First-principles thermochemistry for the combustion of $TiCl_4$ in a methane flame

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Applications

- Opacifier
- 5 million tonnes per year

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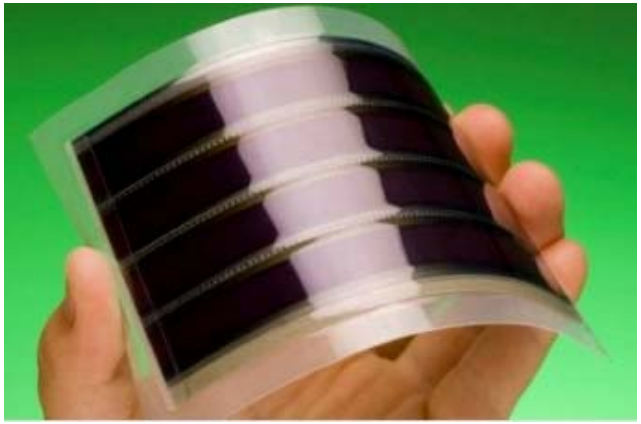
Modern applications



- Solar cells

- Kills bacteria under UV light

- Water splitting under UV light

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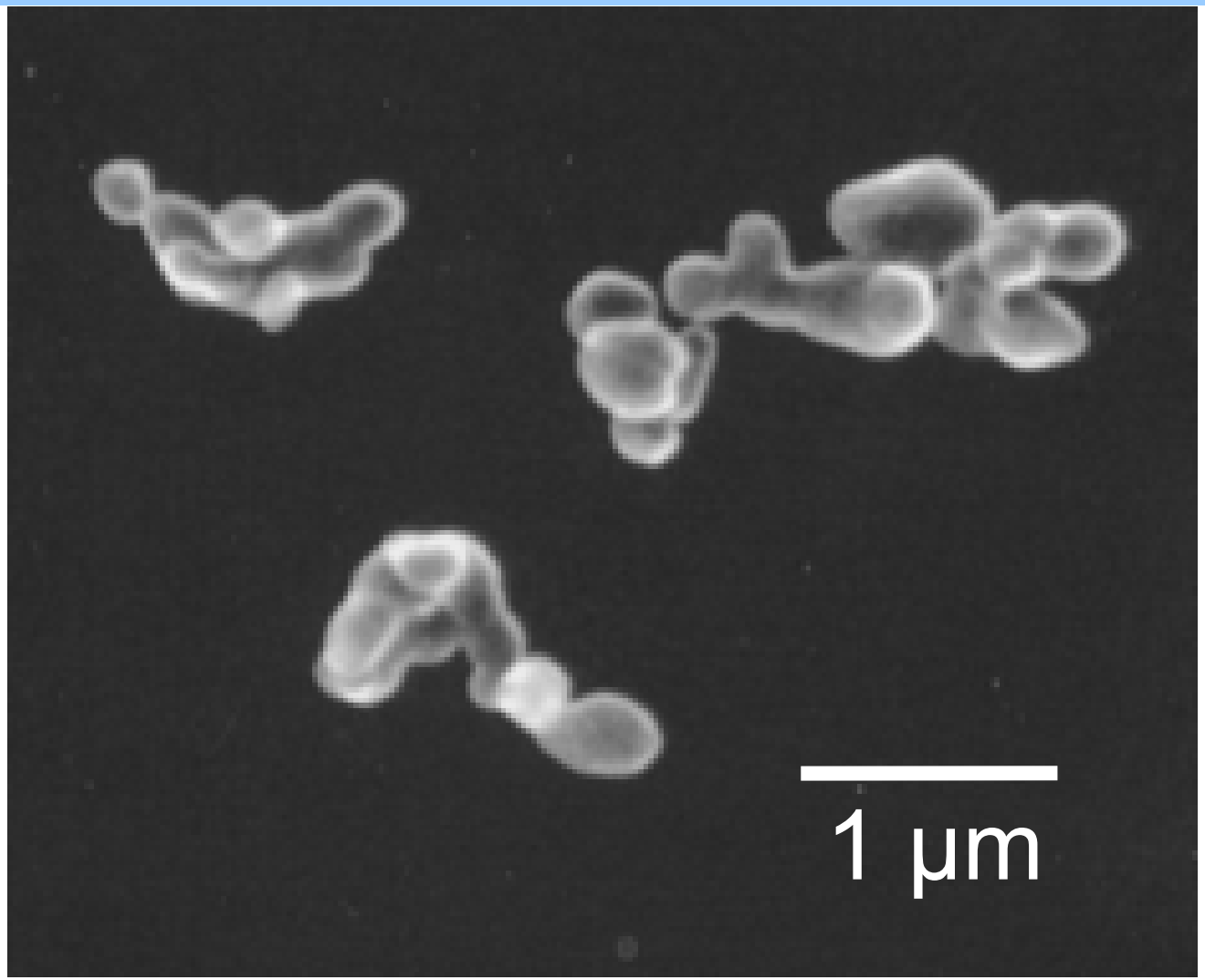
Scanning Electron Microscope



