

Theoretical rate constants may not be useful for kinetics models: The fate of OH in the combustion of a hydrogen/oxygen mixture

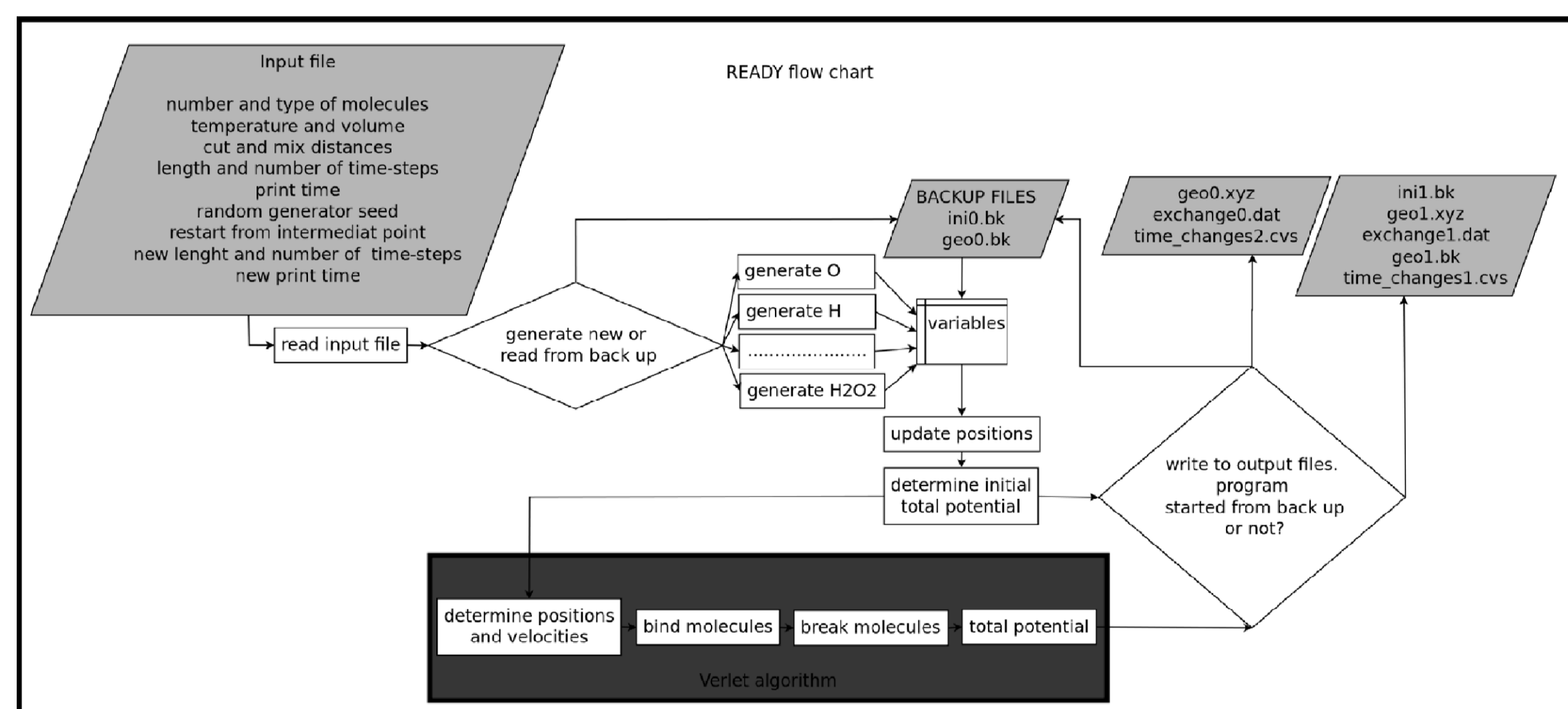


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In a gas phase combustion or explosion, reactants and intermediates can be far from thermal equilibrium, i.e., the number of non-reactive collisions can be small and the energy distribution of the intermediate species will be far from the Boltzmann distribution, depending on the energy distribution at the time of their formation and on the energy transfer in the non-reactive collisions. On the other hand, kinetics models use available kinetic data, rate constants and their variation with temperature, to model complex mechanisms and have been applied to model combustion processes. They rely on the assumption that the number of collisions between reactants and intermediates is large enough to achieve thermal equilibrium. To test this last hypothesis we have followed the evolution of the hydroxyl radical, OH, which is an important and very reactive intermediate, during the combustion of a mixture of oxygen and hydrogen at 3000 K and 2 atm until 3 ns, using the MREADY program.

