Mercury Oxidation by Fly Ash Constituents and Flue Gases and Its Optimization for the Development of Mercury Control Technologies

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Outline

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- Background
  - Mercury emissions
  - Current control strategies
  - Properties
- Aims and schedule
- Characterisation of fly ash samples
- Theoretical studies (modelling)
- Results and discussion
- Experimental set-up
- Summary
- Future work

Background

--- Mercury emissions

- Increasing concerns of mercury emissions due to its toxicity, methylmercury (CH_3Hg)
- 1997 US EPA report:[a]
  - Approximately 158 tons of mercury emitted in the USA;
  - 30% of the total was from coal-fired power plants;
- Mercury control strategies
  - USA: 21 and 70% reduction by 2010 and 2018, respectively; [b]
  - Europe: community strategy concerning mercury; [c]
  - Germany: the first European country regulating mercury emission standard from power plants (0.03mg/m3STP);[d]

a US EPA (1997) Mercury study report to congress, volume I: executive summary
b US EPA (2005) Standards of Performance for New and Existing Stationary Sources: Electric Utility Steam Generating Units (Final role)
c Commission of the European Communities (2005) Communication from the commission to the council and the European Parliament: community strategy concerning mercury
d Federal Ministry for the Environment, Nature Conservation and Nuclear Safety (FMENCNS) (2004) Thirteenth Ordinance on the Implementation of the Federal Immission Control Act (Ordinance on Large Combustion Plants and Gas Turbine Plants – 13.BImSchV)

Background

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--- Current control strategies

- Main forms of mercury leaving stacks:
  - Gaseous element form (Hg^0)
  - Oxidised mercury (Hg^{2+})
  - Particulate bound mercury (Hg_p)

- Hg^0 is difficult to be captured by existing air pollution control devices (APCDs), such as flue gas desulphurisation (FGD) and electrostatic precipitator (ESP) rather than Hg^{2+}

Background

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--- Property comparisons

Property	Elemental mercury, Hg^0	Oxidised mercury, Hg^{2+}
Reactivity	Low	High
Volatility	High	Low
Solubility	Insoluble	High soluble

- It is noted that oxidised mercury is the most suitable form to be captured by existing APCDs for reducing mercury emissions.
- Detailed studies on mercury speciation along the flue gas path are extremely necessary.

Aims

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- Understanding the mechanisms of mercury oxidation along the flue gas path;
- Optimization of mercury oxidation for the development of mercury control technologies.

Project schedule

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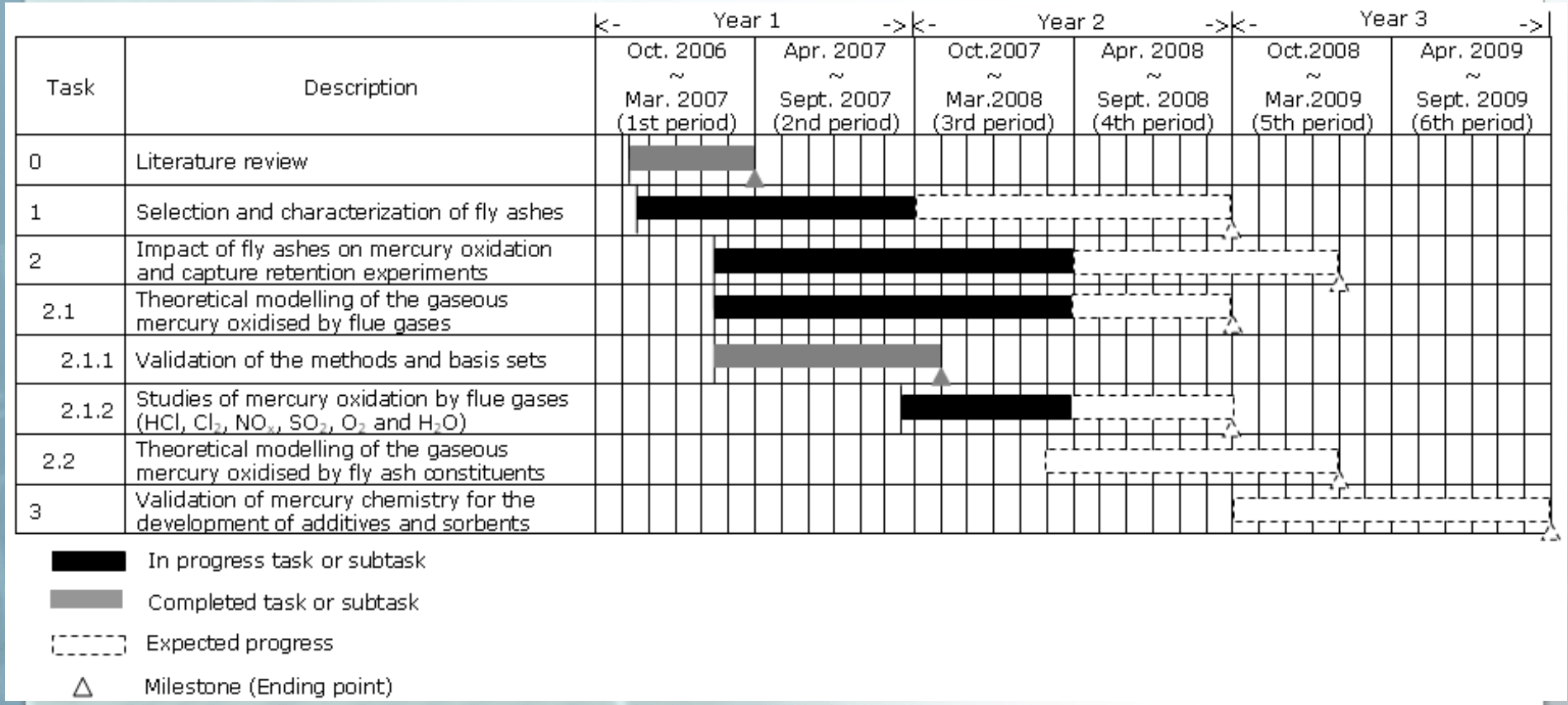

Experimental work

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--- Characterisation of fly ash samples

- Carbon content:
  - 3B2 series: 7.44-42.11%;
  - DD1: 6.8% and DD2: 8.4%;
- Remaining elements (H, N): very low concentrations;
- Particle size distribution:
  - Single model: 3B2/1
  - Bimodal model: 3B2/2, 3B2/3, 3B2/4, DD1 and DD2;

Mercury speciation studies

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- Homogeneous reactions:
  - Taking place between gaseous mercury (Hg^0) and flue gas components, e.g. HCl and SO_2.
- Heterogeneous reactions:
  - Gaseous mercury oxidised by solid oxides present in fly ash constituents, e.g. CaO.

Mercury speciation studies

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--- Mercury chlorination (homogeneous)

No.	Reaction
R1	$Hg + Cl + M \leftrightarrow HgCl + M$
R2	$Hg + Cl_2 \leftrightarrow HgCl + Cl$
R3	$Hg + HCl \leftrightarrow HgCl + H$
R4	$HgCl + Cl_2 \leftrightarrow HgCl_2 + Cl$
R5	$HgCl + Cl \leftrightarrow HgCl_2$
R6	$HgCl + HCl \leftrightarrow HgCl_2 + H$
R7	$Hg + Cl_2 \leftrightarrow HgCl_2$

Source: a. Niksa S., Helble J. J. and Fujiwara N. (2001) Kinetic modeling of homogeneous mercury oxidation: the importance of NO and H2O in predicting oxidation in coal-derived systems, *Environmental Science & Technology*, **35**: p3701-3706; b. Widmer C. N., West J. and Cole A. J. (2000) Thermochemical study of mercury oxidation in utility boiler flue gases, *the 93rd Air & Waste Management Association (A&WMA) Annual Conference and Exhibition*, Salt Lake City, Utah

Modeling profile

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- Software: the latest Gaussian program (G03W)
- Relevant species:

  Hg, HgCl, $HgCl_2$, H, HCl, Cl and Cl_2
- Basis sets for Hg, H and Cl atoms:
  - Hg: SDD, LANL2DZ and 19 basis sets provided by EMSL database (http://bse.pnl.gov/bse/portal), **21** basis sets in total.
  - H and Cl: SDD, LANL2DZ and the largest Pople style basis set, 6-311++G(3df,3pd), **3** basis sets in total.
- Ab initio methods:

  HF, B3LYP, MPn (MP2, MP3 and MP4SDQ), CC (CCD and CCSD), CI (CID and CISD) and QCISD, **10** methods in total.

