

Charge transfer in H_2^+ - $\text{H}(1s)$ collisions.

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Abstract

We present an *ab initio* study of H_2^+ + $\text{H}(1s)$ collisions at H_2^+ impact energies between 0.4 and 50 keV. Cross sections are obtained within the sudden approximation for rotation and vibration of the diatomic molecule. We have found that anisotropy effects are crucial to correctly describe this system in this energy range.

1 Introduction.

The $(\text{H}-\text{H}_2)^+$ system has been considered in many theoretical and experimental works because it is a benchmark in ion-molecule collisions and because its relevance in fusion plasmas. However, while the H^+ + H_2 reaction has been extensively studied, there is little information on the inverse reaction H_2^+ + $\text{H}(1s)$. The available data for this reaction are from the calculations of [1] at impact energies $E < 30$ eV, and the experimental work of [2,3] at impact energies above 20 keV. In this paper, we present calculations carried out for the reaction H_2^+ + $\text{H}(1s)$ by employing the SEIKON [4] approach, which uses the eikonal method and the sudden approximation for rotation and vibration of the diatomic molecule. This method has been applied in previous works [5–7] to obtain charge transfer (CT) cross sections in H^+ + H_2 collisions. In particular, we found in [6], by comparison with the vibronic close-coupling results, that the SEIKON approach is valid for impact energies above 200 eV/amu. Besides, we showed [7] that orientation-averaged cross sections can be accurately approximated by an isotropic calculation where energies and couplings are taken from a fixed orientation of the diatomic target relative to the projectile position vector; this greatly reduces the computational effort. In the present work, we shall describe the first example we found where this approximation breaks down.

In the following sections we use atomic units and we call R the distance from the H nucleus to the center of the H-H internuclear axis; ρ , the H-H internuclear distance; and α , the angle between the vectors \mathbf{R} and $\boldsymbol{\rho}$.

2 Method.

The SEIKON approach is explained in previous works of our group [4]; it uses the impact parameter method (see e.g. [8]), where the position vector \mathbf{R} follows straight-line trajectories, $\mathbf{R} = \mathbf{b} + \mathbf{v}t$, with constant velocity \mathbf{v} and impact parameter \mathbf{b} . The remaining degrees of freedom are treated quantum-mechanically by means of the wave function $\Psi(\mathbf{r}, \boldsymbol{\rho}, t)$, which is a solution of the equation:

$$\left(-\frac{1}{2\mu} \frac{\partial^2}{\partial \rho^2} + H_{\text{elec}} - i \frac{\partial}{\partial t} \Big|_{\mathbf{r}, \boldsymbol{\rho}} \right) \Psi(\mathbf{r}, \boldsymbol{\rho}, t) = 0 \quad (1)$$

where H_{elec} is the clamped-nuclei Born-Oppenheimer electronic Hamiltonian.

The sudden approximation assumes that the initial ro-vibrational wave function $\chi_\nu(\rho)Y_{JM}(\hat{\boldsymbol{\rho}})$ does not appreciably change in the time interval in which the electronic transition takes place, so that Ψ can be written as:

$$\Psi(\mathbf{r}, \boldsymbol{\rho}, t) = \rho^{-1} Y_{JM}(\hat{\boldsymbol{\rho}}) \chi_\nu(\rho) \exp(iU) \times \sum_j a_j(t; \boldsymbol{\rho}) \phi_j(\mathbf{r}; \boldsymbol{\rho}, \mathbf{R}) \exp \left[-i \int_0^t \varepsilon_j dt' \right] \quad (2)$$

where ϕ_j are eigenfunctions of H_{elec} with energies $\varepsilon_j(R, \rho, \alpha)$. In practice, we have evaluated the molecular wave functions by means of a full CI calculation carried out with the program MELD [9]. The term $\exp[iU(\mathbf{r}, t)]$ is a common translation factor [10,11]. The coefficients $a_j(t; \boldsymbol{\rho})$ are obtained by substituting expansion (2) in Eq. (1). For each nuclear trajectory and fixed $\boldsymbol{\rho}$ one obtains:

$$i \frac{da_j}{dt} = \sum_k a_k M_{jk}(\mathbf{R}, \boldsymbol{\rho}) \exp \left[-i \int_0^t (\varepsilon_k - \varepsilon_j) dt' \right] \quad (3)$$

where M_{jk} are the dynamical couplings. These couplings were calculated by means of the numerical differentiation method developed in our laboratory [12,13].