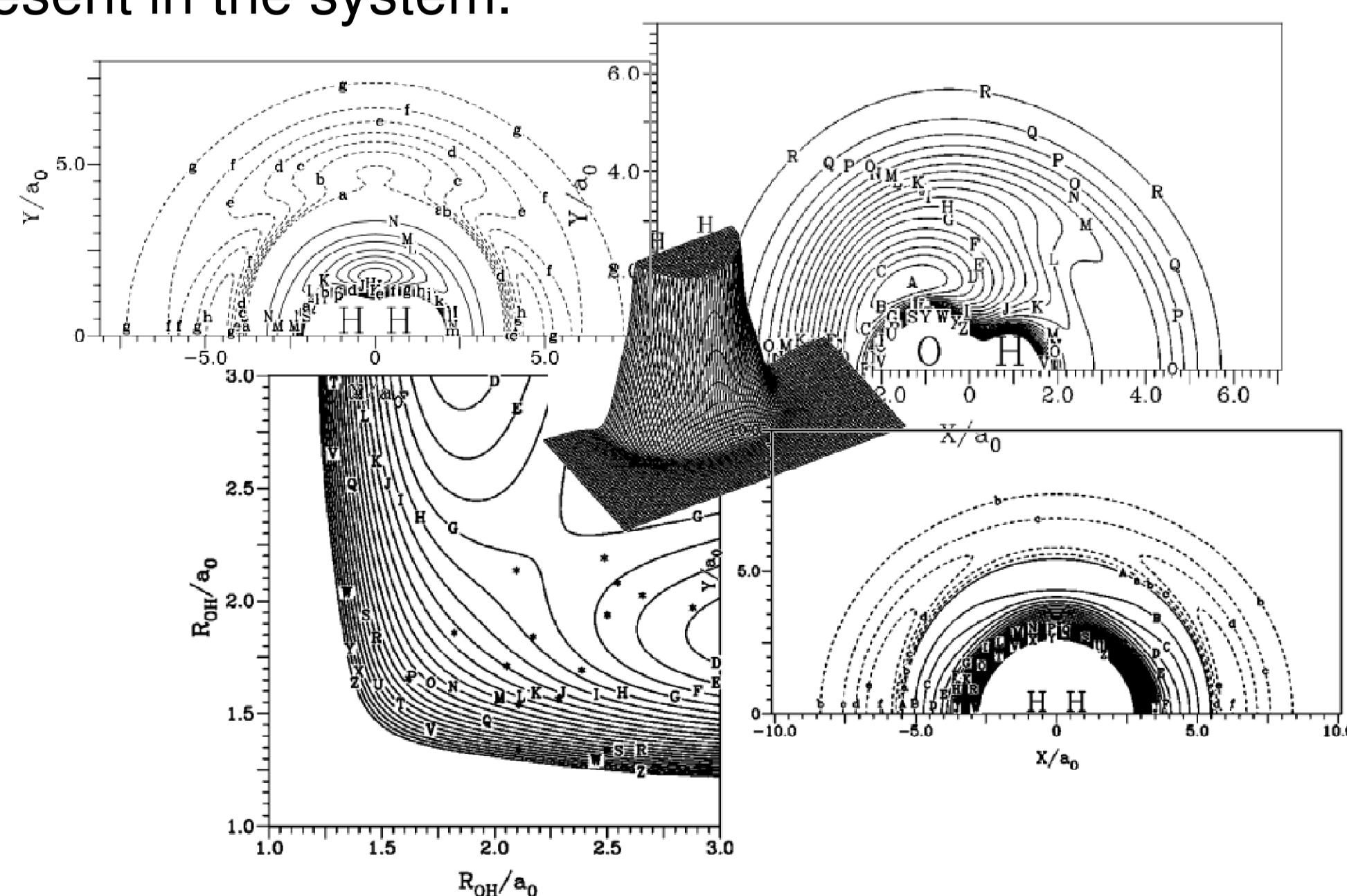
The MReaDy program

Multiple Reactions Dynamics, MREADY, is a program that builds an overall PES for the process in question and performs reactive classical dynamic calculations on it. Starting from a bulk mixture of H₂ and O₂ molecules, the program integrates the equations of motion in a total potential build from 17 accurate potential energy surfaces such as H₄, H₃O, HO₃, H₂O₂ and H₂O among others that should play a role in the combustion process.



Program Flow chart

The MReaDy program uses accurate PESs, reactive and nonreactive, to build a global PES and concurrently integrates the equations of motion of the chemical species present in the system.