Modeling procedure

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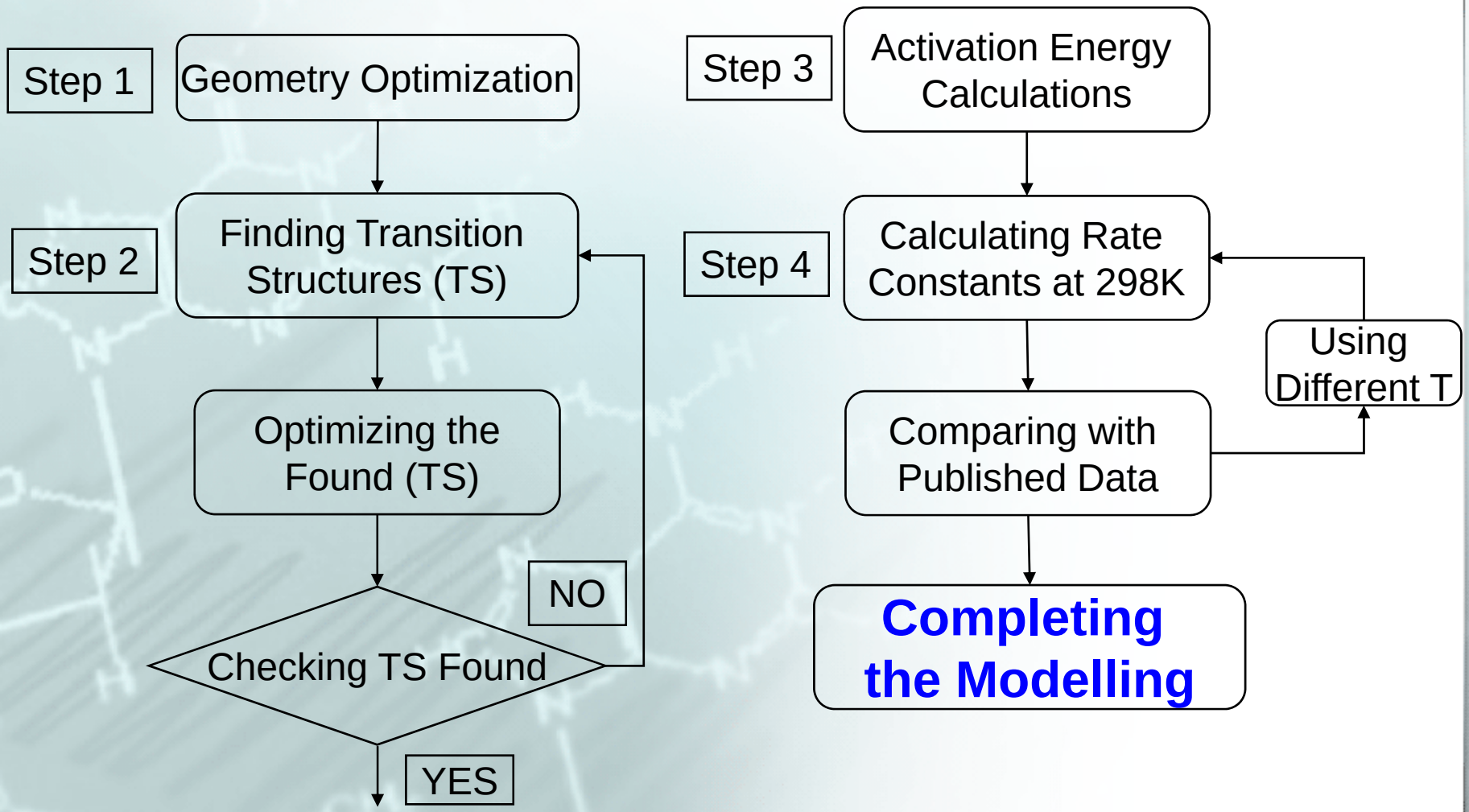

Validation of method and basis set

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Geometry Optimization (Preliminary determination)

- Scenario 1: Hg, H and Cl: SDD & LANL2DZ basis sets.
- Scenario 2: Hg: 19 basis sets provided by EMSL; H & Cl: 6-311++G(3df,3pd)

Second determination

Comparison between theoretical and experimental data in terms of reaction heats (ΔH_{rxn}^{298K}) for the proposed reactions.

Determination Matrix

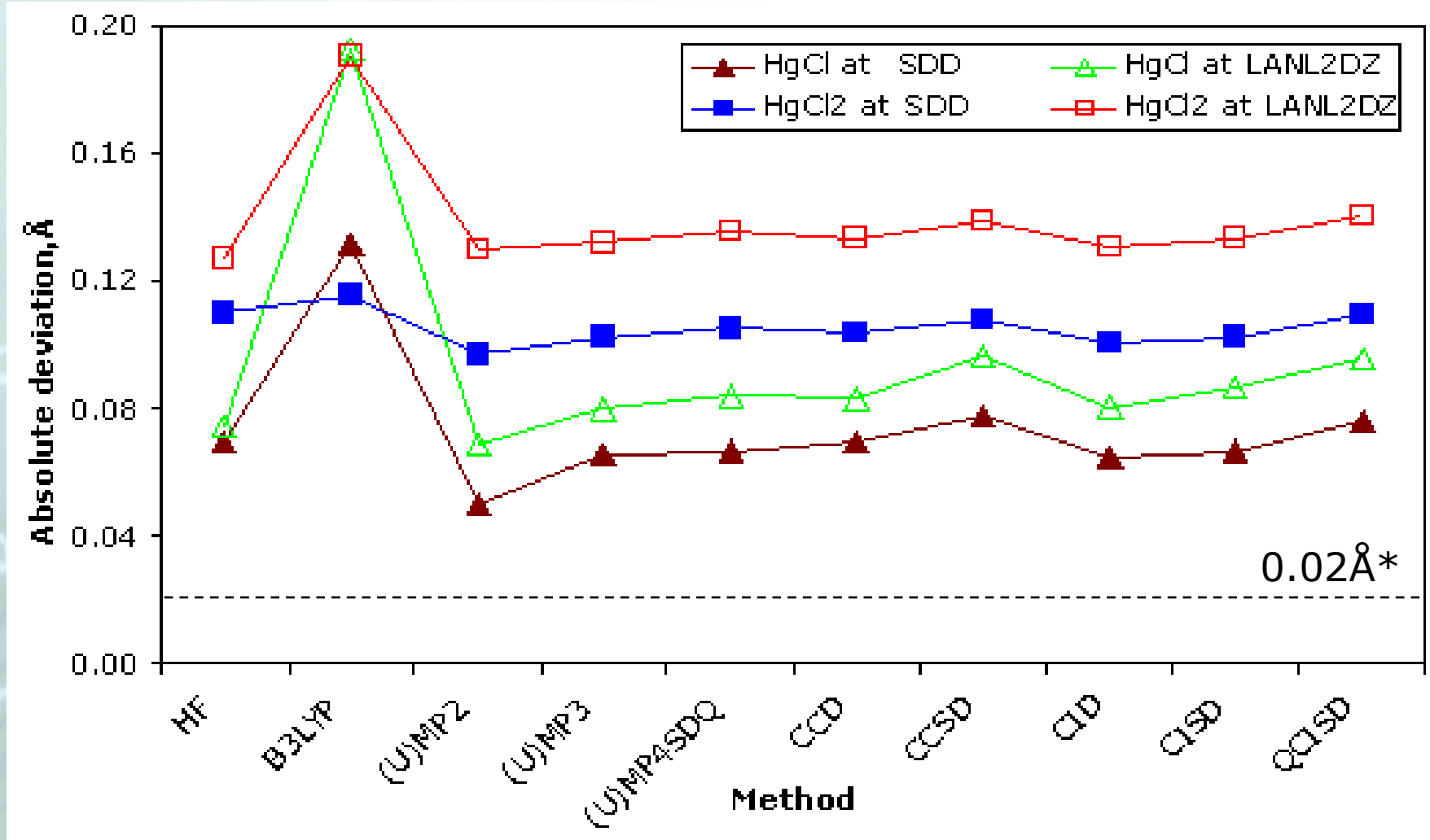
No.	Basis set\method	HF	B3LYP	MP2	MP3	MP4SDQ	CCD	CCSD	CID	CISD	QCISD
1	SDD										
2	LANL2DZ										
3	1992 Stevens										
4	Ahlrichs Coulomb Fitting										
5	aug-cc-pV5Z-PP										
6	aug-cc-pVDZ-PP										
7	aug-cc-pVQZ-PP										
8	aug-cc-pVTZ-PP										
9	cc-pV5Z-PP										
10	cc-pVDZ-PP										
11	cc-pVQZ-PP										
12	cc-pVTZ-PP										
13	cc-pwCV5Z-PP										
14	cc-pwCVDZ-PP										
15	cc-pwCVQZ-PP										
16	cc-pwCVTZ-PP										
17	CRENBL										
18	CRENBS										
19	Stuttgart RLC										
20	Stuttgart RSC 1997										
21	WTBS										

