point calculated corresponds to a relative nuclear velocity of 0.77 a.u., where the applicability of the molecular model itself is questionable.

For impact energies less than 3 keV, the difference between our results and the experimental data of Peart, Grey, and Dolder[8] can be explained as follows: Roughly speaking, at energies beyond 0.1 keV, the neutralization cross section is the sum of three peaks (which flatten considerably as n increases), corresponding to selective population[7] of H($n = 4, 3, 2$) in the vicinity of the crossings between the ionic and covalent molecular potentials. The results of Peart, Grey, and Dolder[8] indicate that the peaks for $n = 4$ and $n = 3$ are located at 0.24 and 1.2 keV, respectively, while our results show that the third peak is canceled out by the ionization reaction. The asymmetry effect will be present for each of the corresponding neutralization reactions.

Finally, as explained in Ref. 3, the radial coupling $\langle \varphi_{g,u}{}^3 | d/dR | \varphi_{g,u}{}^2 \rangle \gg \langle \varphi_{g,u}{}^3 | d/dR | \varphi_{g,u}{}^1 \rangle$; hence for $t \to \infty$ $|a_{g,u}{}^2| \gg |a_{g,u}{}^1|$ and the yield of H($2p$) will be roughly the same as for H($2s$) (the possibility that the former would be much higher than the second has been proposed to settle the controversy).

We thank A. Salin for pointing out this problem to us, and for useful discussions. We also thank V. López for computational assistance. All calculations were carried out at the Centro Coordinado UAM-IBM (Madrid).

---

[1] D. R. Bates and J. T. Lewis, Proc. Phys. Soc. London, Sect. A 68, 173 (1955).

[2] H. S. W. Massey and H. B. Gilbody, *Electronic and Ionic Impact Phenomena* (Oxford Univ. Press, Oxford, 1974), Vol. 4; J. T. Moseley, R. E. Olson, and J. R. Peterson, Case Stud. At. Phys. 5, 1 (1975), and references therein; M. R. Flannery, in *Atomic Processes and Applications*, edited by P. G. Burke and B. L. Moiseiwitsch (North-Holland, Amsterdam, 1976), and references therein; R. K. Janev, Adv. At. Mol. Phys. 12, 1 (1975), and references therein.

[3] F. Borondo, A. Macías, and A. Riera, in Abstracts of the Eighth Colloquium on the Physics of Atomic and Molecular Collisions, Louvain, 1980 (unpublished), and to be published.

[4] E. E. Nikitin, Adv. Quantum Chem. 5, 135 (1970).

[5] J. Hill, J. Geddes, and H. B. Gilbody, J. Phys. B 12, 3341 (1979).

[6] W. Claeys, F. Brouillard, and G. Van Wassenhove, in *Proceedings of the Tenth International Conference on the Physics of Electronic and Atomic Collisions, Paris, 1977*, edited by G. Watel (North-Holland, Amsterdam, 1978), Vol. 1, p. 460.

[7] C. Harel and A. Salin, J. Phys. B 10, 1 (1977).

[8] B. Peart, R. Grey, and K. T. Dolder, J. Phys. B 9, L369 (1976).

[9] The factor $\frac{1}{20}$ used in Ref. 5 is based on the sharing ratio $\frac{2}{3}$ between reactions $H^+ + H^- \to H(1s) + H(2s)$ and $H^+ + H^- \to H(1s) + H(2p)$ taken from the Landau-Zener treatment of Ref. 1. We have shown in Ref. 3 that the Landau-Zener model does not apply in these cases.

[10] W. Kolos and L. Wolniewicz, J. Chem. Phys. 48, 3672 (1968), and 50, 3228 (1969); W. Kolos, Int. J. Quantum Chem. 9, 133 (1975), and J. Mol. Spectrosc. 62, 429 (1976); L. Wolniewicz and K. Dressler, J. Mol. Spectrosc. 67, 416 (1977).

[11] A. Macías and A. Riera, J. Phys. B 10, 861 (1977), and J. Phys. B 11, 1077 (1978).

[12] C. Gaussorgues, D. R. Piacentini, and A. Salin, Comput. Phys. Commun. 10, 223 (1975).

[13] B. Peart, R. Grey, and K. T. Dolder, J. Phys. B 9, 3047 (1976).