The transition probability to a given electronic state can be obtained by applying the closure relation for the set of vibrational states as:

$$P_f(b, v; \hat{\boldsymbol{\rho}}) = \int d\rho \chi_\nu^2 P_f(b, v; \boldsymbol{\rho}) = \int d\rho \chi_\nu^2 |a_f(\infty; \boldsymbol{\rho}) - \delta_{if}|^2 \quad (4)$$

Then, the orientation-dependent cross section for transition to the electronic state f :

$$\sigma_f(v; \hat{\boldsymbol{\rho}}) = 2\pi \int db P_f(b, v; \hat{\boldsymbol{\rho}}) \quad (5)$$

and the corresponding orientation-independent cross section is obtained by integrating over $\hat{\boldsymbol{\rho}}$:

$$\sigma_f(v) = (4\pi)^{-1} \int d\hat{\boldsymbol{\rho}} \sigma_f(v; \hat{\boldsymbol{\rho}}) \quad (6)$$

The integral in the previous equation can be approached by a sum of cross sections evaluated along three representative trajectory orientations, namely those of Fig. 1, as was proposed in [4] (see also [7]):

$$\sigma_f(v) = 3^{-1} [\sigma_f^{\text{I}}(v) + \sigma_f^{\text{II}}(v) + \sigma_f^{\text{III}}(v)] \quad (7)$$

where

$$\sigma_f^{\text{x}}(v) = 2\pi \int db P_f^{\text{x}}(b, v) \quad (8)$$

and $\text{x} \equiv \text{I, II, III}$. Here, $P_f^{\text{I,II,III}}$ are the probabilities for transition to the electronic channel f in the collisions where the trajectory orientations are defined in Fig. 1:

A further simplification can be obtained when both couplings and energies are roughly isotropic. In that case, we define fixed-angle couplings $M_{jk}(R, \rho; \alpha_0)$ and energies $\epsilon_j(R, \rho; \alpha_0)$. By solving the system of differential equations (3), we obtain the angle dependent transition probability $P_f^{\text{iso}}(b, v; \rho, \alpha_0)$, and the corresponding fixed-angle, ρ -dependent cross section, $\sigma_f^{\text{iso}}(v; \rho, \alpha_0)$. The ρ -independent cross section for transition to state f is [see Eq. (4)]:

$$\sigma_f^{\text{iso}}(v; \alpha_0) = \int d\rho \chi_\nu^2 \sigma_f^{\text{iso}}(v; \rho, \alpha_0) \quad (9)$$

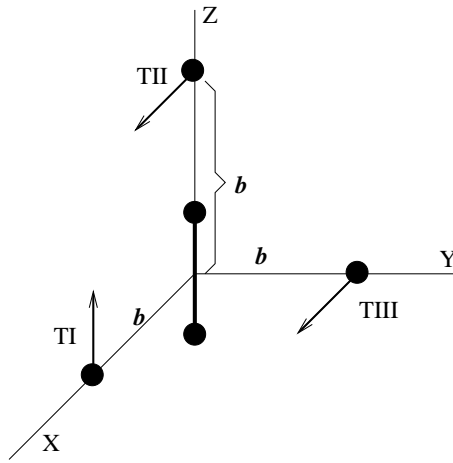


Fig. 1. Geometry of the trajectories TI, TII and TIII used to evaluate the trajectory-averaged cross section in Eq. (7).