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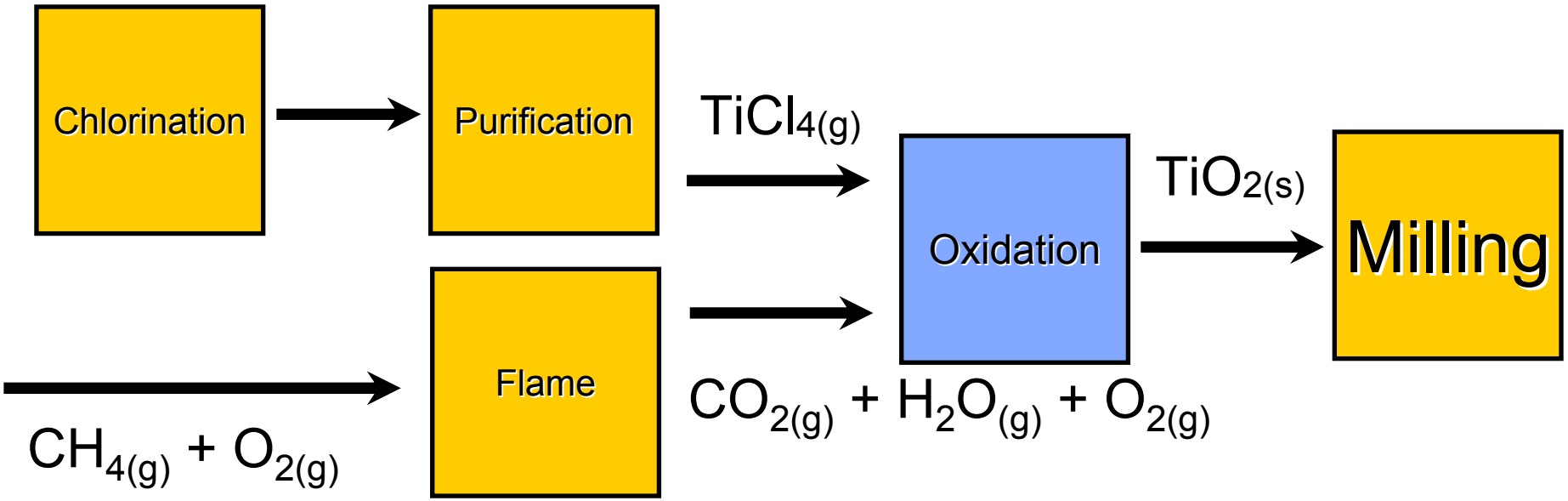
Chloride Process



- $TiCl_{4(g)} + O_{2(g)} \rightarrow TiO_{2(nanoparticles)} + 2\ Cl_{2(g)}$

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H_2O might be important

- TiO_2 can be produced using steam
- H_2O highly reactive
- Some industrial evidence that water might influence particle size distribution
- Aim: Investigate stable species that could be formed from reaction with water

