

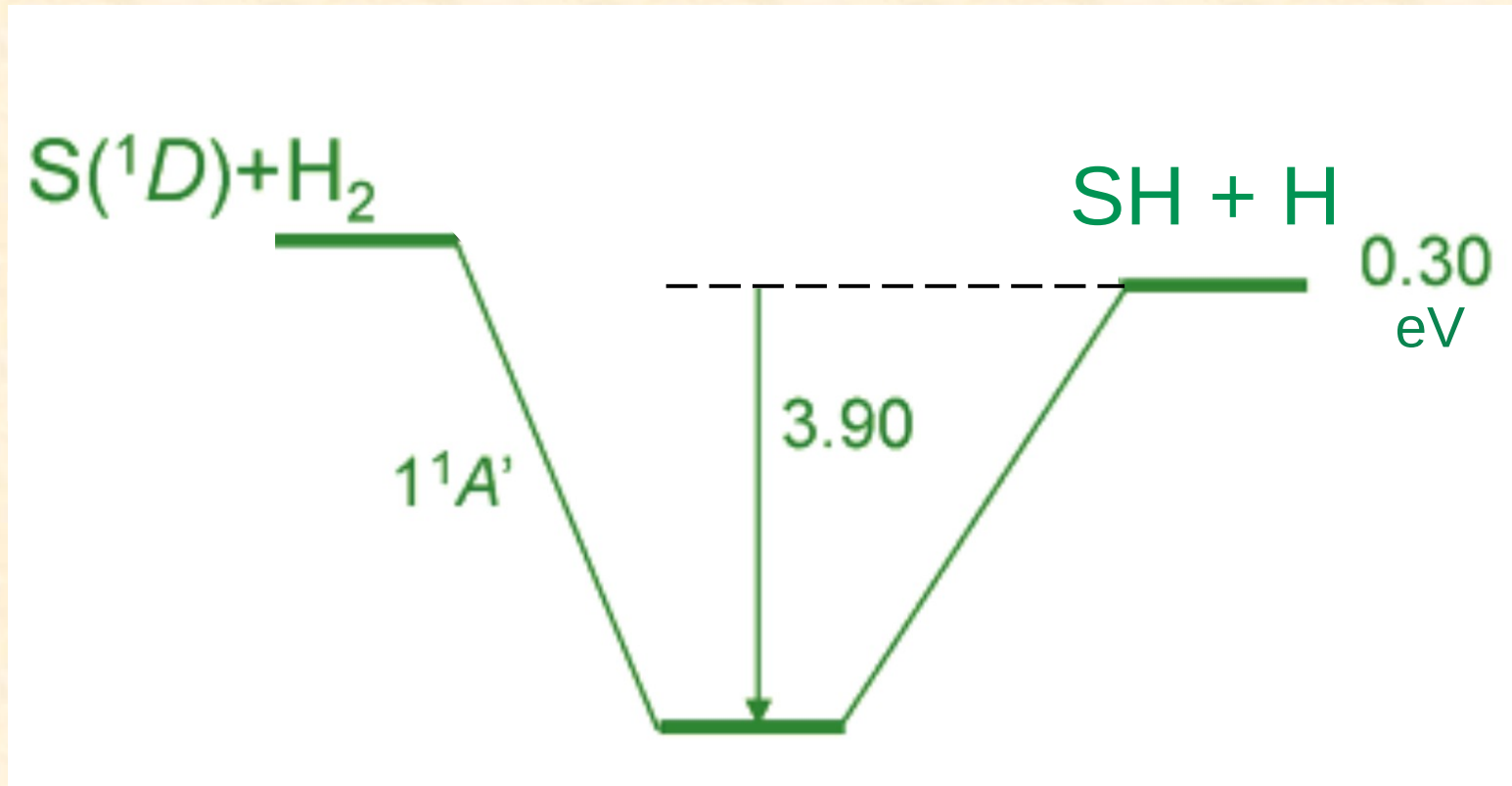
Theoretical dynamics of the $S(^1D)+H_2$ reaction in conditions approaching the cold regime

