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Ro-vibrational excitation of H₂ by H for high temperature regime

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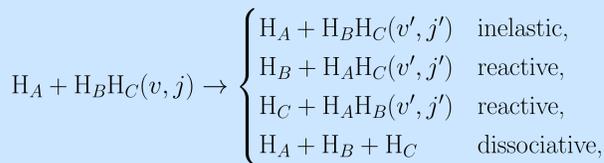
*e-mail : duncan.bossion@umontpellier.fr



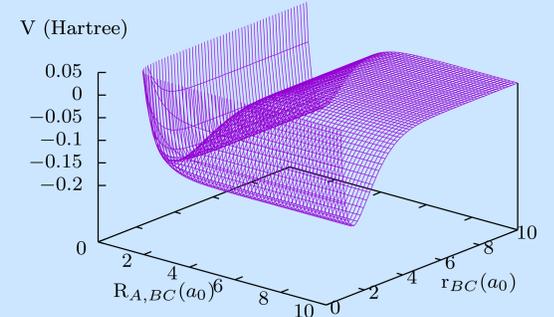
Context : H+H₂ collisions

Accurate knowledge of the abundance of H₂ molecules is crucial for the thermal balance of astrophysical media (early Universe, post-shock regions,...). Need to study the main collisions leading to the formation/destruction of H₂ molecules for temperature ranging from few Kelvins (interstellar medium) to high temperatures (15 000 K). There is low to moderate (5000 K) temperature regime studies using quantum mechanical approaches (TIQM)[1] with an accurate H₃ potential energy surface[3].

Objectives : Study the effects of high energy collisions of H₂ by H compared to low to moderate temperature regimes. Molecular hydrogen is ortho hydrogen (nuclear spin ↑↑ : odd rotational quantum numbers) or para hydrogen (nuclear spin ↑↓ : even rotational quantum numbers).



Ortho-para-H₂ ratio important for the cooling mechanism of H₂,
reactive collision is the only process for the ortho-para-H₂ conversion.



Quasi-Classical Trajectory (QCT) calculation

- State-to-state calculations on our own QCT code,
- Initial ro-vibrational quantum states (v, j) with energies ranging from 0 to 50 000 K,
- Nuclear dynamics solving Hamilton's equations of motion,
- Collisional energies E_{col} ranging from 0.025 Hartree (0.068 eV) to 0.18 Hartree (4.9 eV) every 0.005 Hartree (0.136 eV),
- Assignment of final ro-vibrational state using a standard binning method[4],
- All final ro-vibrational bounded states (v', j') taken into account,
- Cross section function of the reactive probability P_r :

$$P_r(v, j \rightarrow v', j'; b, E_{col}) = \frac{N_r(v', j'; b, E_{col})}{N(v, j; b, E_{col})};$$

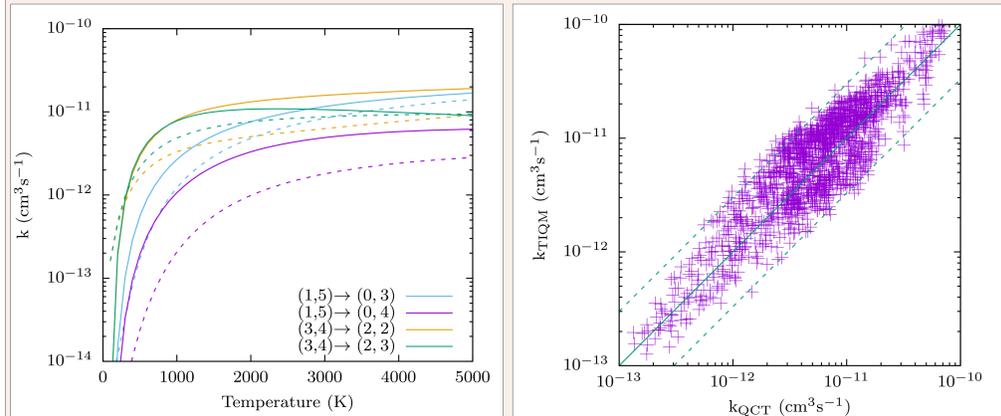
$$\sigma_{v', j' \leftarrow v, j}(E_{col}) = \pi b_{max}^2 P_r(v, j \rightarrow v', j'; E_{col})$$