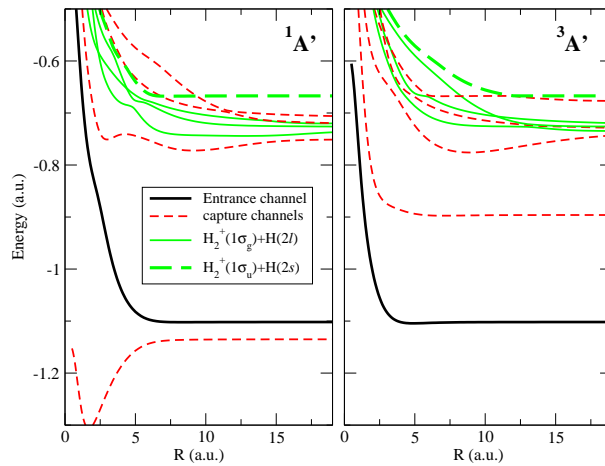


Fig. 2. Potential energy curves for H_3^+ with $\rho = 2.0$ a.u. and $\alpha = 60^\circ$. Left panel: singlet subsystem. Right panel: triplet subsystem.

An approximation to the orientation-averaged cross sections of Eq. (6) is then obtained by averaging the angle-dependent cross sections:

$$\overline{\sigma_f^{\text{iso}}}(v) = \int_0^{\pi/2} d\alpha \sin \alpha \sigma_f^{\text{iso}}(v; \alpha) \quad (10)$$

3 Dynamical calculations

We have carried out calculations in the range of 0.2—50 keV/amu with molecular data calculated keeping $\rho = 2$ a.u. and $\alpha = 60^\circ$, whose PES are depicted in Fig. 2. The states included in the singlet subsystem calculation (ordered

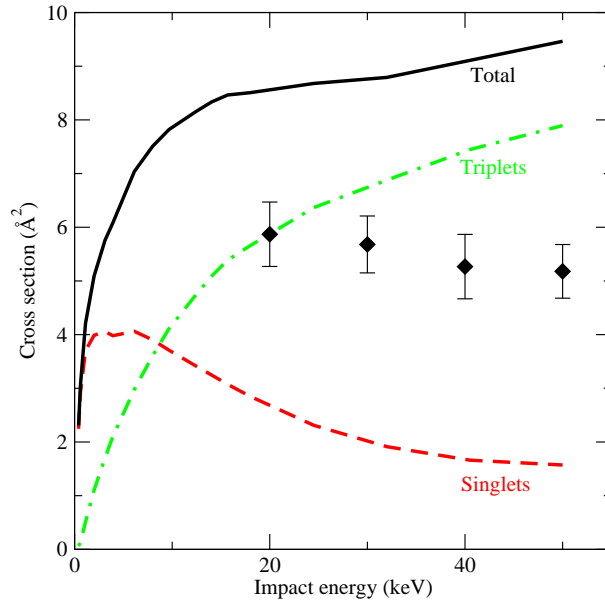


Fig. 3. Cross sections for CT in $\text{H}_2^+ + \text{H}(1s)$ collisions. Lines are the singlets and triplets contribution to the total CT cross section, as indicated in the figure, calculated using the isotropic approximation for $\alpha_0 = 60^\circ$ and $\rho = 2.0$ a.u.. Symbols are the EL cross sections obtained from the sum of the experimental results of Ref. [3] for CT and target and projectile ionization processes.

by increasing energy) are those correlated, at $R \rightarrow \infty$, to $\text{H}_2(1\sigma_g^2; X^1\Sigma_g^+) + \text{H}^+$, $\text{H}_2^+(1\sigma_g; X^2\Sigma_g^+) + \text{H}(1s)$, $\text{H}_2(1\sigma_g1\sigma_u; B^1\Sigma_u^+) + \text{H}^+$, $\text{H}_2^+(1\sigma_g; X^2\Sigma_g^+) + \text{H}(2l)$, $\text{H}_2(1\sigma_g1\pi_u; C^1\Pi_u) + \text{H}^+$, $\text{H}_2(1\sigma_g2\sigma_g; EF^1\Sigma_g^+) + \text{H}^+$ and $\text{H}_2^+(1\sigma_u; B^2\Sigma_u^+) + \text{H}(1s)$, while those in the triplet subsystem are: $\text{H}_2^+(1\sigma_g; X^2\Sigma_g^+) + \text{H}(1s)$, $\text{H}_2(1\sigma_g1\sigma_u; b^3\Sigma_u^+) + \text{H}^+$, $\text{H}_2(1\sigma_g1\pi_u; c^3\Pi_u) + \text{H}^+$, $\text{H}_2(1\sigma_g2\sigma_g; a^3\Sigma_g^+) + \text{H}^+$, $\text{H}_2^+(1\sigma_g; X^2\Sigma_g^+) + \text{H}(2l)$, $\text{H}_2(1\sigma_g2\sigma_u; f^3\Sigma_u^+) + \text{H}^+$, and $\text{H}_2^+(1\sigma_u; B^2\Sigma_u^+) + \text{H}(1s)$. Due to our expansion not containing electronic continuum wave functions, ionization cross sections cannot be separated from CT ones [14]. This means that our results should be compared with the experimental electron-loss (EL) cross sections at energies where ionization is not negligible.