L. Bonnet

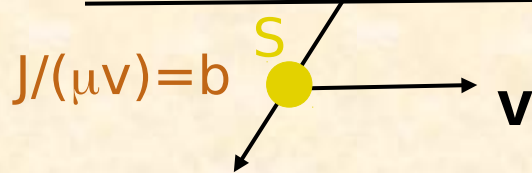


- Quantum nuclear dynamics calculations on ab initio potential energy surfaces are very accurate, but mostly unfeasible for processes involving more than 3 or 4 atoms.
- The quasi-classical trajectory method (QCTM) is a very friendly alternative, easy to code, not limited by the number of atoms and provides 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...).
- For a recent work on the link between S-matrix elements and classical paths : L. Bonnet, J. Chem. Phys. 158, 114112 (2023).
- 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.

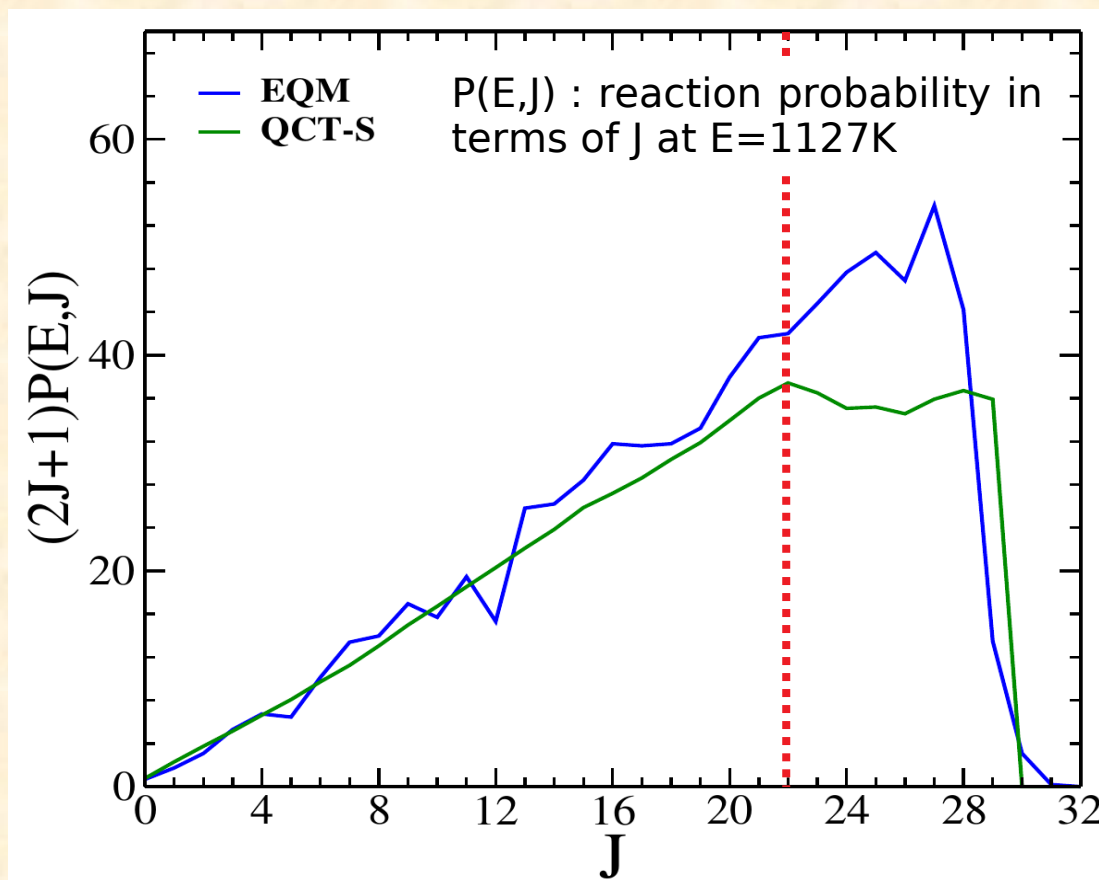
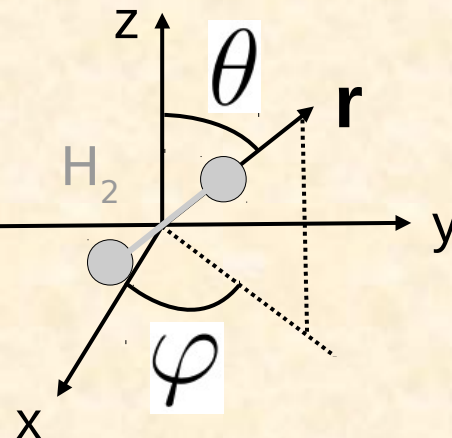
→ Potential energy profile :