PESs currently implemented in the MReaDy program

H ₂ (¹ Σ)	H ₂ (³ Σ)	O ₂ (³ Σ)	O ₂ (¹ Δ)
HO(² Π)	HO ₂ (² A'')	H ₂ O(¹ A')	H ₂ O(³ A'')
O ₃ (¹ A ₁)	H ₃ (²)	H ₄ (¹ B ₁)	H ₂ O ₂ (¹ A)
H ₂ O ₂ (³ A)	O ₄ (³ A)	H ₃ O	HO ₃ (² A)

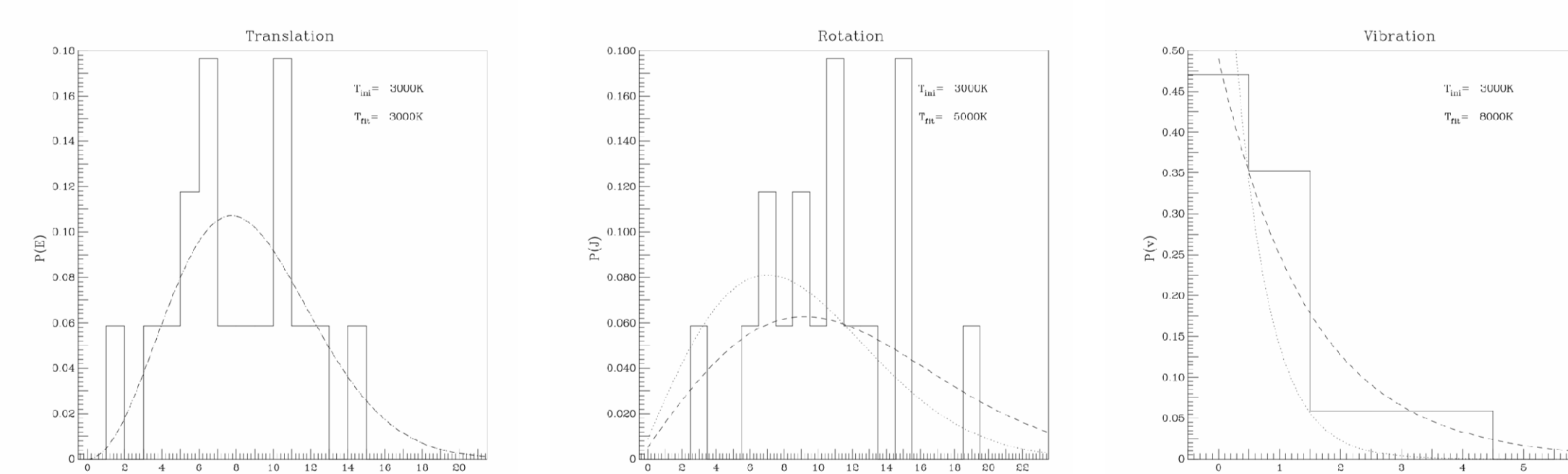
In the absence of accurate PESs, non-reactive collisions are treated using pair-additive repulsive potentials in order to account for the energy transfer between colliding partners.

Preliminary Results

Computed		Translational	Rotational	Vibrational
Formed	energy/J	0.3511E-19	0.4147E-19	0.7436E-19
	fraction	0.2326	0.2748	0.4926
2 ps ~ 100 col.	energy/J	0.5158E-19	0.5110E-19	1.0280E-19
	fraction	0.2510	0.2487	0.5003

Statistical		Translational	Rotational	Vibrational
1000K	energy/J	0.2071E-19	0.1381E-19	0.3752E-19
	fraction	0.2875	0.1916	0.5201
3000K	energy/J	0.6213E-19	0.4142E-19	0.5199E-19
	fraction	0.3994	0.2663	0.3342
5000K	energy/J	1.0355E-19	0.6903E-19	0.7558E-19
	fraction	0.4173	0.2782	0.3045
7000K	energy/J	1.4497E-19	0.9665E-19	1.0136E-19
	fraction	0.4227	0.2818	0.2955
9000K	energy/J	1.864E-19	1.2426E-19	1.2794E-19
	fraction	0.4250	0.2833	0.2917

OH energy distribution



OH energy distribution after 2 ns

Conclusion

in spite of the occurrence of a large number of collisions, these are more efficient in rotational and translational energy transfer than in vibrational quenching. As a consequence, the OH radical seems to be vibrationally excited, having an average energy which is twice the rotational. This result, which is expected to have a significant contribution to the reaction rate constants involving this radical, has recently been confirmed experimentally [2].

References

- [1] C. Mogo and J. Brandão, *Journal of Computational Chemistry*, **2014**, *35*, 1330.
- [2] O.V. Skrebkov, *Journal of Modern Physics*, **2014**, *5*, 1806.

Acknowledgement

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