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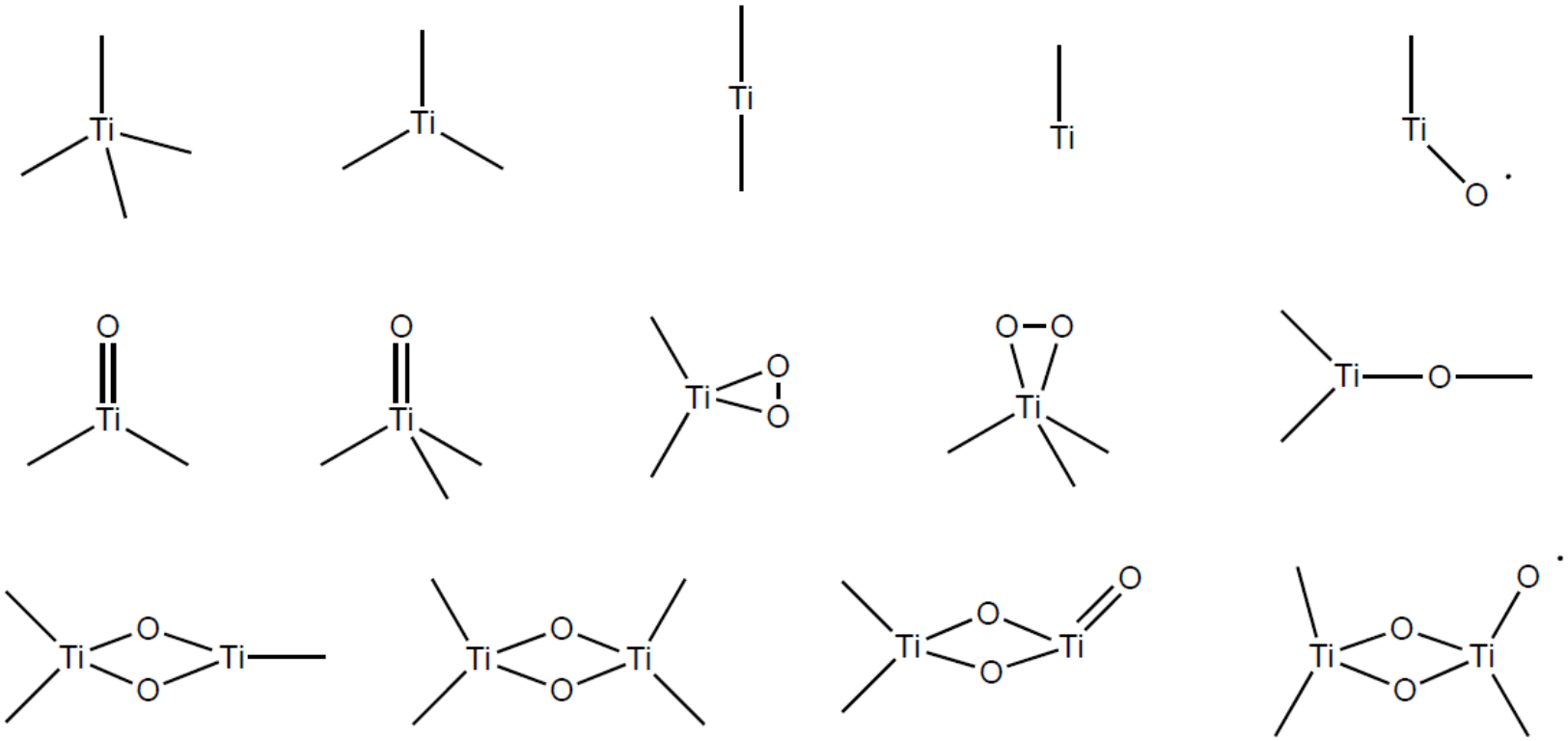
Species in literature