- State-to-state rate constant :

$$k_{v', j' \leftarrow v, j}(T) = \left(\frac{8k_B T}{\pi \mu_{A,BC}} \right)^{1/2} \frac{1}{(k_B T)^2} \int_0^\infty \sigma_{v', j' \leftarrow v, j}(E_{col}) E_{col} \exp\left(-\frac{E_{col}}{k_B T}\right) dE_{col}$$

b impact parameter, N_r number of reactive trajectories, N total number of trajectories, k_B boltzman constant and $\mu_{A,BC}$ the reduced mass of the system.

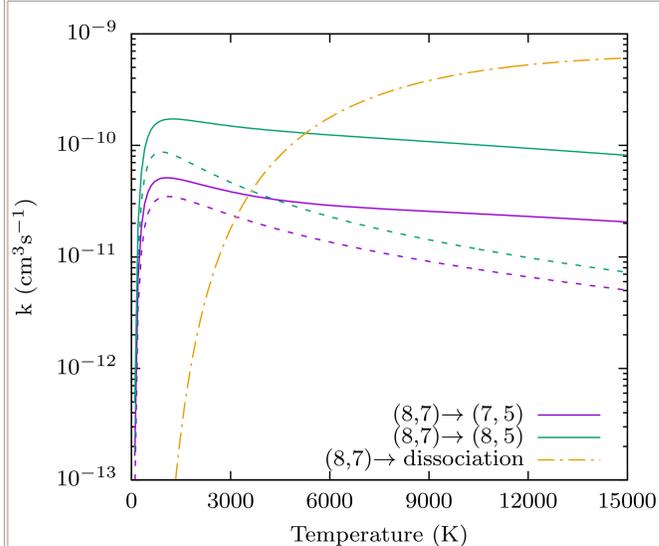
Comparison QCT-TIQM



Left : rate constants results for QCT (solid lines) and TIQM (dashed lines), $(v, j) \rightarrow (v', j')$; right : comparison between QCT and TIQM rate constants at 5000 K.

- Agreement between TIQM[1] and QCT calculations below a factor of 3 for spin conversion process (reactive collisions) as for spin conservation process (inelastic + reactive collisions),
- Allows to extend the QCT calculations above the energies reachable using quantum methods.

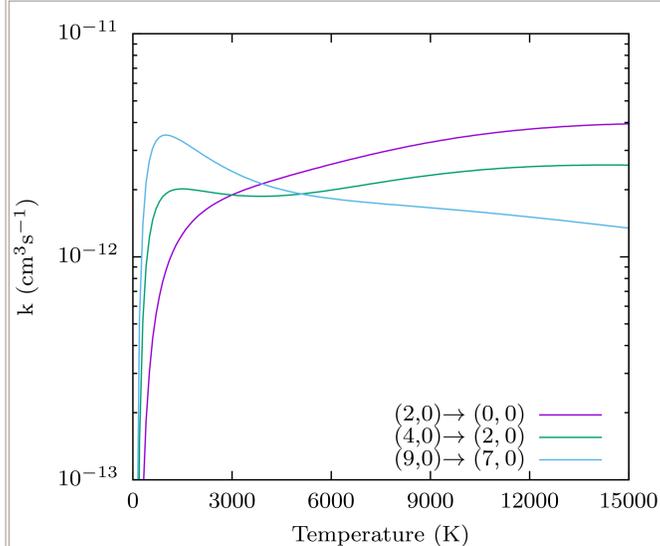
Dissociation and reactive process



QCT rate constants, solid lines : spin conserving transitions, dashed lines : reactive process, dotted-dashed line : dissociation process, $(v, j) \rightarrow (v', j')$.