The calculated cross sections obtained for $\alpha_0 = 60^\circ$ and $\rho = 2.0$ a.u. (that is, the equilibrium distance yielding the Franck-Condon (FC) approximation), are presented in Fig. 3 for the singlet, triplet and combined systems; they clearly disagree with the EL cross sections obtained from the experimental results of Ref. [3], and the discrepancy comes from the triplet contribution, which does not fall as energy increases above 20 keV.

We have also carried out calculations by applying the sudden approximation (Eq. (4)), both with $\nu = 0$ and $\nu = 1$, and for $\alpha_0 = 60^\circ$, which yielded results very close to the FC ones. Therefore, we conclude that the discrepancy with the experiment, at these energies, is not due to vibrational effects or to vibrational excitation in the H_2^+ beam.

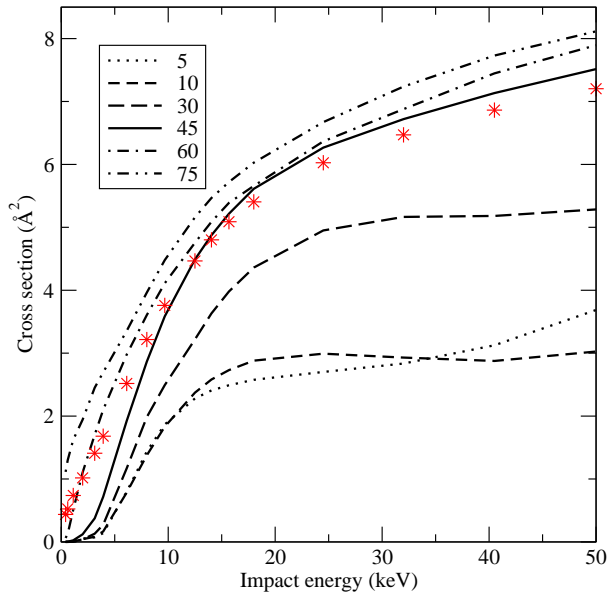


Fig. 4. Total cross sections (only triplets) for CT calculated using the FC ($\rho = 2$ a.u.) and the isotropic approximations for several values of the angle α (in degrees), as indicated in the figure. \star is the ρ -dependent isotropic average (see Eq. (10)).

The remaining approximation in our treatment is the isotropic approximation; To study the influence of anisotropy effects on the cross section, we first study the variation with α of the ρ -dependent cross sections. A first test is shown in Fig. 4, where we have plotted the contribution of the triplet subsystem to the CT cross section $\sigma_{CT}^{iso}(v; \rho = 2, \alpha)$ for several values of α . When the impact energy is not small, the triplet contribution dominates the cross section and, in this subsystem, the transition takes place in the neighborhood of $R = 2$ a.u., where the PES and couplings are highly anisotropic, leading to a variation with α of the cross section. However, the α average of the procedure of Eq. (10) yields a cross section very close to the value calculated with $\alpha_0 = 45^\circ$, and therefore does not explain the disagreement with the experiment. We thus concluded, that a possibility of error lays in the angle averaging of Eq. (10). Accordingly, we have evaluated trajectory-averaged cross sections using the procedure of Eq. (7).

