Towards the quantum mechanical calculation of reaction rates

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J.F.J.Janssen[1], J.L.G. Suijker[2], J. Van Dijk[1]
[1] *Department of Applied Physics, Eindhoven University of Technology, PO Box 513, NL-5600 MB, Eindhoven, The Netherlands*
[2] *Philips Lighting B.V., BG Light Sources & Electronics, P.O. Box 80020, NL-5600 JM, Eindhoven, The Netherlands*

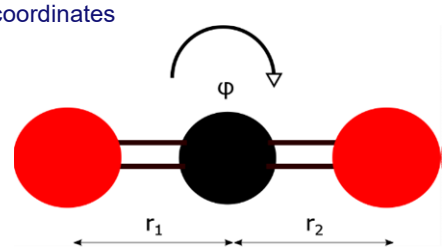
Contact: j.f.j.janssen@tue.nl

Introduction

The high CO_2 concentration in the air is driving global warming. Methods for the destruction of CO_2 molecules are investigated to limit its concentration. The most promising method uses vibrational pumping. The vibrational-vibrational reactions are poorly understood and occur in PLASIMO's CO_2 global model via empirical scaling relations. The quality of these relations is unknown. For that reason a quantum mechanical calculation of these rates is investigated. The main bottleneck is the calculation of the 11D potential.

Possible configurations

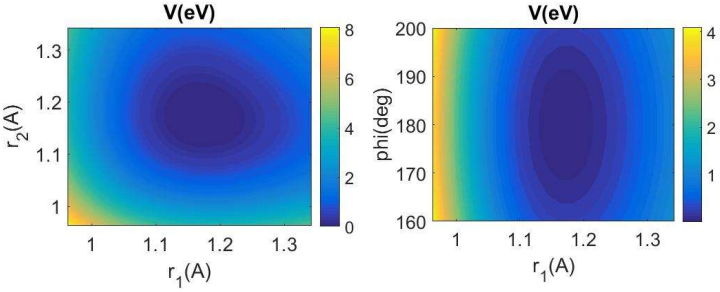
The internal structure of a CO_2 molecule can be described with 3 coordinates



An interaction between two of these CO_2 molecules therefore already contains 6 degrees of freedom. The remaining degrees of freedom include the separation between the center of mass (COM) of both molecules, the rotation along the COM of molecule 2 and the rotation of molecule 2 around molecule 1

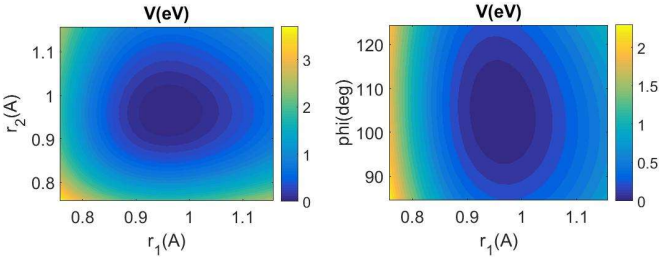
Potential surface CO_2

As a first step the potential energy surface for a single molecule is calculated. The left figure shows results for the variation of r_1 and r_2 and the right figure for r_1 and phi.



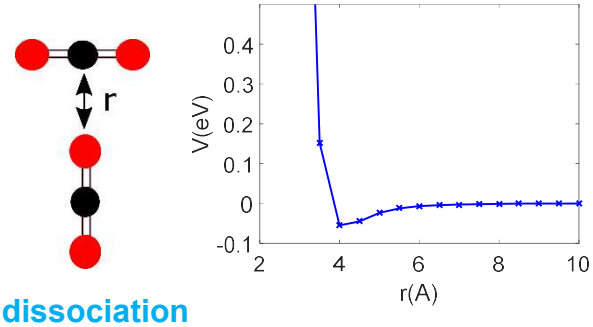
Potential surface H_2O

Since the final goal of the project is to create CH_4 the impact of H_2O on the chemistry is important as well.



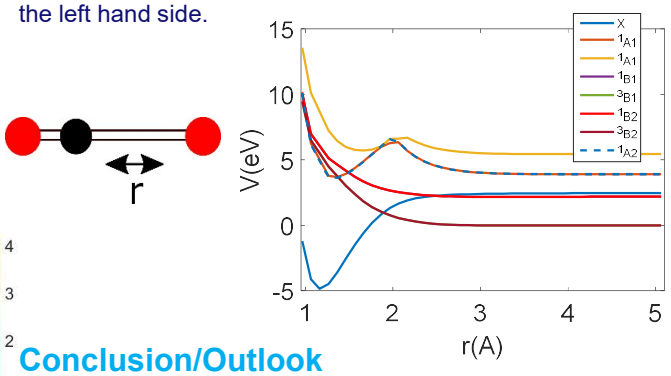
Interaction of two CO_2 molecules

Two CO_2 molecules collide as indicated in the drawing on the left hand side.



CO_2 dissociation

The potential energy curves for the CO_2 molecule are calculated for the dissociation as indicated in the figure on the left hand side.



Conclusion/Outlook

The CCSD procedure gives reliable results for the calculation of the potential energy. Further work focusses on using the optimal basis set and determining the 11D grid in such a way that all features can be captured while the calculation time remains reasonable.