- West et al (2009), Combustion and Flame

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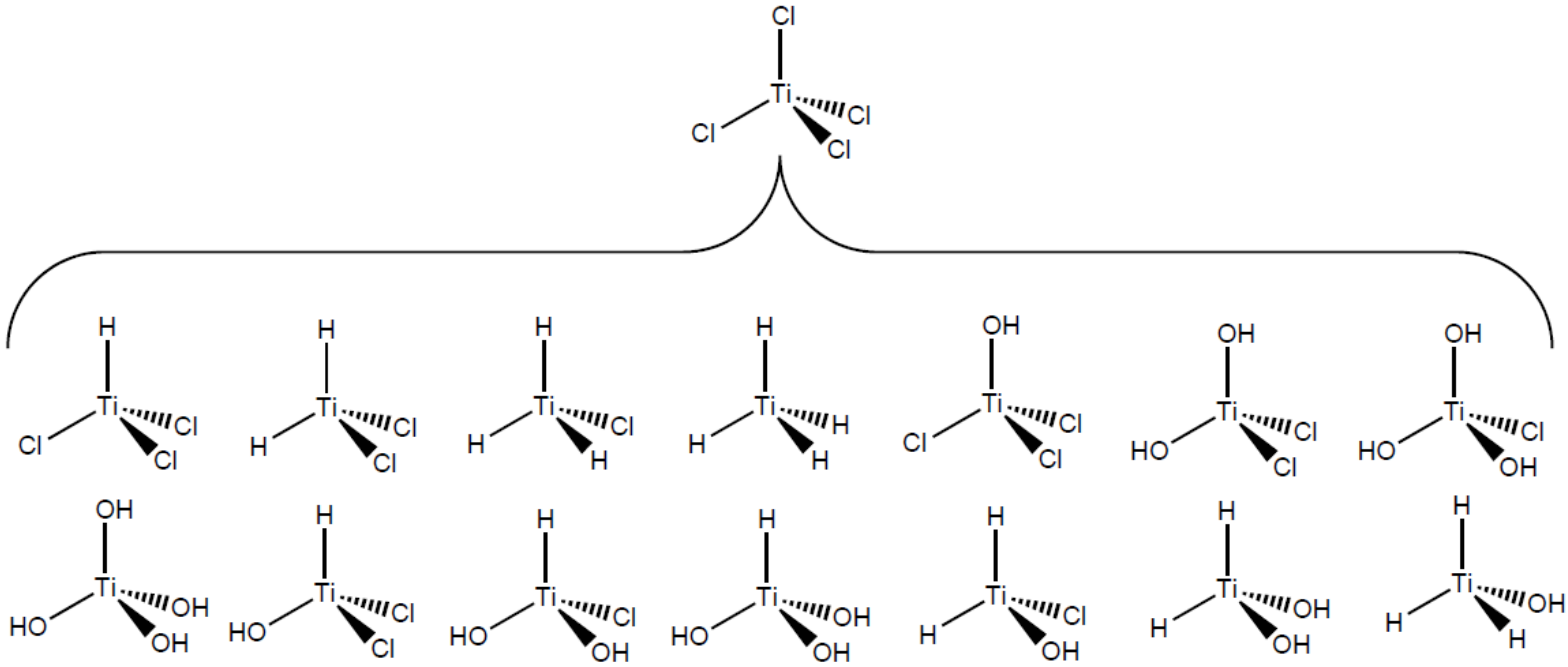
Species generation



- Take multiplicities from original species

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New species

- The algorithm on the previous slide produced over 300 possible species
- A number of these were duplicates
- After duplicates removed we were left with over 200 geometries
- Next step is to screen these species for stable or important molecules

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Quantum calculations

$$\hat{H}\Psi = E\Psi$$

$$\hat{H}_{elec} = -\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2 - \sum_{i=1}^{N}\sum_{A=1}^{M}\frac{Z_A}{r_{iA}} + \sum_{i=1}^{N}\sum_{j>i}^{N}\frac{1}{r_{ij}}$$

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Density Functional Theory

- One to one mapping between ground state electron wavefunction and electron density
- Functional calculates energy given electron density
- Minimise energy to get geometry of ground state

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Gaussian

- Gaussian03 used throughout
- We use B97-1/6-311+G(d,p) for geometry optimization and for calculating vibrational frequencies
- 141 species remain

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Thermochemistry

- Use data from quantum calculations to calculate thermochemistry (H, S, G etc)
- Rigid rotor harmonic oscillator approximation
- Errors due to enthalpy of formation are the largest

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Enthalpy of formation

Species	$\Delta_f H^\circ_{298.15\,K}$ kJ/mol
TiOCl	-274
$TiOCl_2$	-598
$TiOC_3$	-639
TiO_2Cl_2	-558
TiO_2Cl_3	-774
$Ti_2O_2Cl_3$	-1257
$Ti_2O_2Cl_4$	-1552
$Ti_2O_3Cl_2$	-1331
$Ti_2O_3Cl_3$	-1418
$Ti_2O_2Cl_5$	-1272
$Ti_2O_2Cl_6$	-1503
$TiCl_4$	-763.16
$TiCl_3$	-539.32
$TiCl_2$	-237.23
TiO_2	-305.43
ClOCl	87.86
OClO	104.60
ClOH	-74.48
H_2O	-241.83
HCl	-92.31
OH	38.99
Cl	121.30
O	249.18