Given the complexity of applying Eq. (7), which would require the parametrization of multiple conical intersections to generate energies and dynamical couplings for a large number of projectile trajectories, we have tested the possibility of reducing the basis set to a 3-state basis, for the singlet subsystem, that includes the entrance channel and the exit channels dissociating into $H_2(X^1\Sigma_g^+) + H^+$ and $H_2(B^1\Sigma_u^+) + H^+$, and a 2-state basis for the triplet subsystem, with the entrance channel and the exit channel that dissociates into $H_2(b^3\Sigma_u^+) + H^+$. The difficulty with this procedure is that one can only compare then inelastic cross sections which contain a sizeable contribution coming from excitation. Nevertheless, we have found that the extra states in

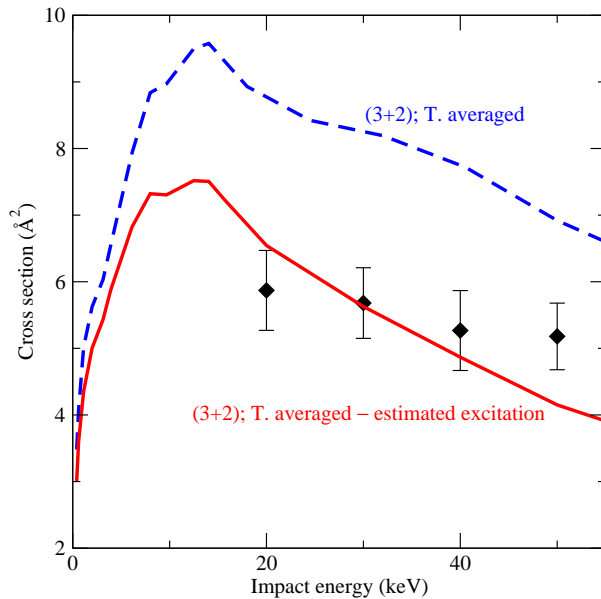


Fig. 5. FC trajectory-averaged (dashed line) total cross sections for CT calculated using the (3+2) (singlets+triplets) molecular basis (see text). The solid line is the “net estimated” (see text) EL cross section contained in the (3+2) calculation. Symbols for the experimental data as in Fig. 3.

the (9+9)-basis respect the (3+2) one, are populated mainly in a two-step mechanism via the first excited state. Therefore, any anisotropic effect on the (9+9) calculations would be also observed in a calculation using the smaller basis.

Our results, using Eq. (7) with the (3+2) molecular basis are displayed in Fig. 5, along with the experimental EL cross sections. It can be noted that the trajectory-averaged cross sections show an energy dependence similar to that of the experimental values. The difference between our results and the experiments can be explained from the fact that the reduced basis set does not include either target or projectile excitation channels, so that, as explained before, the data of Fig. 5 would really correspond to an inelastic cross section. To estimate the contribution from excitation to this cross section we can assume that the ratio between excitation and inelastic cross section obtained with the large (9+9) basis set is similar to that with the reduced basis. Furthermore, the ratio obtained with the large basis is approximately constant for the different orientations, so that it is reasonable to assume that it also holds for an anisotropic calculation. By using this ratio, we obtain our final estimated EL cross section, which is presented in the same figure.

We have also studied the reason why Eq. (7) should be used rather than Eq. (10) to perform the angle averaging. The main difference stands from trajectory effects, which are particularly relevant for the present system, because the coupling terms between the entrance channel, $H_2^+(1\sigma_g)+H(1s)$, and

the CT one, $H_2(1\sigma_g 1\sigma_u)+H^+$, vanish along trajectory TIII, for symmetry reasons. This lowers the CT cross section in triplets considerably because the mentioned CT channel is the dominant one.

4 Concluding remarks

We have calculated the electron-loss cross sections in collisions of $H_2^+ + H(1s)$ using several approximations in the dynamical treatment. We have seen that it is crucial to account explicitly for the anisotropy of the system in the dynamical treatment. This anisotropy is important in the present case because at high impact energies the CT cross section is dominated by the triplets subsystem, and it so happens that the CT channel that is energetically closest belongs to a different irreducible representation to that of the entrance channel for some nuclear geometries of C_{2v} symmetry. We thus have an additional selection rule for these geometries and this lowers the cross section. The two features (transitions at small R , and an additional selection rule) determine the brake-down of the simple angle-averaging of Eq. (10).

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