exceptional agreement. In addition, agreement is good for the theoretical and experimental probabilities for the dissociation reaction that accompanies chemisorption of H₂ on platinum (illustrated in Fig. 1). This is strong evidence for the applicability of the theory. The comparison also suggests that an electronically adiabatic theory — a theory that considers electronically excited states as insignificant — is sufficient to predict and explain the experimental observables for this reaction.

Examination of the potential energy surface provides an explanation as to why the electronically adiabatic theory is sufficient. The energy available to the reactants is not significantly enhanced as the chemisorption energy is relatively small. This seems to be a general feature for the interaction of H₂ with metal surfaces. It is related to the fact that H₂ cannot easily accept electrons from the metal, in contrast to molecules such as NO. Other calculations on the probability of electronic excitations in H₂/metal systems confirm this view.

The one slight weakness is that density functional theory has been used to calculate the potential energy surface. Comparison with highly accurate ab initio quantum chemistry calculations for simple gas phase reactions shows that density functional theory does not always predict reaction barriers accurately. But the extensive comparisons that have now been done between theory and experiment for the H₂/metal system do suggest that the density functionals used for this system are reliable.

The conclusions of this study are good news for the theoretical treatment of scattering and reactions of molecules such as H₂ on metal surfaces. The use of the idea of the potential energy surface has held up well and the prospects for extending this type of rigorous quantum theory to other molecule–surface systems are promising. This might include dissociations of more complicated — and highly industrially relevant — molecules such as NH₃ and CH₄ on platinum and other metals.

REFERENCES