West *et. al.*, Combust Flame, 2009

NIST database

- Reasonably sparse literature data
- Choice of reaction critical
- Ideally we could use isodesmic reactions:
  - Number of each bond type unchanged by reaction

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Automatic isodesmic script

- Originally developed for Phadungsukanan et al, J. Phys. Chem. A, 2009, for Si species.
- Express reaction as set of linear equations for each bond.
- Use linear programming package to minimize total bond changes.

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Isodesmic reactions

Species	$\Delta_f H^\circ_{0\,K}$ kJ/mol	$\Delta_f H^\circ_{298.15\,K}$ kJ/mol	Standard Deviation kJ/mol	No. of reactions	No. of bond changes
$TiCl_3OH$	−941	−917	14	6	0
$Ti_2O_2Cl_3OH$	−1741	−1708	14	4	0
$Ti_2OCl_4(OH)_2$	−1936	−1893	56	6	0
$TiCl_2OH$	−719	−699	24	6	0
$TiOClOH$	−742	−724	34	7	0
$TiCl_2(OH)_2$	−1079	−1054	28	6	0
$TiOCl_2OH$	−793	−770	28	6	0
Ti_2O_3ClOH	−1545	−1518	64	6	0
$Ti_2O_2Cl_2(OH)_2$	−1866	−1831	43	6	0
$TiCl(OH)_2$	−850	−829	29	6	0

- Used a script to automatically find isodesmic reactions and take averages
- Main errors due to absence of Ti-H bond in database

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Equilibrium compositions

- Cantera
- Use NASA polynomials calculated in this work
- Other polynomials taken from the literature
- NIST/NASA databases

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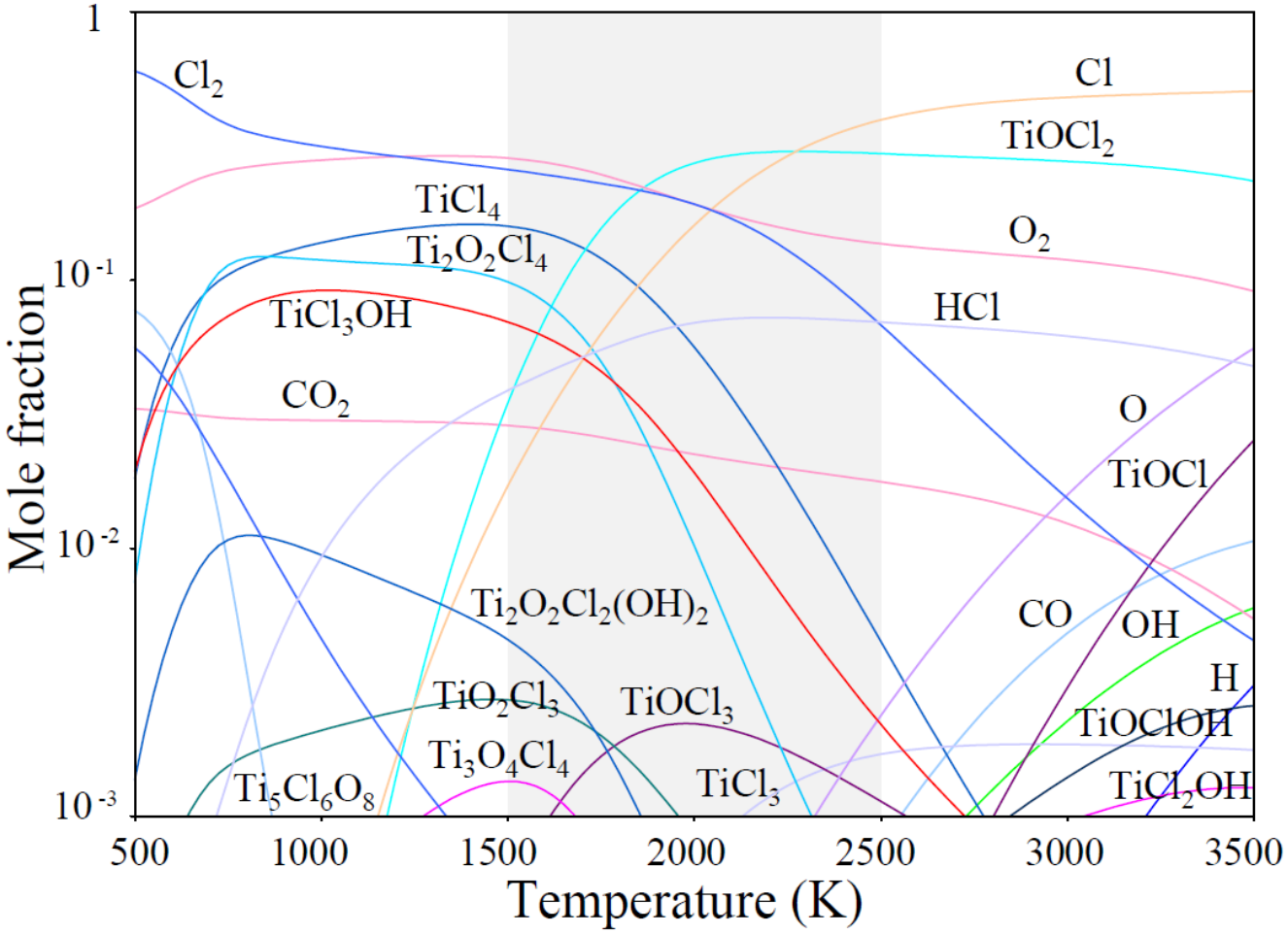
Mole fractions