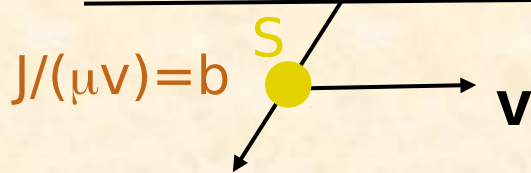
→ Initial conditions:



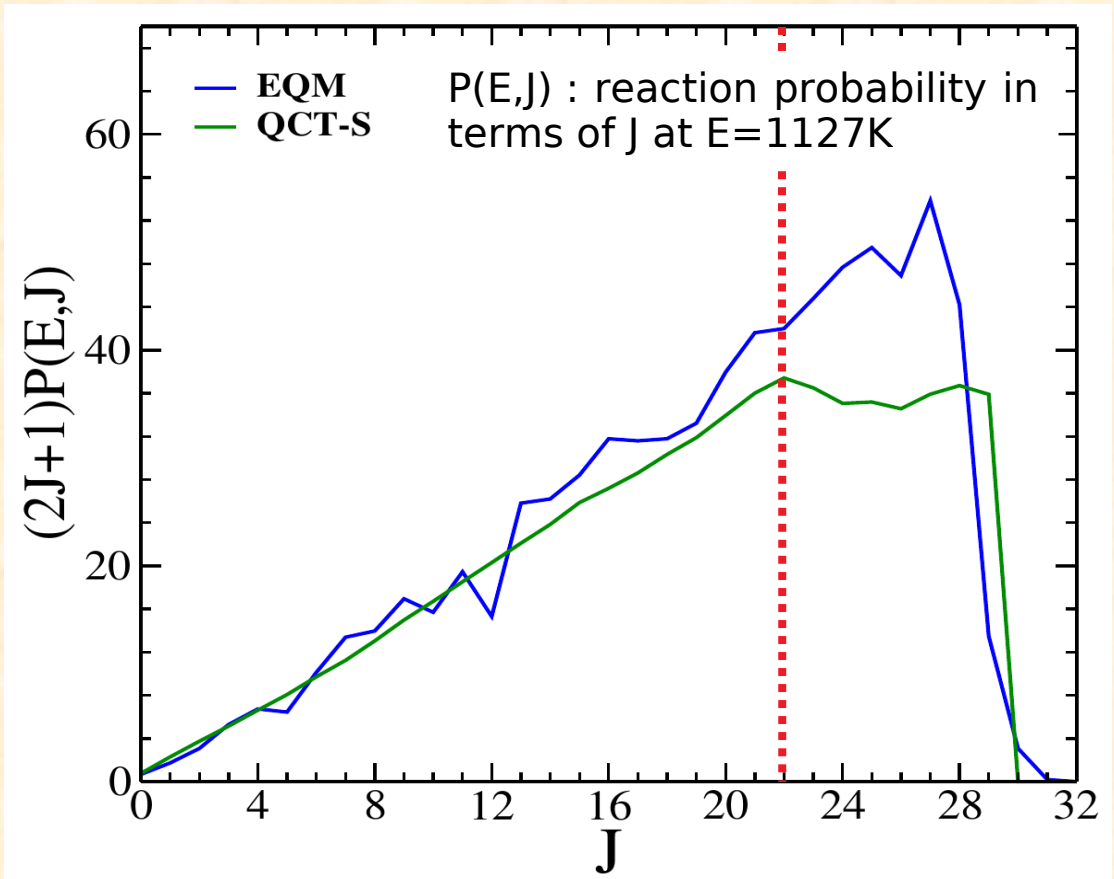
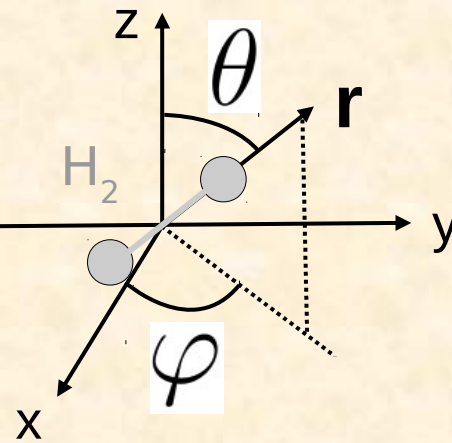
J : total angular momentum