Scenario 1 (20 runs)

Scenario 2 (190 runs)

Geometry Optimization

--- Scenario 1



* Ref: Foresman B. J. and Frisch Æ. (**1996**) Exploring Chemistry with Electronic Structure Methods, 2nd Ed., Gaussian Inc., Pittsburgh, PA, p118

Geometry Optimization

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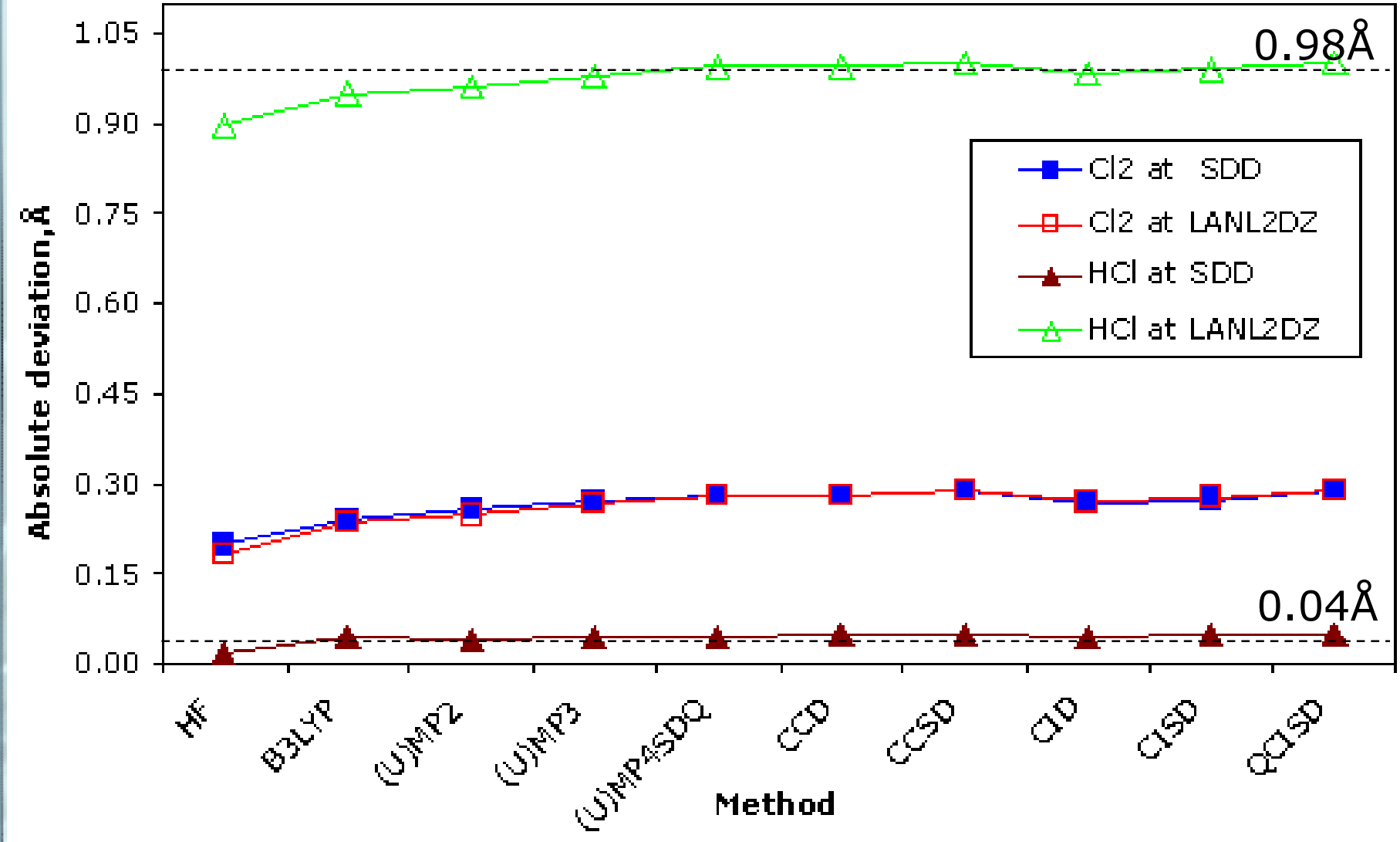
--- Scenario 1



Determination Matrix

No.	Basis set\method	HF	B3LYP	MP2	MP3	MP4SDQ	CCD	CCSD	CID	CISD	QCISD
1	SDD										
2	LANL2DZ										
3	1992 Stevens										
4	Ahlrichs Coulomb Fitting										
5	aug-cc-pV5Z-PP										
6	aug-cc-pVDZ-PP										
7	aug-cc-pVQZ-PP										
8	aug-cc-pVTZ-PP										
9	cc-pV5Z-PP										
10	cc-pVDZ-PP										
11	cc-pVQZ-PP										
12	cc-pVTZ-PP										
13	cc-pwCV5Z-PP										
14	cc-pwCVDZ-PP										
15	cc-pwCVQZ-PP										
16	cc-pwCVTZ-PP										
17	CRENBL										
18	CRENBS										
19	Stuttgart RLC										
20	Stuttgart RSC 1997										
21	WTBS										

Geometry Optimization

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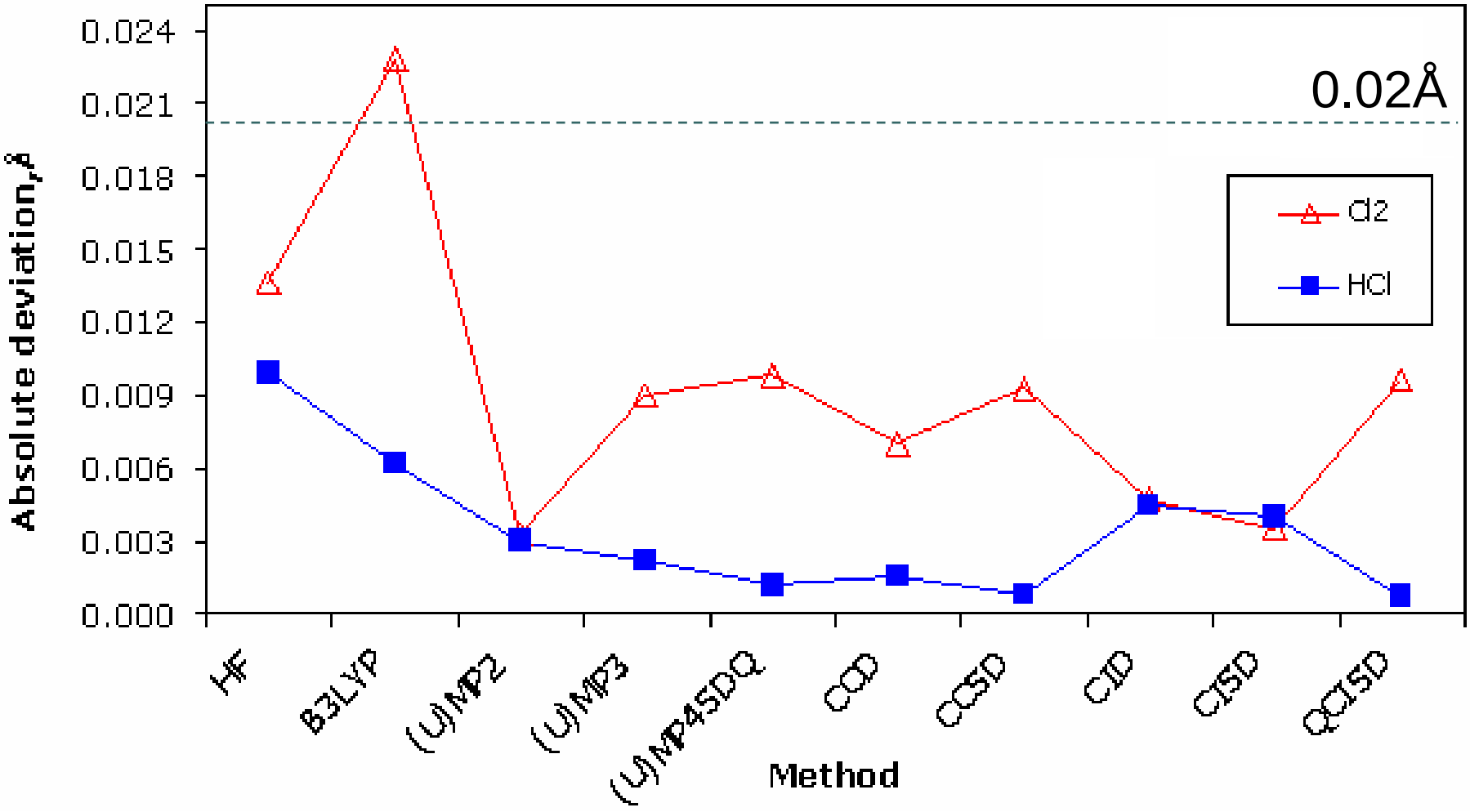
--- Scenario 2