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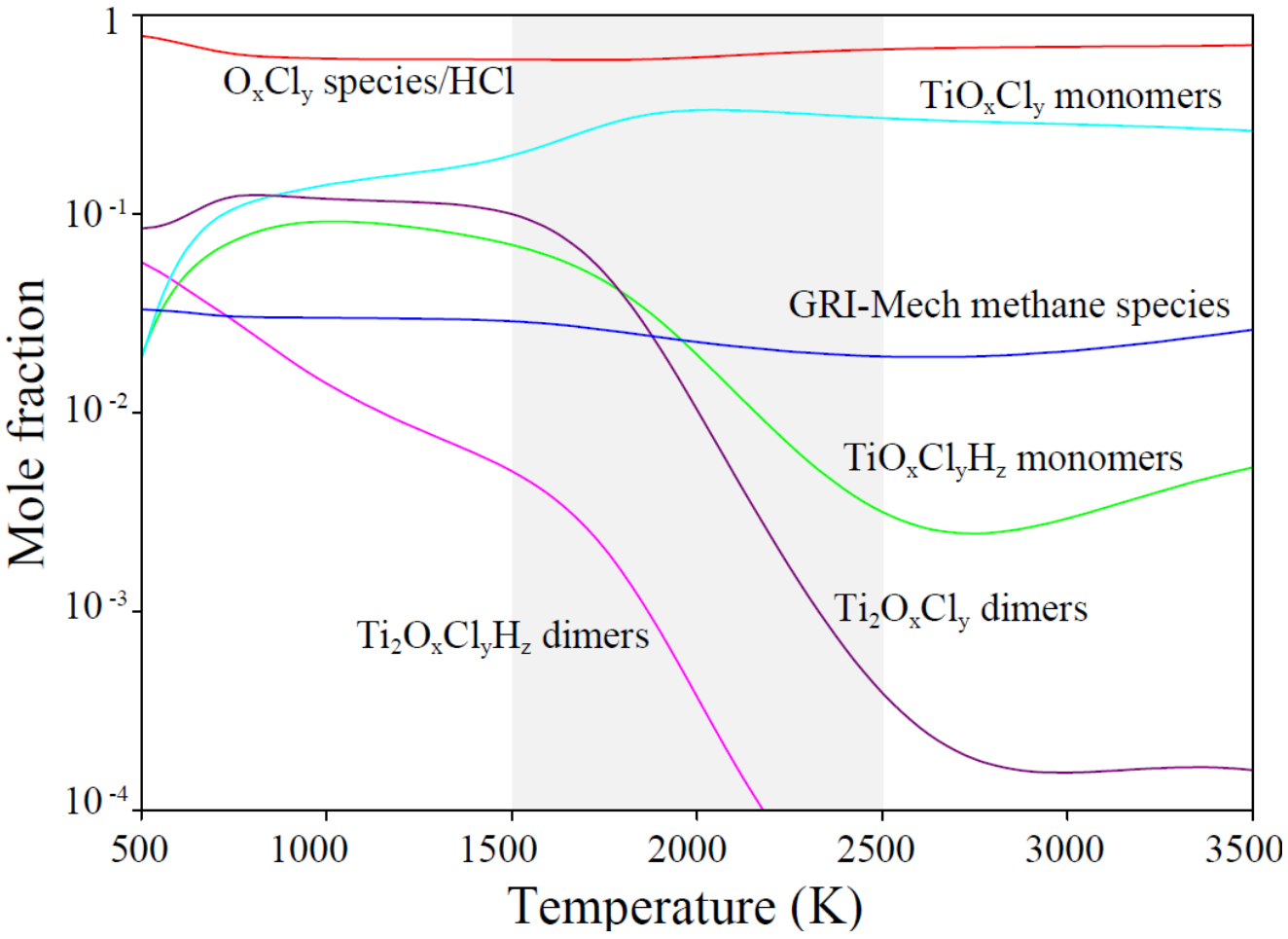
Collated mole fractions