→ Initial conditions:

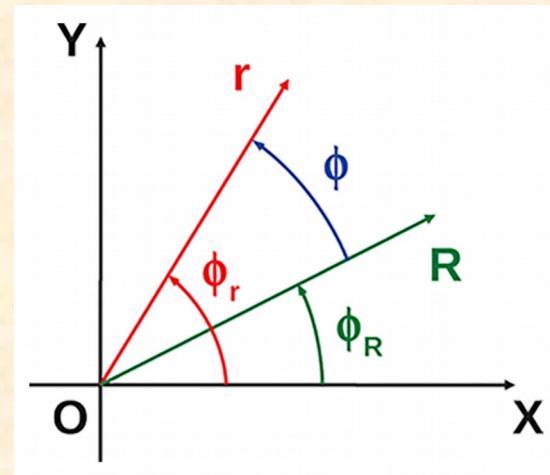
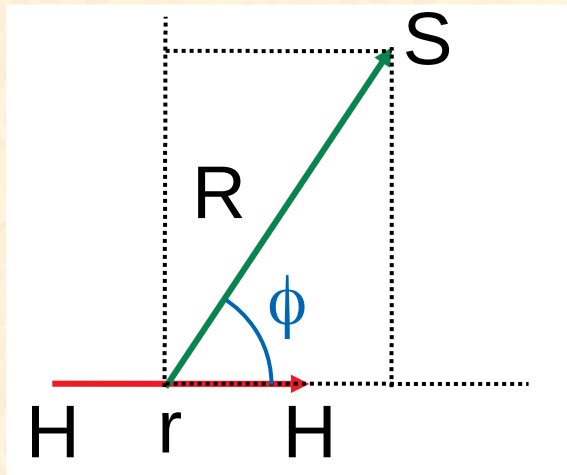


J : total angular momentum



Coplanar dynamics :