- Dissociation dominates the state-to-state transitions (spin conservation and conversion processes) above few thousands of Kelvins for the collisions involving quantum states of internal energies above 3.5 eV,
- De-excitation rate constants increase with the internal energy of the final quantum state,
- Rate constant for the reactive process dominates the collisions around 1000 to 3000 K,
- Inelastic process dominates for low total energy collisions (low collisional energy and/or low initial state energy) and also for the high temperature regime (high collisional energy and/or high initial state energy).

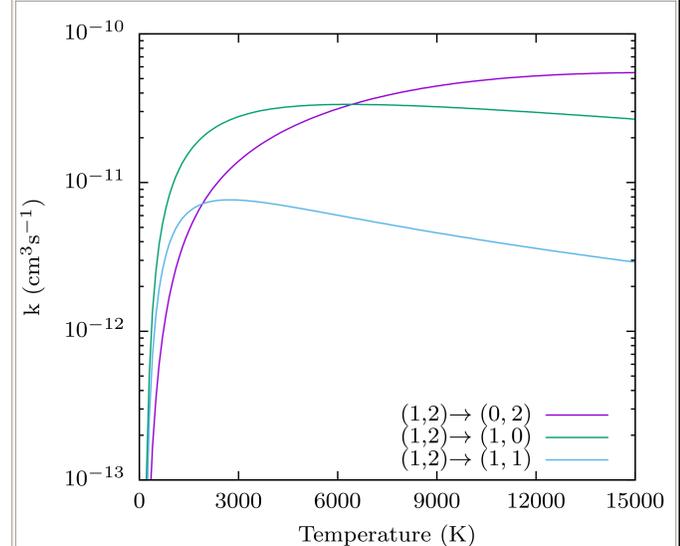
Pure vibrational de-excitation



QCT rate constants for $\Delta v = 2$, purely vibrational de-excitations, $(v, j) \rightarrow (v', j')$.

- Initial internal energy (ro-vibrational state) of the molecule contributes the most to the rate constant at low to moderate temperature collisions,
- Collisional energy leads the rate constant at high temperature (compared to internal energy),
- Leads to a crossing between high internal energy rate constants and high collisional energy rate constants,
- Concerning high internal energy states (see $(4, 0) \rightarrow (2, 0)$) : inelastic collisions dominates high temperature (with dissociation) \rightarrow minimum of the rate constant around 5000 K,
- Similar for ro-vibrational de-excitations (for small Δj).

High energy ro-vibrational study



QCT rate constants, ro-vibrational versus purely rotational de-excitations, $(v, j) \rightarrow (v', j')$.

- Ortho-para-H₂ and para-ortho-H₂ conversion processes (only reactive collisions) always slower than spin conservation processes (reactive + inelastic collisions) as expected[2] for all the temperature range considered,
- Purely rotational de-excitations faster than ro-vibrational de-excitations for low collisional energy collisions,
- For high collisional energy collisions (lot of energy to store into internal energy) as $\Delta E_v > \Delta E_j$, ro-vibrational de-excitations faster,
- Leads to a crossing between purely rotational de-excitation and ro-vibrational de-excitation rate constants moving to higher temperature with higher initial internal energy.

Conclusion

- Low to moderate temperature rate constants behavior should not be extrapolated for high temperature regime due to a non-monotonic evolution of the state-to-state rate constants,
- Dissociation process cannot be neglected for the high temperature regime[4].

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2. S.L. Mielke, B.C. Garrett, K.A. Peterson, J. Chem. Phys., 116, 4142 (2002)
3. D.G. Truhlar, J.T. Muckermann in R.B. Bernstein ed., Atom-Molecule Collision Theory,
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