Theoretical studies of reactive scattering processes involving the H_2 reaction complex

J Hörnquist[1]*, P Hedvall[1] Å Larson[1] and A E Orel[2]

[1]Department of Physics, Stockholm University, AlbaNova University Center, SE-106 91 Stockholm, Sweden
[2]Department of Chemical Engineering, University of California, Davis, California 95616, USA

Synopsis We study mutual neutralization of $H^+ + H^-$ *ab initio* and fully quantum mechanically including effects which have not previously been considered such as rotational couplings and autoionization from electronic resonant states. A quasidiabatic model is developed to investigate the role of autoionization and higher excited states. This model can also be used to study a variety of other processes and is here applied in a study of associative ionization in collisions of $H^+ + H^-$ and $H(1s) + H(ns)$.

The mutual neutralization process $H^+ + H^- \rightarrow H(1s) + H(n)$, where n is the principal quantum number, is important for understanding H_2 formation in the early universe [1]. Here, this process is studied *ab initio* and fully quantum mechanically and the total and differential cross sections as well as the branching ratios are calculated. These calculations include effects which have not previously been considered, such as rotational couplings that couple $^1\Sigma^+_{g/u}$ states to $^1\Pi_{g/u}$ states, excited states correlating with the $n \geq 4$ asymptotic limits and autoionization from electronic resonant states. We use accurate *ab initio* potential curves and couplings to describe the lower electronic states while a quasidiabatic model is developed to include the lowest electronic resonant state in each relevant symmetry as well as an arbitrary number of Rydberg states. With this model, we investigate the importance of higher excited states and the role of autoionization. While the inclusion of rotational couplings is found to be important, the effect of autoionization and higher excited states is shown to be small for this particular system [2].

Since the model includes couplings between bound electronic states as well as electronic resonant states and couplings to the ionization continuum, it can also be used to study other processes such as double charge transfer, dissociative recombination, resonant ion-pair formation and associative ionization. We also present the results of a study of the associative ionization processes $H^+ + H^- \rightarrow H_2^+ + e^-$ and $H(1s) + H(ns) \rightarrow H_2^+ + e^-$. For these processes we investigate the importance of non-local effects by including a non-local complex potential.

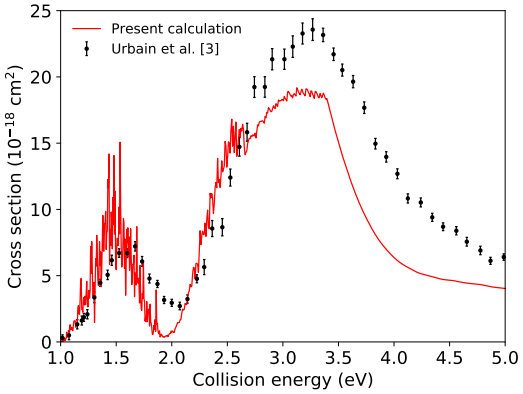

Figure 1. Calculated $H(1s)+H(2s)$ associative ionization cross section compared with the measurement of Ref. [3].

References

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*E-mail: johan.hornquist@fysik.su.se