$$\theta = \pi/2$$

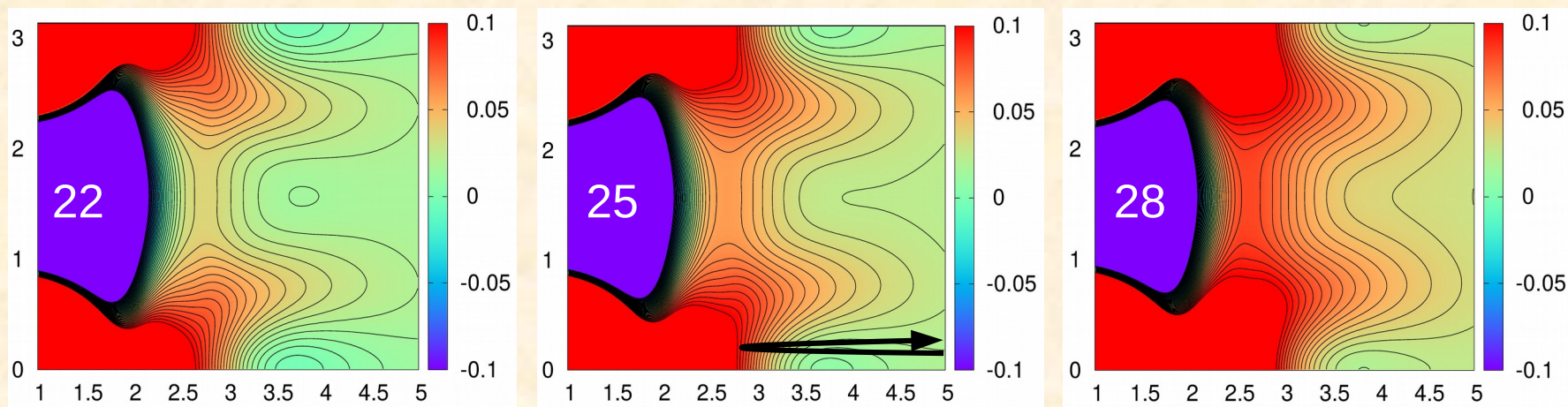
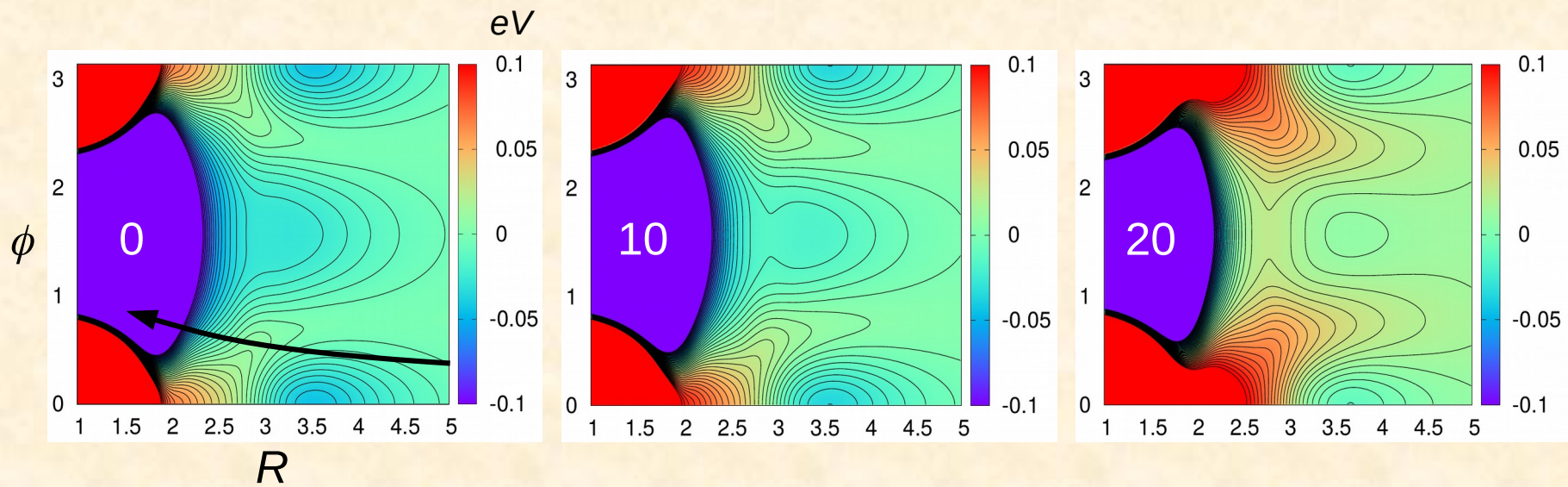