Geometry Optimization --- Scenario 2

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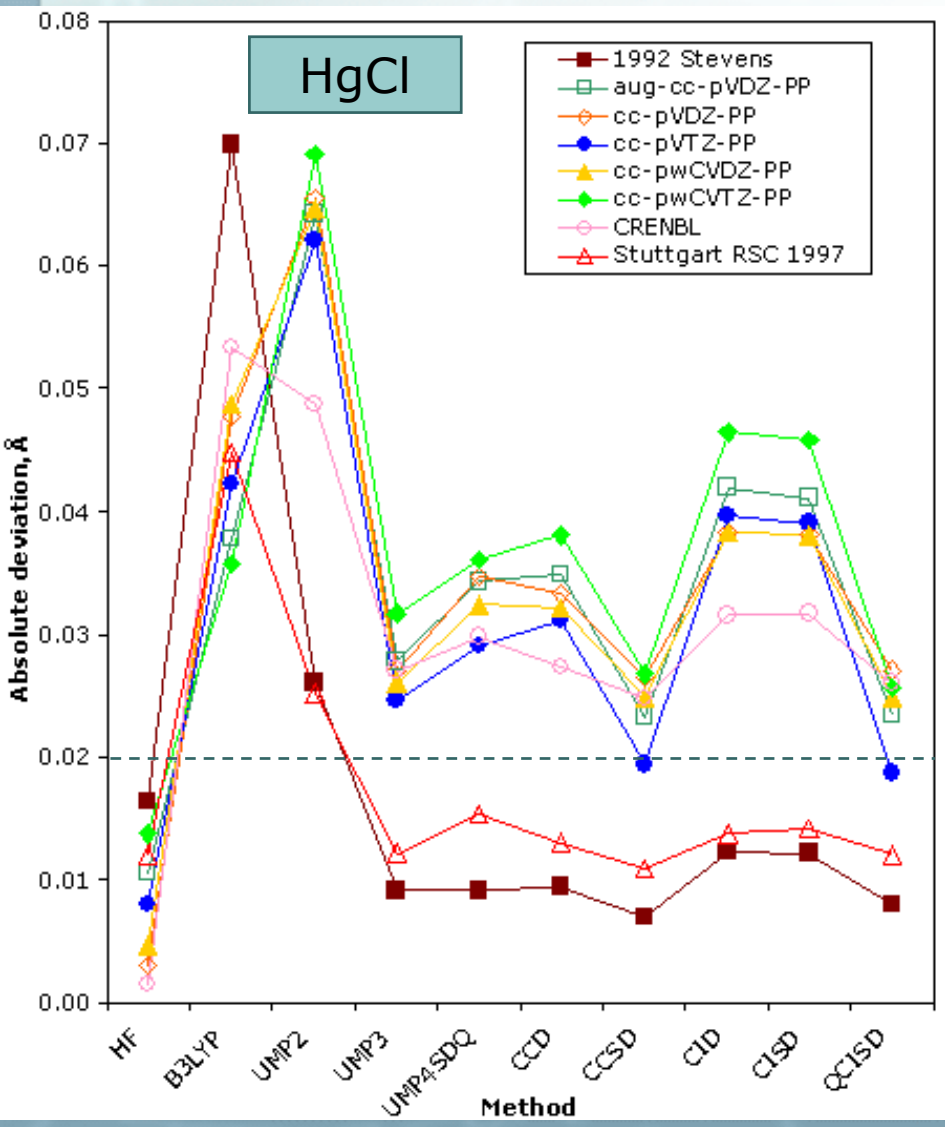