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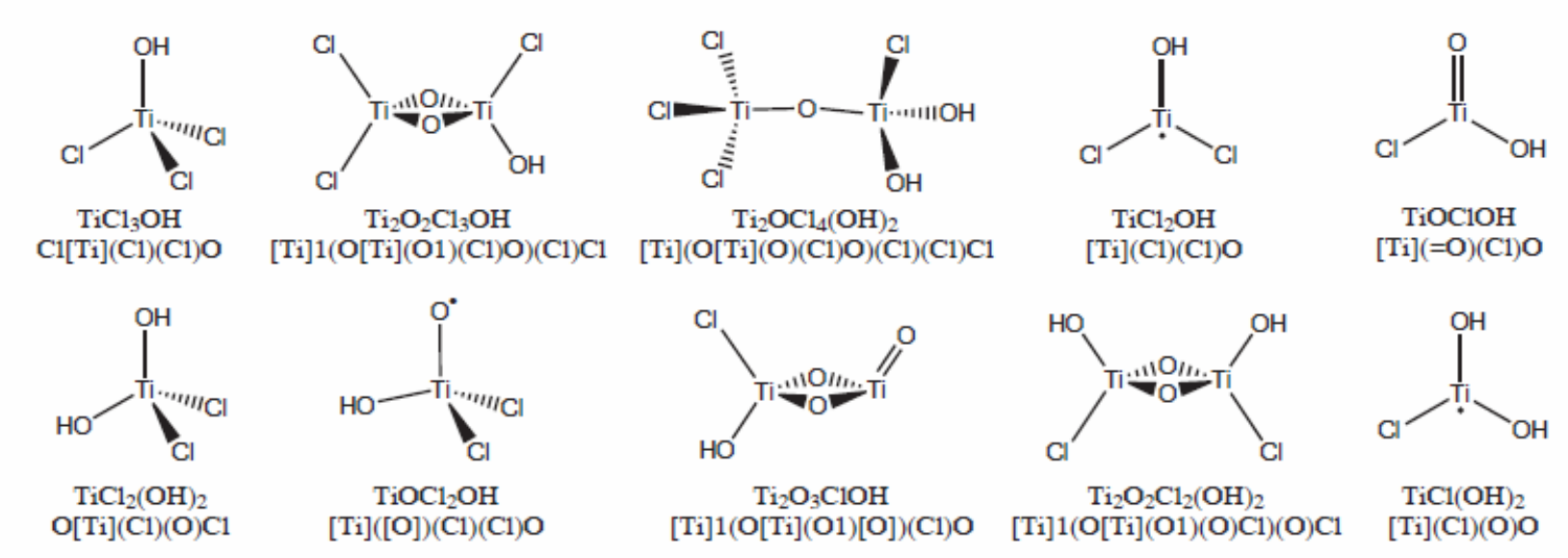
Top ten species



- A number of species are present in high concentration
- H likely to influence kinetics

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Conclusions

- Hydrogen containing species are stable and will exist at industrial and experimental conditions.

