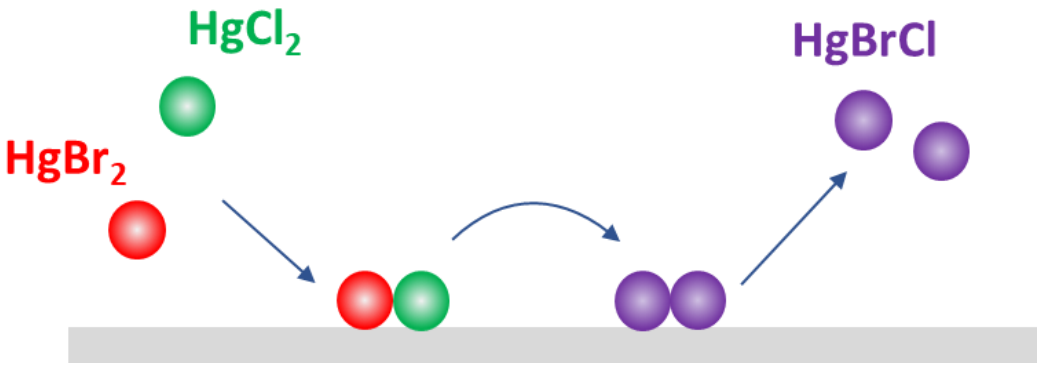
NJIT New Jersey's Science & Technology University

Surface reactions can alter both perceived and actual composition of atmospheric Hg(II)

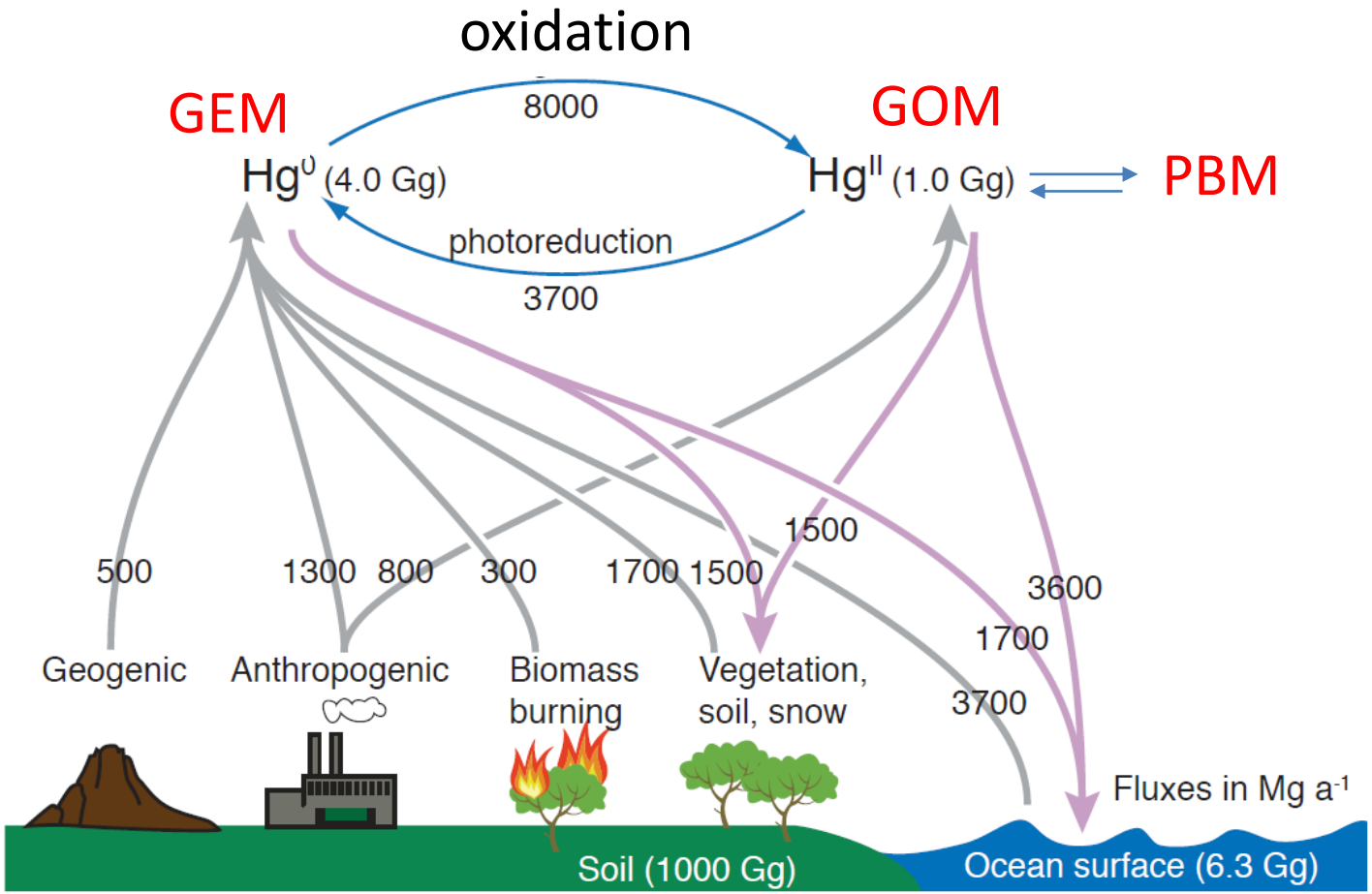
Alexei Khalizov and Na Mao
New Jersey Institute of Technology