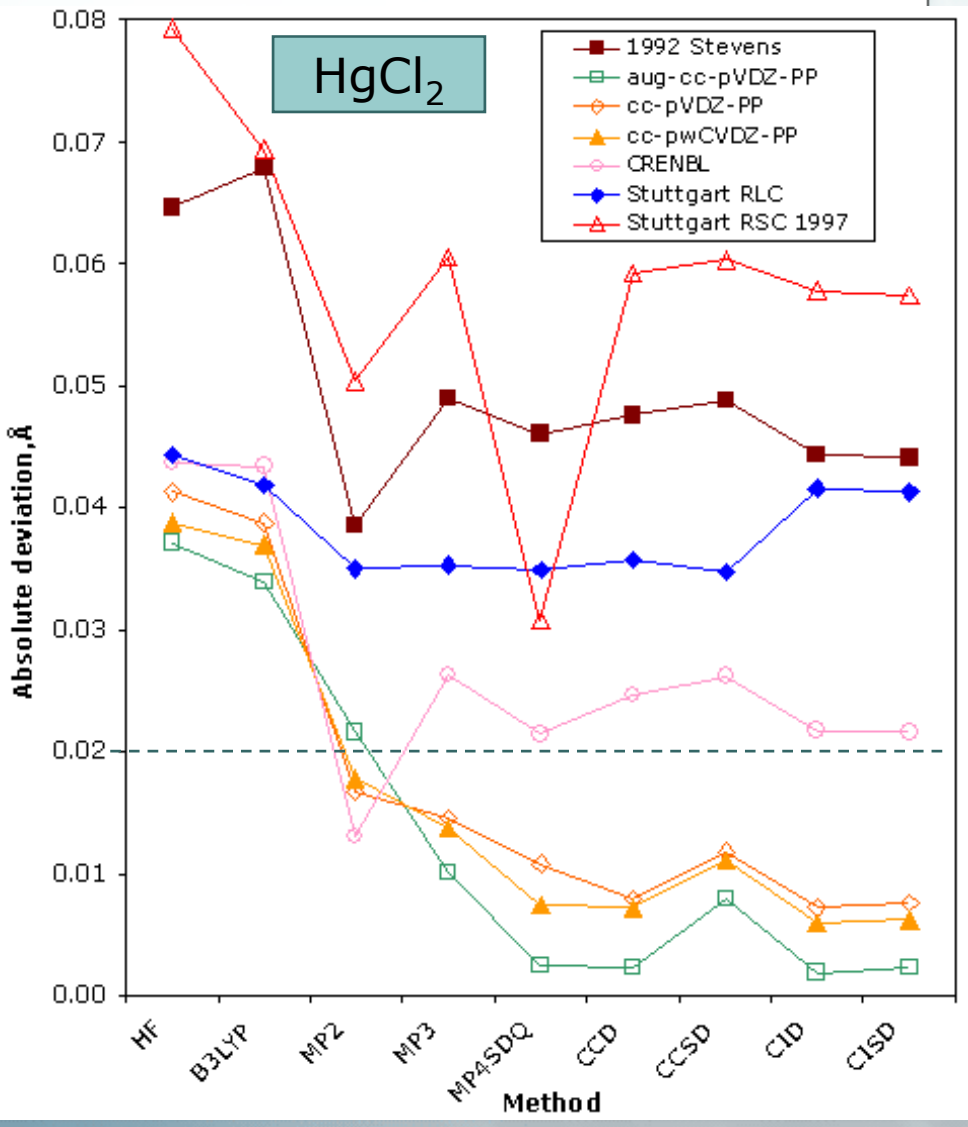

Geometry Optimization

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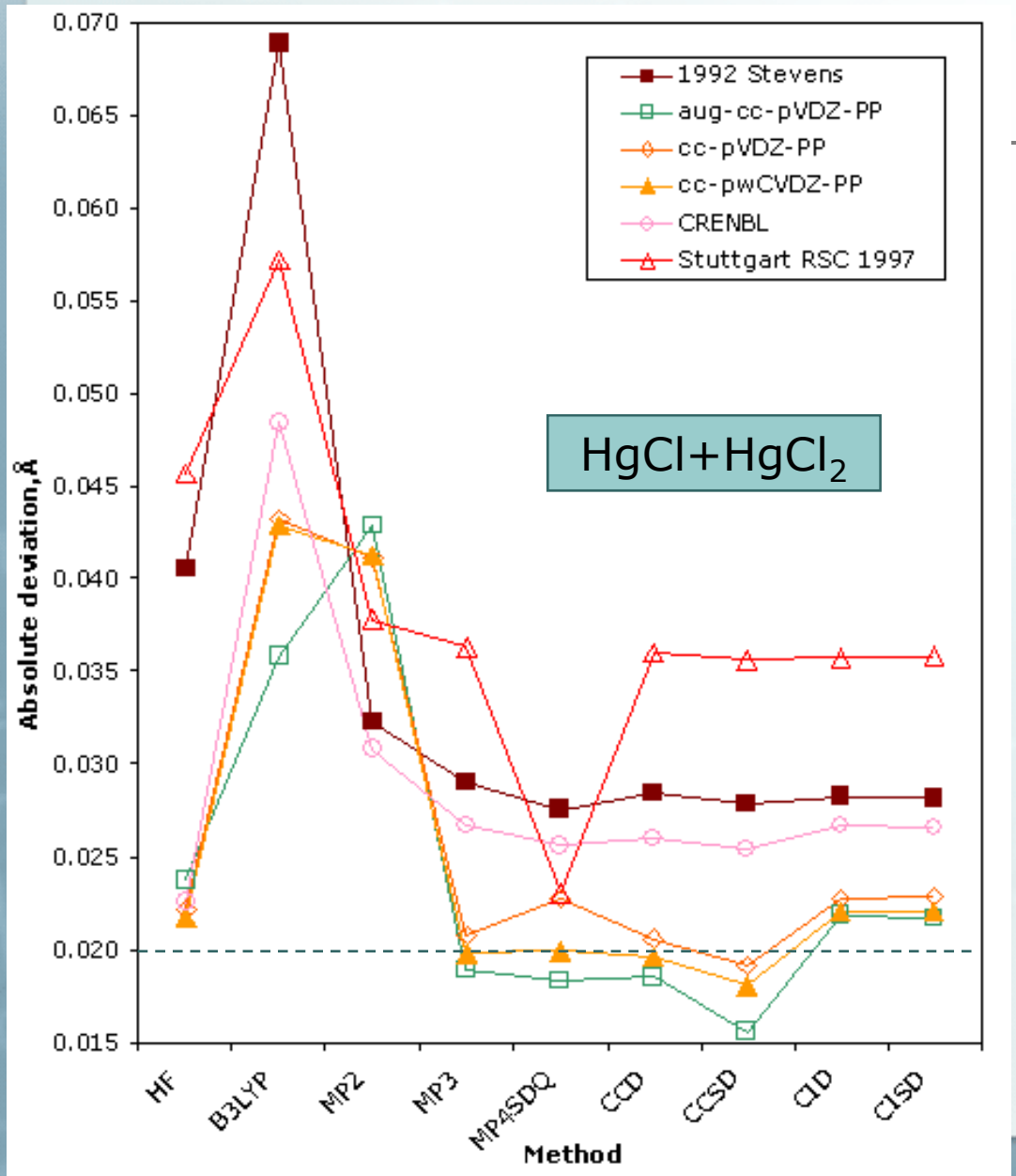

--- Scenario 2

Average absolute deviation of Hg-Cl bond length =

(absolute deviation of HgCl +absolute deviation of $HgCl_2$)/2

Determination Matrix

No.	Basis set\method	HF	B3LYP	MP2	MP3	MP4SDQ	CCD	CCSD	CID	CISD	QCISD
1	SDD										
2	LANL2DZ										
3	1992 Stevens					√		√		√	√
4	Ahlrichs Coulomb Fitting										
5	aug-cc-pV5Z-PP										
6	aug-cc-pVDZ-PP					√		√		√	√
7	aug-cc-pVQZ-PP										
8	aug-cc-pVTZ-PP										
9	cc-pV5Z-PP										
10	cc-pVDZ-PP										
11	cc-pVQZ-PP										
12	cc-pVTZ-PP					√		√		√	√
13	cc-pwCV5Z-PP										
14	cc-pwCVDZ-PP					√		√		√	√
15	cc-pwCVQZ-PP										
16	cc-pwCVTZ-PP										
17	CRENBL					√		√		√	√
18	CRENBS										
19	Stuttgart RLC										
20	Stuttgart RSC 1997										
21	WTBS										

20 combinations

Further Determination

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-- Calculated results

Comparison of theoretical and experimental ΔH_{rxn}^{298K} (kJ/mol) at the 1992 Steven's basis set

No.	Reaction	Method				NIST* experiment
		QCISD	MP4SDQ	CCSD	CISD	
R1	Hg+Cl+M-->HgCl+M	-110.98	-110.76	-111.06	-65.92	-104.23
R2	$Hg+Cl_2$-->HgCl+Cl	94.52	96.29	94.09	67.17	138.37
R3	Hg+HCl-->HgCl+H	311.05	-	310.98	344.82	327.38
R4	$HgCl+Cl_2$-->$HgCl_2$+Cl	-123.22	-125.13	-123.40	-93.41	-103.44
R5	HgCl+Cl-->$HgCl_2$	-328.72	-332.17	-328.56	-226.51	-346.04
R6	HgCl+HCl-->$HgCl_2$+H	93.31	-	93.48	184.24	85.57
R7	$Hg+Cl_2$-->$HgCl_2$	-234.21	-235.89	-234.46	-159.34	-207.67
Average absolute error		19.76	-	19.95	57.64	

-: not determined

*: The National Institute of Standards and Technology, http://webbook.nist.gov/

Further Determination

The University of Nottingham

-- Calculated results

Comparison of theoretical and experimental ΔH_{rxn}^{298K}(kJ/mol) at the aug-cc-pVDZ-PP basis set

No.	Reaction	Method				NIST* experiment
		QCISD	MP4SDQ	CCSD	CISD	
R1	Hg+Cl+M-->HgCl+M	-78.68	-72.78	-77.73	16.99	-104.23
R2	$Hg+Cl_2$-->HgCl+Cl	126.82	134.27	127.42	150.09	138.37
R3	Hg+HCl-->HgCl+H	343.36	-	344.31	427.74	327.38
R4	$HgCl+Cl_2$-->$HgCl_2$+Cl	-115.13	-119.83	-115.29	-50.75	-103.44
R5	HgCl+Cl-->$HgCl_2$	-320.63	-326.88	-320.44	-183.85	-346.04
R6	HgCl+HCl-->$HgCl_2$+H	101.41	-	101.60	226.90	85.57
R7	$Hg+Cl_2$-->$HgCl_2$	-193.81	-192.61	-193.02	-33.76	-207.67
Average absolute error		17.12	-	17.50	109.06	

-: not determined

*: The National Institute of Standards and Technology, http://webbook.nist.gov/

Further Determination

The University of Nottingham

-- Calculated results

Comparison of theoretical and experimental ΔH_{rxn}^{298K} (kJ/mol) at the cc-pVTZ-PP basis set

No.	Reaction	Method				NIST* experiment
		QCISD	MP4SDQ	CCSD	CISD	
R1	Hg+Cl+M-->HgCl+M	-76.20	-70.40	-74.80	38.38	-104.23
R2	$Hg+Cl_2$-->HgCl+Cl	129.30	136.64	130.35	171.48	138.37
R3	Hg+HCl-->HgCl+H	345.83	-	347.24	449.13	327.38
R4	$HgCl+Cl_2$-->$HgCl_2$+Cl	-112.68	-117.22	-112.89	-32.19	-103.44
R5	HgCl+Cl-->$HgCl_2$	-318.18	-324.26	-318.04	-165.29	-346.04
R6	HgCl+HCl-->$HgCl_2$+H	103.86	-	104.00	245.45	85.57
R7	$Hg+Cl_2$-->$HgCl_2$	-188.88	-187.62	-187.69	6.19	-207.67
Average absolute error		18.53	-	19.02	131.89	

-: not determined

*: The National Institute of Standards and Technology, http://webbook.nist.gov/

Further Determination

The University of Nottingham

-- Calculated results

Comparison of theoretical and experimental ΔH_{rxn}^{298K}(kJ/mol) at the cc-pwCVDZ-PP basis set

No.	Reaction	Method				NIST* experiment
		QCISD	MP4SDQ	CCSD	CISD	
R1	Hg+Cl+M-->HgCl+M	-84.00	-79.50	-82.81	16.49	-104.23
R2	$Hg+Cl_2$-->HgCl+Cl	121.50	127.54	122.35	149.58	138.37
R3	Hg+HCl-->HgCl+H	338.03	-	339.23	427.23	327.38
R4	$HgCl+Cl_2$-->$HgCl_2$+Cl	-112.16	-115.75	-112.22	-41.81	-103.44
R5	HgCl+Cl-->$HgCl_2$	-317.66	-322.80	-317.37	-174.91	-346.04
R6	HgCl+HCl-->$HgCl_2$+H	104.37	-	104.67	235.84	85.57
R7	$Hg+Cl_2$-->$HgCl_2$	-196.16	-195.25	-195.03	-25.32	-207.67
Average absolute error		16.45	-	16.93	113.88	

