Calculating Chemical Rate Constants in Plasma Conditions

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Introduction

Rate constants are necessary for many calculations of interest to plasma physicists, in both academia and industry (e.g., [1]). This poster details the first steps towards a fast and robust computational method to calculate rate constants for chemical reactions using deMonNano [2], a density functional tight binding (DFT-B) computer program. Experimental literature containing rate constants is lacking for reactions in plasma conditions, and it is hoped that with this method it will be possible to calculate the rate constants for any neutral reaction in plasma conditions in order to populate the Quantemol Database (QDB) [3].

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Step 1: Set Up

The computational method should work with neutral species in plasma conditions of >1,000 K and <100 mTorr, and the chemical reactions should be of the form:

A + B → C + D
or
A + B → C

The latter has been tested with the system $SiH_2 + SiH_4 \rightarrow Si_2H_6$, the results of which are discussed here.

25,000 DFT-B molecular dynamics simulations were performed with deMonNano by firing SiH_2 at SiH_4 and recording if the simulation resulted in the formation of Si_2H_6.

To allow full sampling of possible collision configurations a z-matrix was used to set the initial geometries. The schematic below shows how the molecules are randomised, with the impact parameter (b), two angles (α), four dihedral angles (γ), and the velocity of the SiH_2 (ν) randomised for each collision simulation.

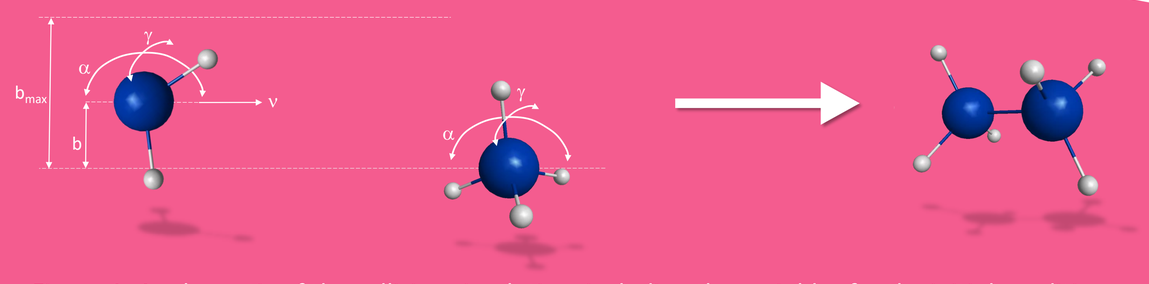

Figure 1: A schematic of the collision simulation, including the variables for the initial conditions.

Computational Method

Step 2: DFT-B

deMonNano is a density functional tight-binding (DFT-B) computer program. DFT-B uses a linear scaling technique for both storage and operations. As DFT-B uses pre-calculated parameter files and does not require computation of integrals, it is a very fast and computationally efficient method.

All calculations were performed with DFT-B and self consistent charge (SCC). A Nosé-Hoover bath was used, and the temperature of the bath was set at the temperature of the reaction (either 300 K or 600 K). The molecules were allowed to vibrationally equilibrate before the initial velocity was implemented. The pressure used was the deMonNano standard of 0.1 MPa.

Mathematical Equation

$$k = \frac{\sum[(N\nu)2\pi b]b_{max}}{\sum N_{tot}}$$

k = Rate constant ($cm^3\ s^{-1}$)
N = 1 (success) or 0 (failure)
$\mathbf{N_{tot}}$ = Total number of event simulations
b = Impact parameter (cm)
$\boldsymbol{b_{max}}$ = Maximum *b* sampled (cm)
ν = Velocity (cm/s)

The rate constants are calculated using the mathematical equation shown above. For unsuccessful simulations, when Si_2H_6 is not formed, the numerator is always equal to zero. The $b(b_{max})$ term gives a higher weighting to the larger b parameters, as they make up a larger area of the reaction cross-section and hence a higher probability of occurring.

Step 3: Data Analysis

Results

The rate constants calculated with deMonNano at 300 K and 600 K are shown below in Table 1, where they are also compared to experimentally determined rate constants from literature [4]. The calculated rate constants are correct to the same order of magnitude for both 300 K and 600 K, which is an excellent result for this level of theory.

Table 1: Comparison of rate constants calculated with deMonNano (column 'DFT-B') with experimentally determined rate constants from literature [4].

300 K		600 K	
DFT-B	**Experimental**	**DFT-B**	**Experimental**
1.06×10^{-9} $cm^3\ s^{-1}$	2.13×10^{-10} $cm^3\ s^{-1}$	8.61×10^{-10} $cm^3\ s^{-1}$	5.4×10^{-11} $cm^3\ s^{-1}$

Conclusion

The rate constants calculated with deMonNano at 300 K and 600 K are in good agreement with the experimental literature values, and can be calculated quickly for the $SiH_2 + SiH_4 \rightarrow Si_2H_6$ system at pressures of 0.1 MPa. The calculated and experimental rate constants show the same trend with temperature, hence it would be possible to extrapolate rate constant values to temperatures which have not been experimentally determined in order to populate the QDB.

References

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