- $TiCl_3OH$, $Ti_2O_2Cl_3OH$, $Ti_2OCl_4(OH)_2$, $TiCl_2OH$, $TiOClOH$, $TiCl_2(OH)_2$, $TiOCl_2OH$, Ti_2O_3ClOH, $Ti_2O_2Cl_2(OH)_2$, and $TiCl(OH)_2$ are highlighted as ten of the most stable $Ti_iO_jCl_kH_l$ species for industrial conditions.

- $TiCl_3OH$ is the most abundant new species.

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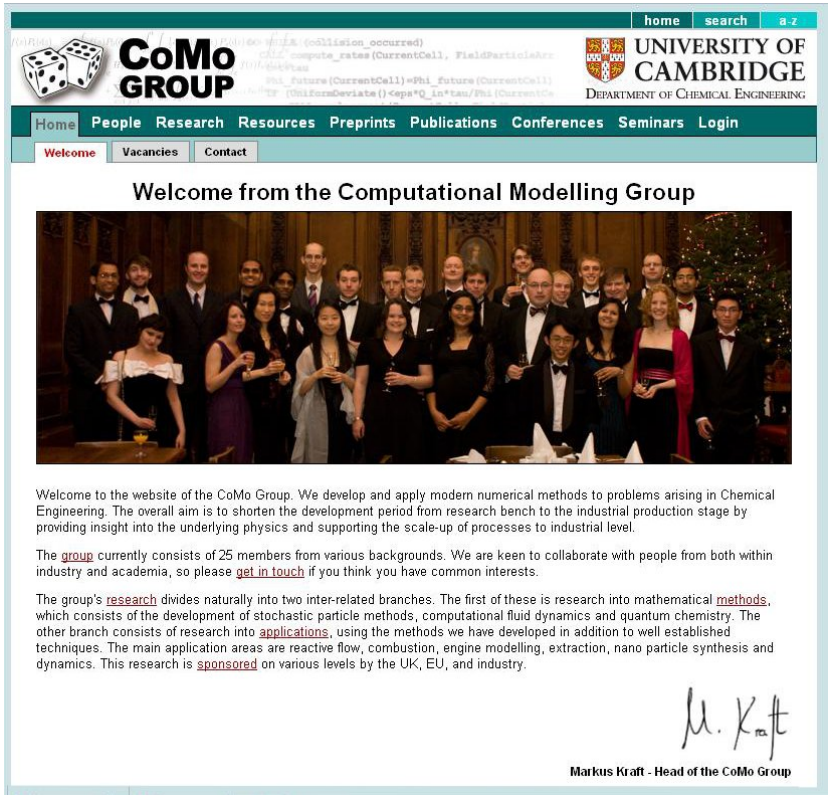
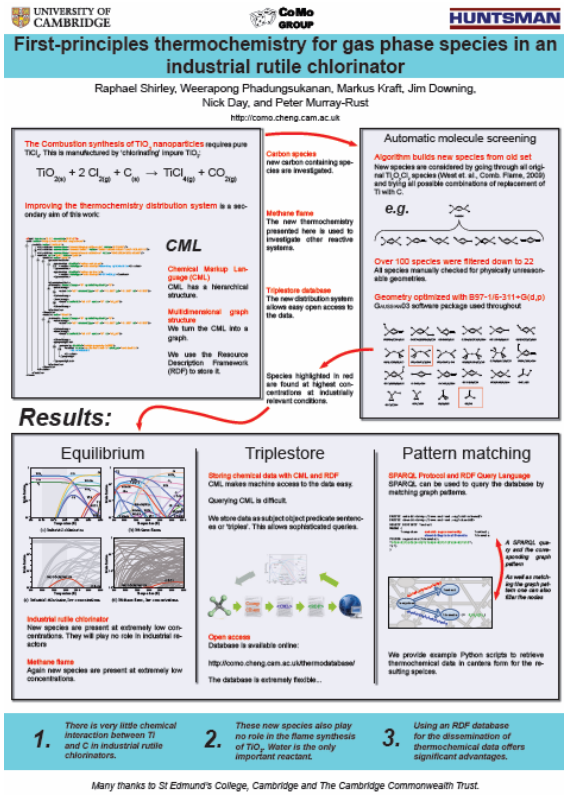
Thank you





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