-: not determined

*: The National Institute of Standards and Technology, http://webbook.nist.gov/

Further Determination

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-- Calculated results

Comparison of theoretical and experimental ΔH_{rxn}^{298K} (kJ/mol) at the CRENBL basis set

No.	Reaction	Method				NIST* experiment
		QCISD	MP4SDQ	CCSD	CISD	
R1	Hg+Cl+M-->HgCl+M	-97.27	-95.84	-97.06	-43.74	-104.23
R2	$Hg+Cl_2$-->HgCl+Cl	108.24	111.21	108.09	89.36	138.37
R3	Hg+HCl-->HgCl+H	324.77	-	324.98	367.01	327.38
R4	$HgCl+Cl_2$-->$HgCl_2$+Cl	-121.42	-116.35	-121.45	-86.11	-103.44
R5	HgCl+Cl-->$HgCl_2$	-326.92	-323.40	-326.61	-219.21	-346.04
R6	HgCl+HCl-->$HgCl_2$+H	95.11	-	95.43	191.54	85.57
R7	$Hg+Cl_2$-->$HgCl_2$	-218.69	-212.19	-218.51	-129.85	-207.67
Average absolute error		13.91	-	14.00	68.15	

-: not determined

*: The National Institute of Standards and Technology, http://webbook.nist.gov/

Further Determination

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-- Calculated results

Comparison of theoretical and experimental ΔH_{rxn}^{298K} (kJ/mol) in terms of average absolute error

No.	Basis set	Method			
		QCISD	MP4SDQ	CCSD	CISD
3	1992 Steven's	19.76	-	19.95	57.64
6	aug-cc-pVDZ-PP	17.12	-	17.50	109.06
12	cc-pVTZ-PP	18.53	-	19.02	131.89
14	cc-pwCVDZ-PP	16.45	-	16.93	113.88
17	CRENBL	13.91	-	14.00	68.15

-: not determined

Determination Matrix

No.	Basis set\method	HF	B3LYP	MP2	MP3	MP4SDQ	CCD	CCSD	CID	CISD	QCISD
1	SDD										
2	LANL2DZ										
3	1992 Stevens					√		√		√	√
4	Ahlrichs Coulomb Fitting										
5	aug-cc-pV5Z-PP										
6	aug-cc-pVDZ-PP					√		√		√	√
7	aug-cc-pVQZ-PP										
8	aug-cc-pVTZ-PP										
9	cc-pV5Z-PP										
10	cc-pVDZ-PP										
11	cc-pVQZ-PP										
12	cc-pVTZ-PP					√		√		√	√
13	cc-pwCV5Z-PP										
14	cc-pwCVDZ-PP					√		√		√	√
15	cc-pwCVQZ-PP										
16	cc-pwCVTZ-PP										
17	CRENBL					√		√		√	√
18	CRENBS										
19	Stuttgart RLC										
20	Stuttgart RSC 1997										
21	WTBS										

20 combinations

Determination Matrix

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QCISD/1992, QCISD/CRENBL and CCSD/CRENBL

Mercury speciation studies

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--- Mercury chlorination (homogeneous)

No.	Reaction
R1	$Hg + Cl + M \leftrightarrow HgCl + M$
R2	$Hg + Cl_2 \leftrightarrow HgCl + Cl$
R3	$Hg + HCl \leftrightarrow HgCl + H$
R4	$HgCl + Cl_2 \leftrightarrow HgCl_2 + Cl$
R5	$HgCl + Cl \leftrightarrow HgCl_2$
R6	$HgCl + HCl \leftrightarrow HgCl_2 + H$
R7	$Hg + Cl_2 \leftrightarrow HgCl_2$

Source: a. Niksa S., Helble J. J. and Fujiwara N. (2001) Kinetic modeling of homogeneous mercury oxidation: the importance of NO and H2O in predicting oxidation in coal-derived systems, *Environmental Science & Technology*, **35**: p3701-3706; b. Widmer C. N., West J. and Cole A. J. (2000) Thermochemical study of mercury oxidation in utility boiler flue gases, *the 93rd Air & Waste Management Association (A&WMA) Annual Conference and Exhibition*, Salt Lake City, Utah

$HgCl+HCl \leftrightarrow HgCl_2+H$

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--- Predicted geometries

Unit: bond length, Å; bond angle, degree. T=298K

	QCISD/1992	QCISD/CRENBL	CCSD/CRENBL	Expt.
HgCl	2.412	2.394	2.3952	2.42[a]
HCl	1.274	1.274	1.2738	1.2746[b]
$HgCl_2$	2.3003, ∠180°	2.2777, ∠180°	2.2781, ∠180°	2.252[b], ∠180°
TS (Hg-Cl-Cl--H)	Cl-Hg: 2.3241; Hg-Cl: 2.3763 Cl-H: 1.781; ∠ClHgCl: 180° ∠HgClH: 180°	Cl-Hg: 2.3025; Hg-Cl: 2.3631 Cl-H: 1.7689; ∠ClHgCl: 180° ∠HgClH: 180°	Cl-Hg: 2.3029; Hg-Cl: 2.3636 Cl-H: 1.7685; ∠ClHgCl: 180° ∠HgClH: 180°	Not available

[a] Ref: Bhartiya B. J., Behere H. S. and Rao L. P. M. (1990) Dissociation energies of HgCl, HgBr and HgI from potential energy curves, *Journal of quantitative spectroscopy & radiative transfer*, **43**(1): p95-98;
[b] Ref: Lide R. D. ed. (2007) Bond Lengths and Angles in Gas-phase Molecules, in CRC Handbook of Chemistry and Physics, Internet Version, 87th Edition, Taylor and Francis, Boca Raton, FL

$HgCl+HCl \leftrightarrow HgCl_2+H$

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--- Predicted thermodynamic and kinetic

T=298K	QCISD/1992	QCISD/CRENBL	CCSD/CRENBL	Expt.
Frequencies, cm^{-1}				
HgCl	289.0268	285.5	285.0	292.61[a]
HCl	3024.7	3024.7	3026.1	2989.74[a]
$HgCl_2$	97.3, 97.3, 338.2,392.1	93.7, 93.7, 347.4, 397.1	94.0, 94.0, 347.3, 397.0	75, 75, 363, 413[b]
TS (Hg-Cl-Cl--H)	77.4, 77.4, 214.6, 214.6, 330.4, 360.6, -1038.5	73.6, 73.6, 198.6, 198.6, 339.8, 364.7, -1057.6	73.8, 73.8, 199.1, 199.1, 339.6, 364.6, -1062.9	Not available
Reaction heat ΔH_{rxn}, kJ/mol				
Forward	93.163	94.949	95.283	85.57[d]
Activation energy, kJ/mol				
Forward	121.024	125.901	126.497	Not available
Reverse	27.864	30.957	31.217	

[a] Ref: Herzberg G. (1939) Molecular spectra and molecular structure I. Spectra of diatomic molecules, D. Van Nostrand Company, New York; [b] Ref: Herzberg G. (1966) Molecular spectra and molecular structure III Electronic spectra and electronic structure of polyatomic molecules, D. Van Nostrand Company, Inc. New York; [c] Ref: National Institute of Standards and Technology (NIST)

$HgCl+HCl \leftrightarrow HgCl_2+H$

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--- Comparison of k

T=298K	Method/basis set	Rate constant, $cm^3/mol\ s$	
		Forward	Reverse
This work	QCISD/1992	4.561×10^{-11}	3.940×10^{8}
	QCISD/CRENBL	7.434×10^{-12}	1.275×10^{8}
	CCSD/CRENBL	5.798×10^{-12}	1.145×10^{8}
Wilcox and Blowers (2004)	QCISD/1992	3.919×10^{-12}	-
	QCISD/1997	8.864×10^{-10}	-
Niksa et al. (2001)	-	7.154×10^{-5}	-
Widmer et al. (2000)	-	8.657×10^{-2}	-

$HgCl+HCl \leftrightarrow HgCl_2+H$

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--- Theoretical rate constant (K=25-1200°C)

- QCISD/1992:

$$k_{forward} = 5.273 \times 10^{11} e^{\frac{-15089}{T}} \text{ and } k_{reverse} = 1.271 \times 10^{14} e^{\frac{-3651.7}{T}}$$

