Theoretical dynamics of the S($^1$D)+H$_2$ reaction in conditions approaching the cold regime

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Quantum nuclear dynamics calculations on ab initio potential energy surfaces are very accurate, but mostly unfeasible for processes involving more than 3 or 4 atoms.

The quasi-classical trajectory method (QCTM) is a very friendly alternative, easy to code, not limited by the number of atoms and provides insight. Obviously, QCTM lacks realism when quantum effects arise.

For about two decades, we try to incorporate quantum corrections in QCTM in the light of the semiclassical theory of molecular scattering (Miller, Marcus, Heller...).


Here, we discuss a major effect seen in the benchmark insertion reaction $S(^1D) + H_2(v=j=0)$ under conditions approaching the cold regime. This effect is due to ro-vibrationally adiabatic non reactive trajectories.
Potential energy profile:

\[ S^{(1D)} + H_2 \rightarrow 1^{1}A' \rightarrow 3.90 \text{ eV} \rightarrow \text{SH} + H \rightarrow 0.30 \text{ eV} \]
Initial conditions:

\[ J/\mu \nu = b \]

\( J \): total angular momentum
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\[ J/(\mu v) = b \]

\( J \) : total angular momentum

\( \theta = \pi/2 \)

Coplanar dynamics:

\[ q = p/2 \]

Graph showing reaction probability in terms of \( J \) at \( E = 1127K \).
\( R > 2.5 \, \text{Å} \)

\[ H \approx E_v + H_{TR} \]

\[ H_{TR} \approx \frac{P^2}{2\mu} + \frac{j^2}{2mr_e^2} + V_J(R, \phi) \]

\[ V_J(R, \phi) = V(R, r_e, \phi) + \frac{J^2}{2(\mu R^2 + mr_e^2)} \]
Let us ignore ro-vibrationally adiabatic non reactive trajectories: Adiabaticity Correction (AC).

A clear justification of this correction is still lacking...
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