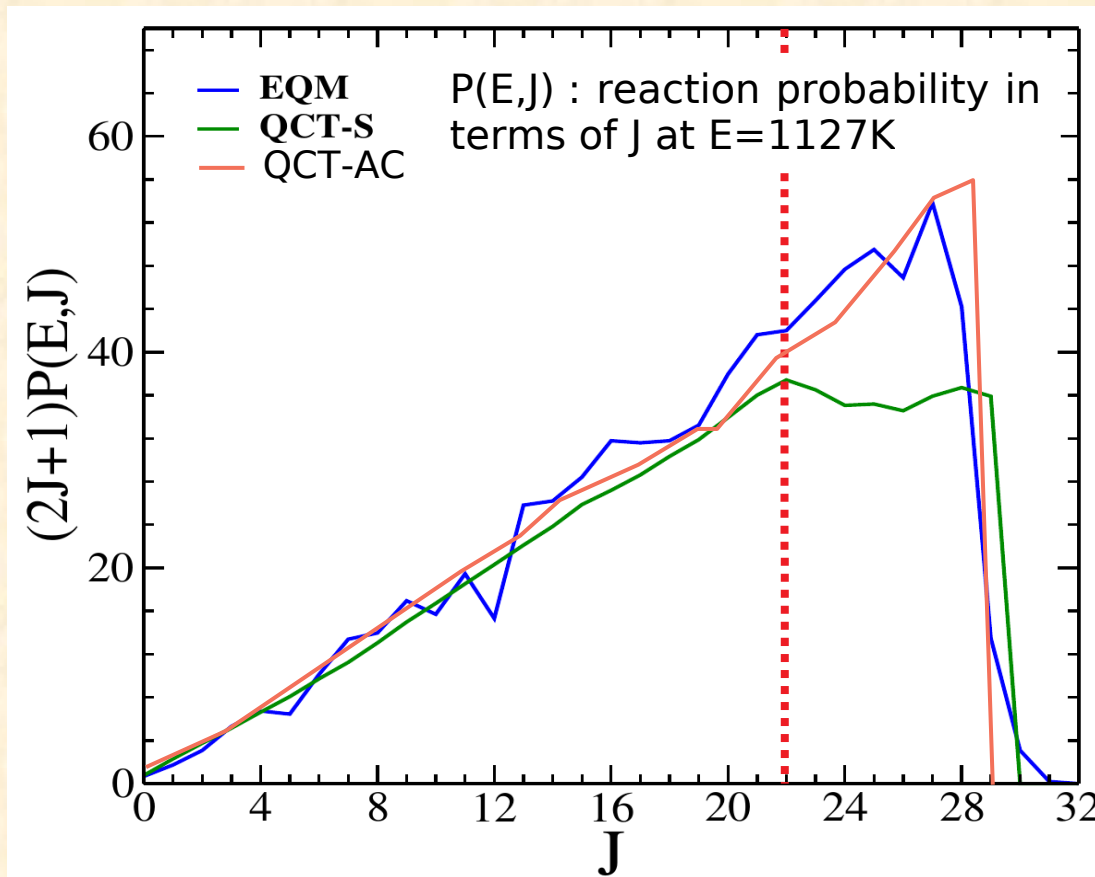
$$R > 2.5 \text{ \AA}$$

$$H \approx E_v + H_{TR}$$

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

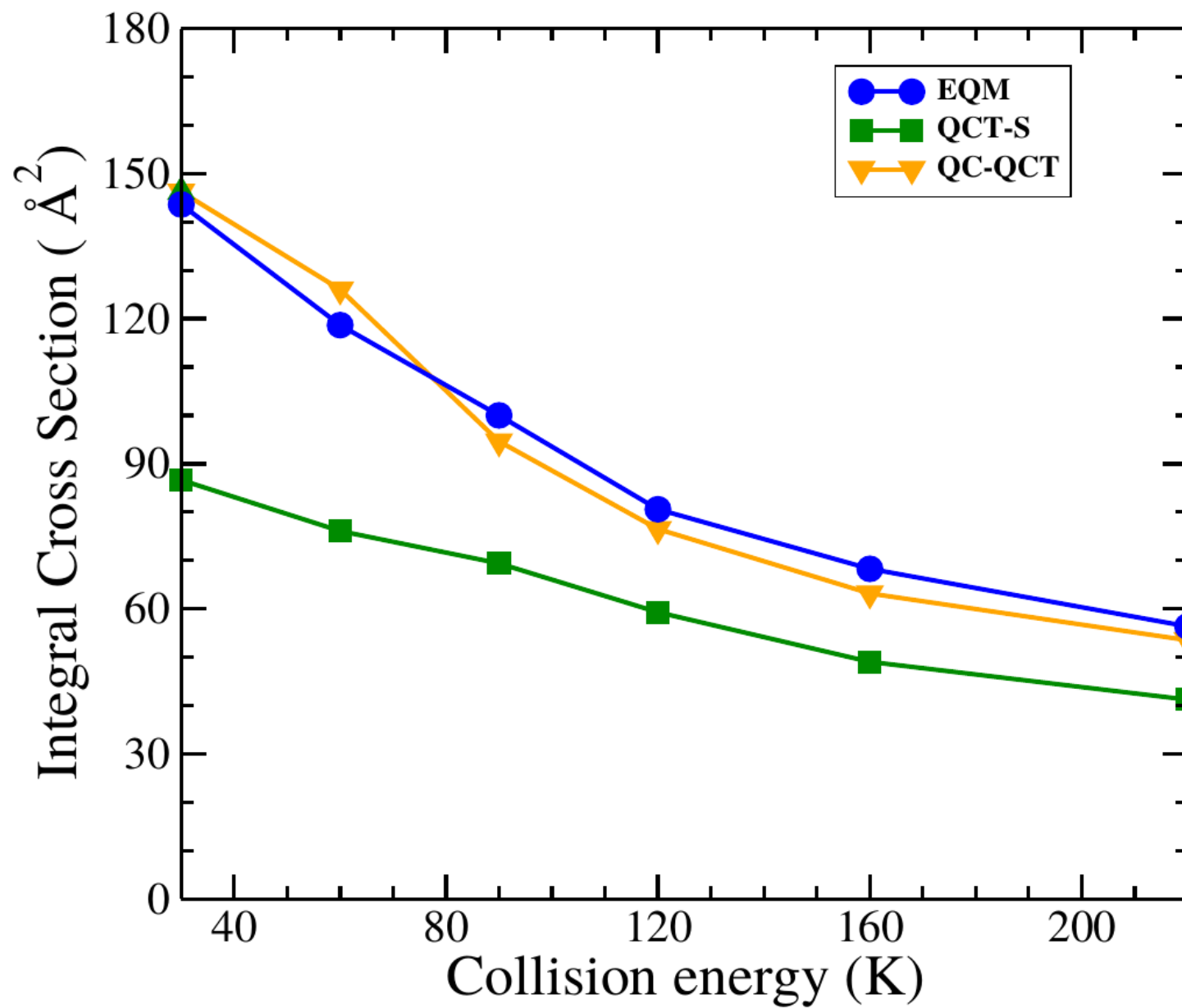
$$V_J(R, \phi) = V(R, r_e, \phi) + \frac{J^2}{2(\mu R^2 + mr_e^2)}$$





→ Let us ignore ro-vibrationally adiabatic non reactive trajectories : Adiabaticity Correction (AC).

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



Maurice Monnerville, Lille

Pascal Larrégaray, Bordeaux

Cédric Crespos, Bordeaux

Laura Viaud, Bordeaux