- QCISD/CRENBL:

$$k_{forward} = 6.447 \times 10^{11} e^{\frac{-15684}{T}} \text{ and } k_{reverse} = 1.516 \times 10^{14} e^{\frac{-4035.2}{T}}$$

- CCSD/CRENBL:

$$k_{forward} = 6.363 \times 10^{11} e^{\frac{-15753}{T}} \text{ and } k_{reverse} = 1.506 \times 10^{14} e^{\frac{-4064.8}{T}}$$

Arrhenius equation: $k = A\exp(-E_a / RT)$

$HgCl+HCl \leftrightarrow HgCl_2+H$

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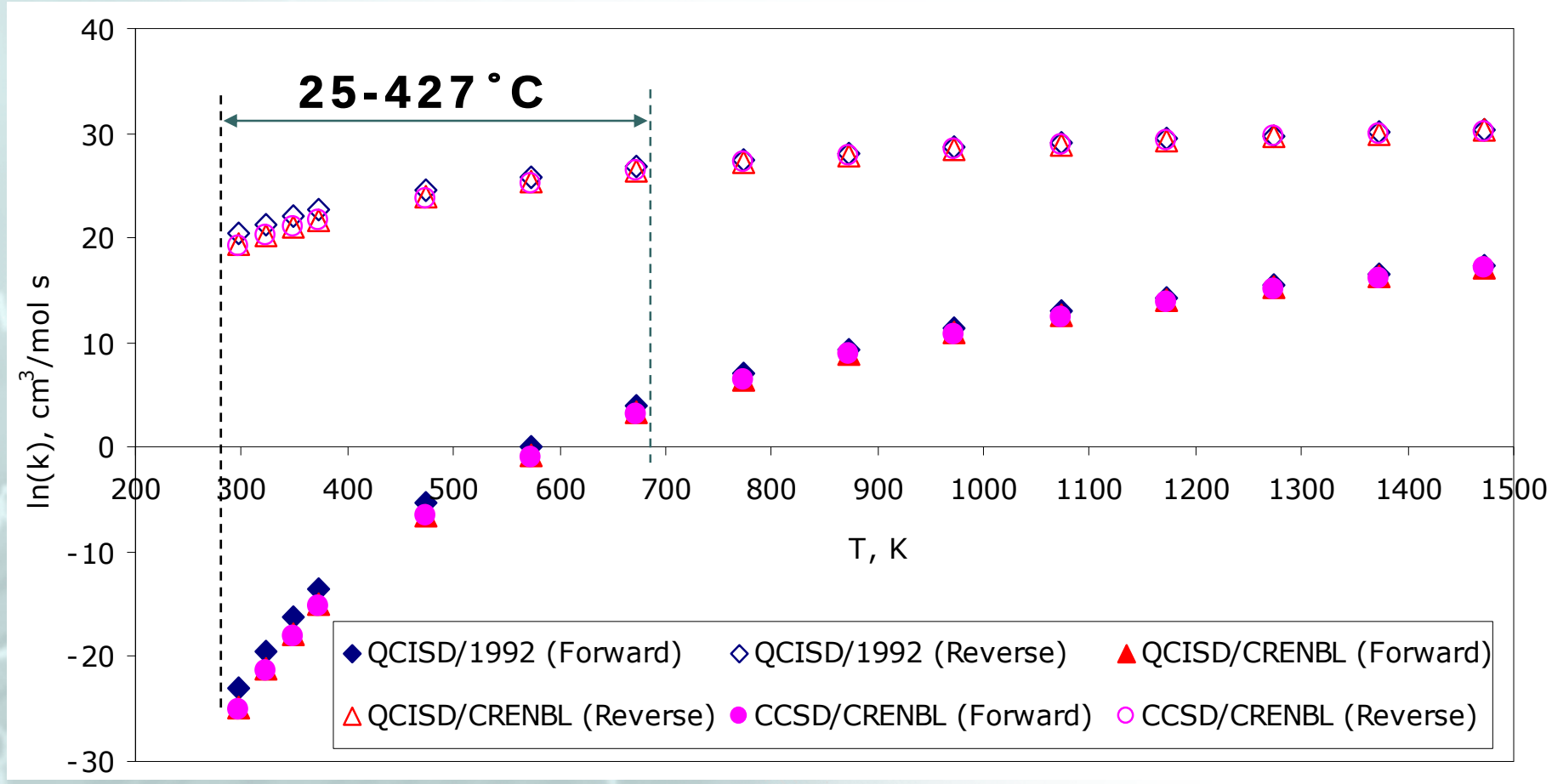
--- Temperature profile



$HgCl+HCl \leftrightarrow HgCl_2+H$

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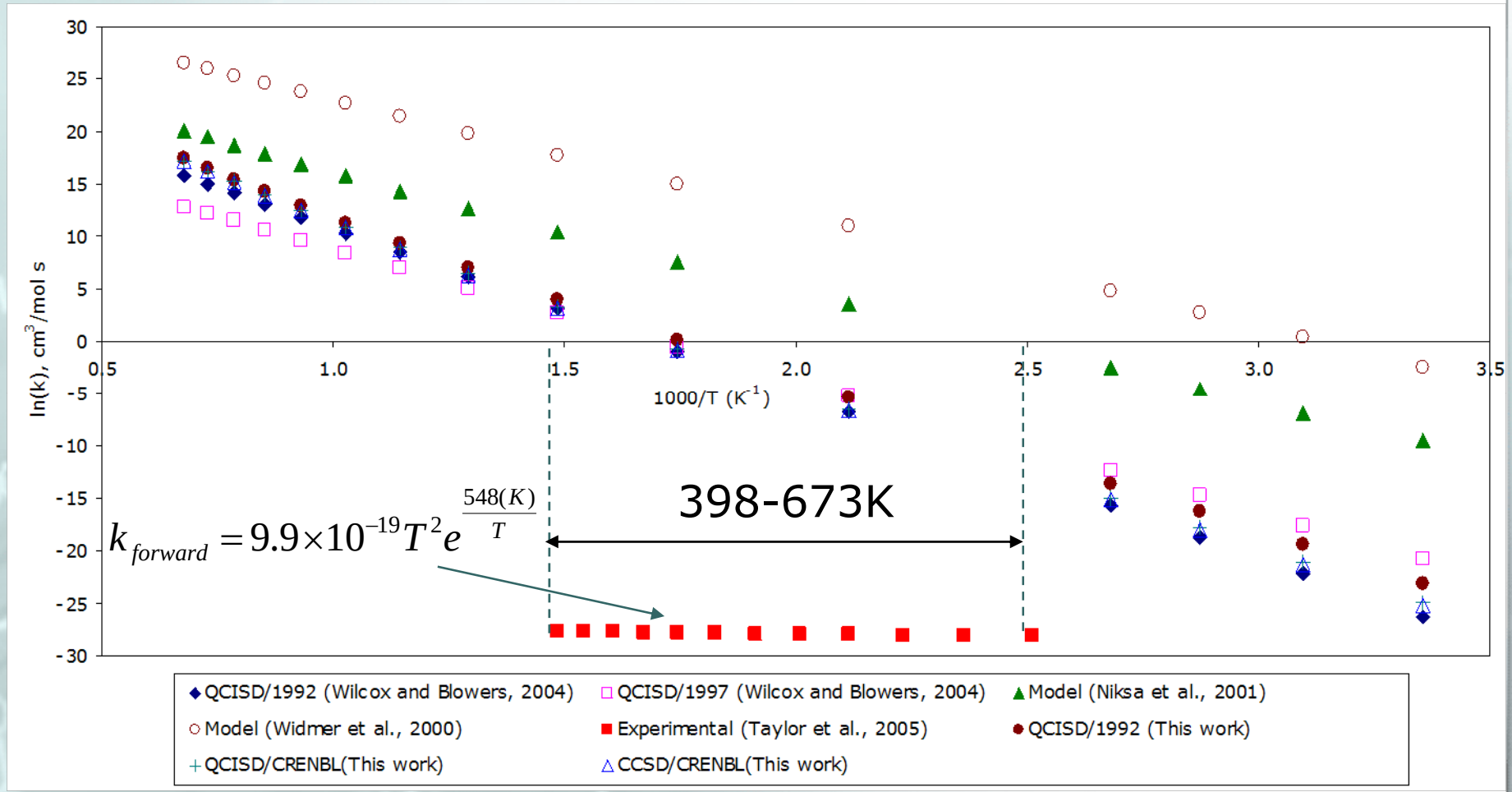
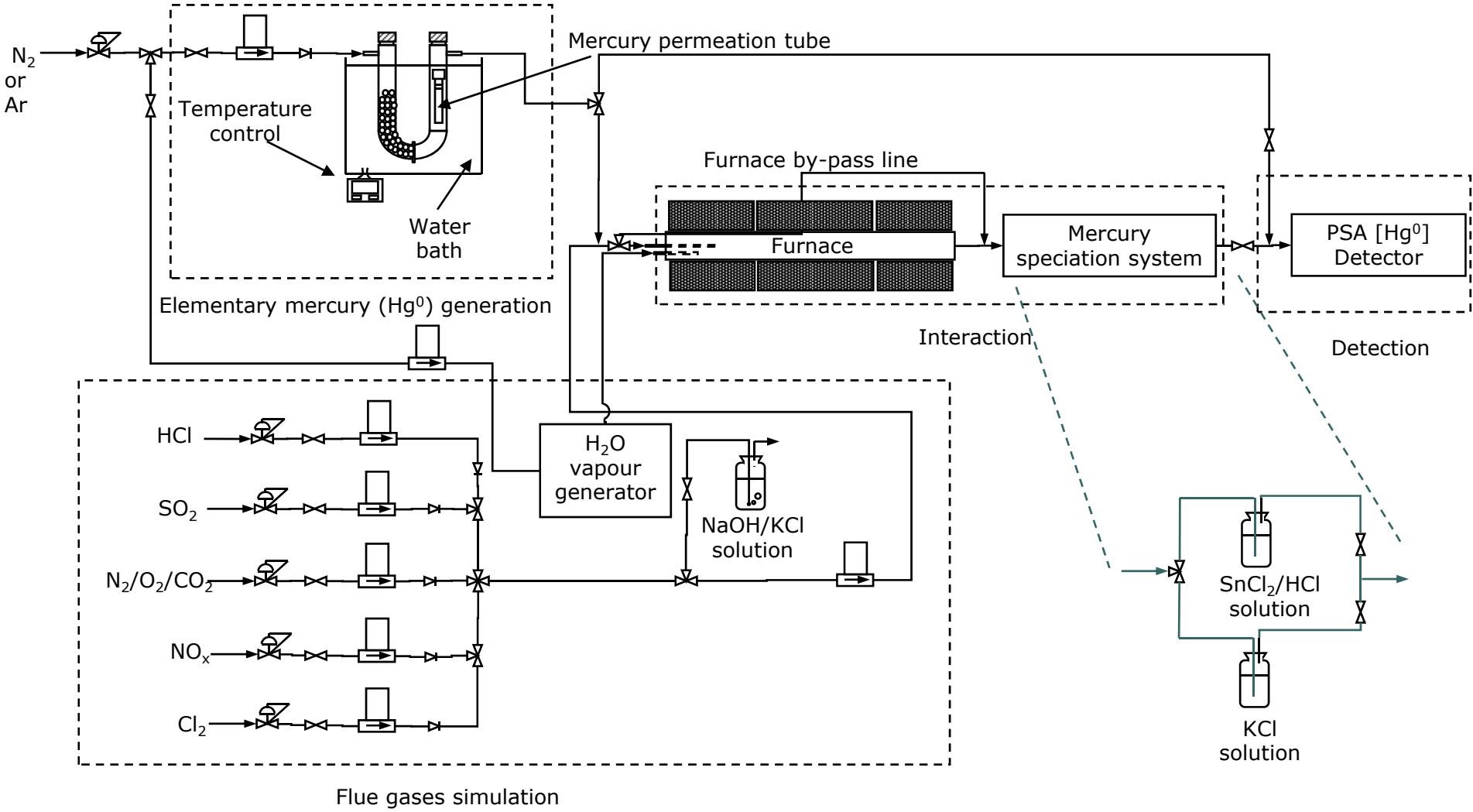
--- Comparison of models



