PERSPECTIVES: REACTION DYNAMICS

Bending or Breaking the Rules?

David E. Manolopoulos

On page 715 of this issue, Alexander *et al.* (*1*) consider the dynamics of an elementary chemical reaction. Unusually, they do so without making the assumption that the Born-Oppenheimer approximation—a key simplifying step in quantum mechanics that underlies the way we think about molecules—holds. The results point to an unresolved discrepancy between experiment and theory.

The Born-Oppenheimer approximation (*2*) is based on the observation that, because electrons are over a thousand times less massive than nuclei, they move much more quickly in a molecule. Hence, when the nuclei move, the electrons adjust almost instantaneously to the new nuclear positions. In quantum mechanical terms, this means that the electronic wavefunction evolves adiabatically (without changing state) as the nuclei move, whereas the nuclei experience a time-averaged potential from the electrons. The motion of the electrons can therefore be separated from that of the nuclei, simplifying the theoretical description of a molecule.

The Born-Oppenheimer approximation is known to fail in some situations, especially where excited electronic states are involved. The internal conversion between two singlet electronic states in a photochemical reaction is a textbook example of an electronically nonadiabatic transition (*3*). However, the adiabatic approximation is generally believed to be a reliable tool for predicting the outcome of bimolecular reactive collisions (*4, 5*), and the vast majority of theoretical studies of bimolecular reactions has been carried out within the framework of this approximation.

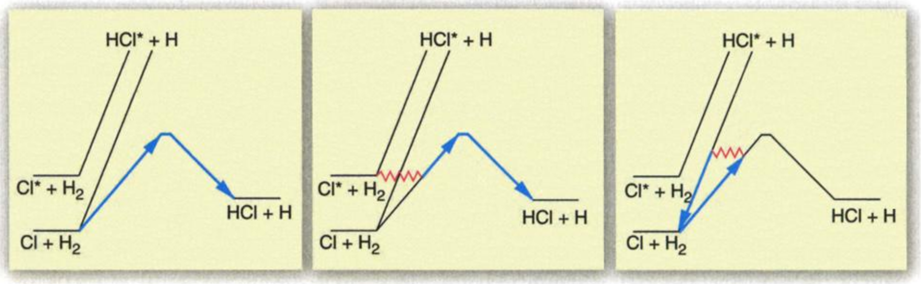
Alexander *et al.* break this mold (*1*). In their state-of-the-art electronic structure and quantum scattering calculations of the reaction between a chlorine atom and molecular hydrogen

$$\mathrm{Cl} + \mathrm{H_2} \rightarrow \mathrm{HCl} + \mathrm{H} \qquad (1)$$

they explicitly allow for the effect of electronic nonadiabaticity. The first model calculations of this kind were performed many years ago (*6*, *7*), and the underlying theory has been established for some time (*8*). However, full ab initio calculations of electronic nonadiabaticity have previously only been performed for the reactions between a chlorine atom and hydrogen chloride (*9*) and between a fluorine atom and molecular hydrogen (*10*).

The motivation for studying the reaction of Cl with H_2 comes from a recent experiment by Liu and co-workers (*11*), who found that the spin-orbit excited state of the chlorine atom, Cl*, was more reactive than the ground state, Cl. This result is surprising, because it breaks the rule that the adiabatically-allowed reaction pathway always dominates (*4, 5*). The reaction of Cl* with H_2 can only produce the ground state of the HCl molecule via an electronically nonadiabatic transition, whereas the reaction of Cl with H_2 to form HCl can proceed adiabatically (see the figure).

The calculations reported by Alexander *et al.* reveal an electronically nonadiabatic effect in the Cl + H_2 reaction, although it is not as pronounced as that seen by Liu and co-workers. The calculations predict that the reactivity of the ground state Cl atom will be reduced by an electronically nonadiabatic transition in the reactant valley. This nonadiabatic transition (see the figure) gives rise to inelastic scattering back to the Cl + H_2 reactants, a process that competes with the forward reaction. Electronic nonadiabaticity is thus found to have an indirect effect on the reactivity by enhancing inelastic scattering.



Adiabatic and nonadiabatic pathways. (Left) Adiabatic reaction of Cl with H_2. **(Middle)** Nonadiabatic reaction of Cl* with H_2. **(Right)** Nonadiabatic inelastic scattering pathway identified by Alexander *et al.* (*1*). Nonadiabatic transitions are represented by zigzag lines, excited electronic states by stars.

This result is consistent with earlier theoretical work on nonadiabatic effects in inelastic collisions between halogen atoms and molecular hydrogen. The classic example is the inelastic energy transfer process

$$\mathrm{F^*} + \mathrm{H_2}(j = 0) \rightarrow \mathrm{F} + \mathrm{H_2}(j = 2) \qquad (2)$$

in which the spin-orbit energy of a fluorine atom is transferred into rotational energy of a hydrogen molecule, increasing its rotational quantum number j from 0 to 2. This process was predicted to be very efficient in early calculations by Rebentrost and Lester (*7*), whose prediction has been confirmed by more exact calculations (*10*). It is so efficient because the relevant electronic time scale—Planck's constant divided by the fluorine atom spin-orbit splitting—is comparable in this case to the time scale of the nuclear motion.

The calculations of Alexander *et al.* do not, however, agree with the experiments of Liu and co-workers (*11*) with regard to the reactivity of Cl*. Despite the predicted decrease in Cl reactivity as a result of nonadiabatic inelastic scattering, the calculations find Cl to be substantially more reactive than Cl* at all but the very lowest collision energies (*1*). The theoretical results thus favor the usual adiabatic reaction pathway (*4*, *5*).

The discrepancy between experiment and theory is substantial: The calculations imply that the Cl + H_2 reaction obeys the adiabatic rule, whereas the experimental observations suggest otherwise. Tanaka *et al.* previously observed an exception to the adiabatic rule in an experimental study of the reaction between an argon cation (Ar^+) and a hydrogen molecule (*12*). The cation Ar^+ has the same number of electrons as Cl and a very similar nuclear mass and spin-orbit splitting. Their study lends support to the experimental observations of Liu and co-workers, but the arguments in favor of the theoretical result are equally strong. It remains to be seen how the disagreement will be resolved.

References

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The author is in the Physical and Theoretical Chemistry Laboratory, South Parks Road, Oxford OX1 3QZ, UK. E-mail: mano@physchem.ox.ac.uk