Experimental set up



A Schematic diagram for mercury speciation studies

Experimental set-up

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Additional equipment

Experimental set-up

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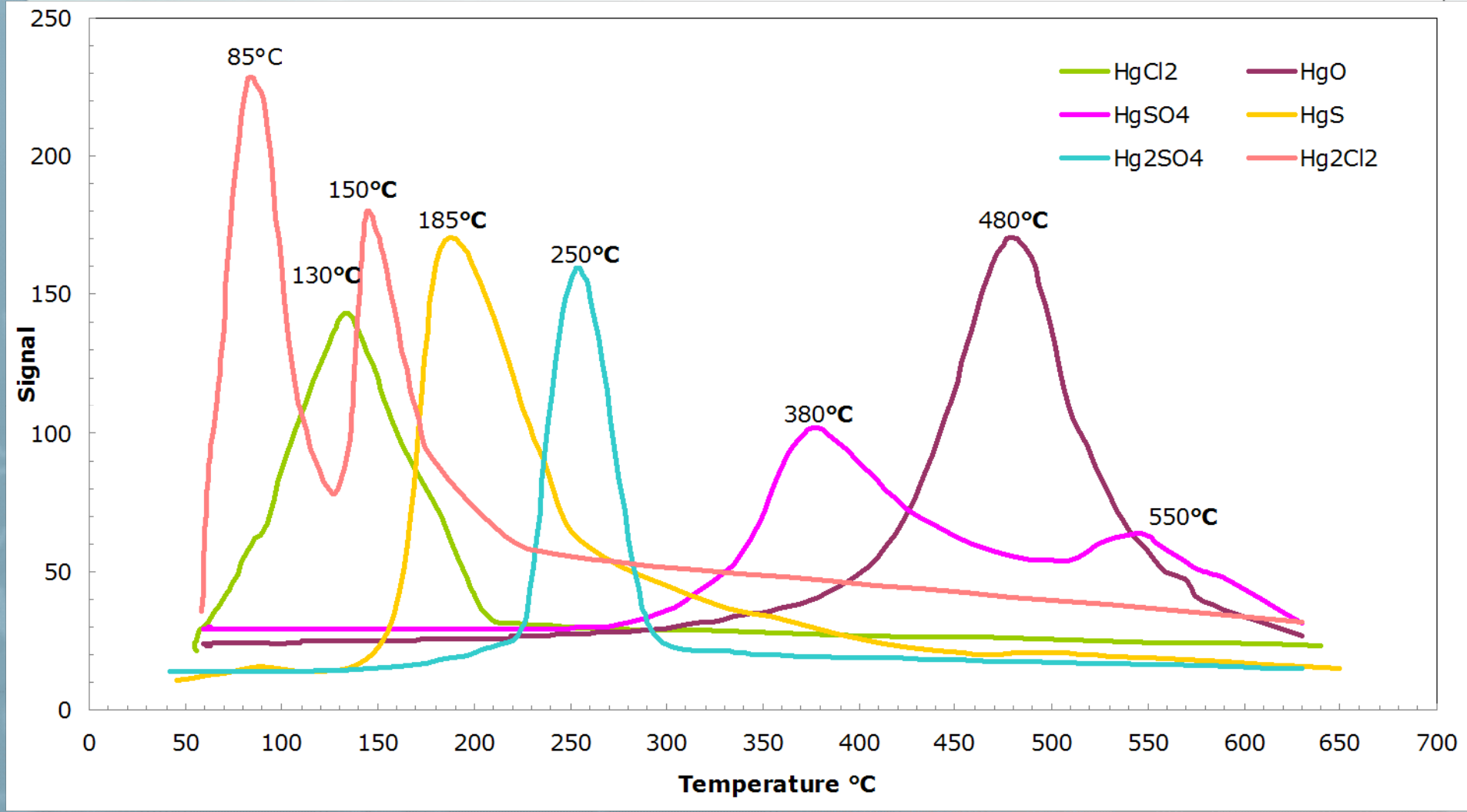
Fingerprints for mercury compounds



Summary

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- Six fly ash samples were characterised by ultimate and proximate analyses, LOI value and particle size distribution.
- The validation of method and basis set was completed and three combinations were considered to be accurate for this project.
- One mercury chlorination reaction, $HgCl+HCl \leftrightarrow HgCl_2+H$, was completed using the three chosen combination.
- The reverse reaction is favoured in the low temperature range (25-427°C).
- An experimental set-up is being commissioned

Future work

- Complete the theoretical study on homogeneous reactions taking place between gaseous elemental mercury and flue gas components, including mercury chlorination (Task 2.1).
- Complete commission of experimental set up and determine rate constants to validate theoretical model
- Start modelling in heterogeneous reactions taking place gaseous elemental mercury and fly ashes (Task 2.2).
- Evaluate the effects of individual material on mercury oxidation (Task 3)

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Thank You
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Question?