khalizov@njit.edu

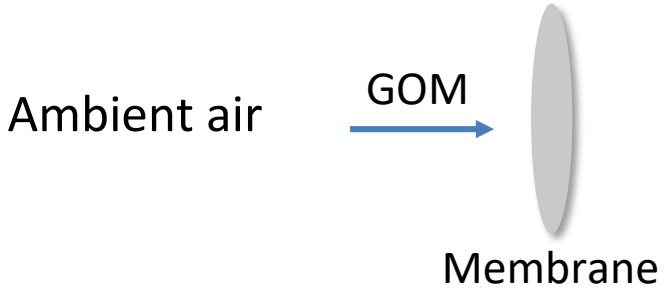
Molecular speciation of Hg(II)

Mao, et al., Heterogeneous Chemistry of Mercuric Chloride on Inorganic Salt Surfaces. The Journal of Physical Chemistry A, 2021. 125(18): p. 3943-3952.

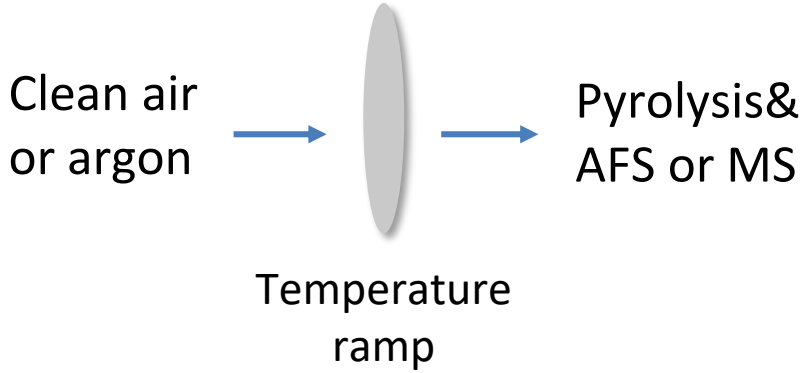


Holmes, et al., Global atmospheric model for mercury including oxidation by bromine atoms. Atmospheric Chemistry and Physics 2010. 10(24): p. 12037-12057.

Step 1: adsorption



Step 2: desorption and analysis



Do these approaches work?

Predicted GOM molecules don't appear to be volatile or thermally stable

$$Hg + Br \rightarrow HgBr$$

$$HgBr + NO_2 \rightarrow \mathbf{BrHgONO}$$

$$HgBr + HO_2 \rightarrow \mathbf{BrHgOOH}$$

$$BrHgONO + h\nu \rightarrow BrHgO + NO$$

$$BrHgO + CH_4 \rightarrow \mathbf{BrHgOH} + CH_3$$

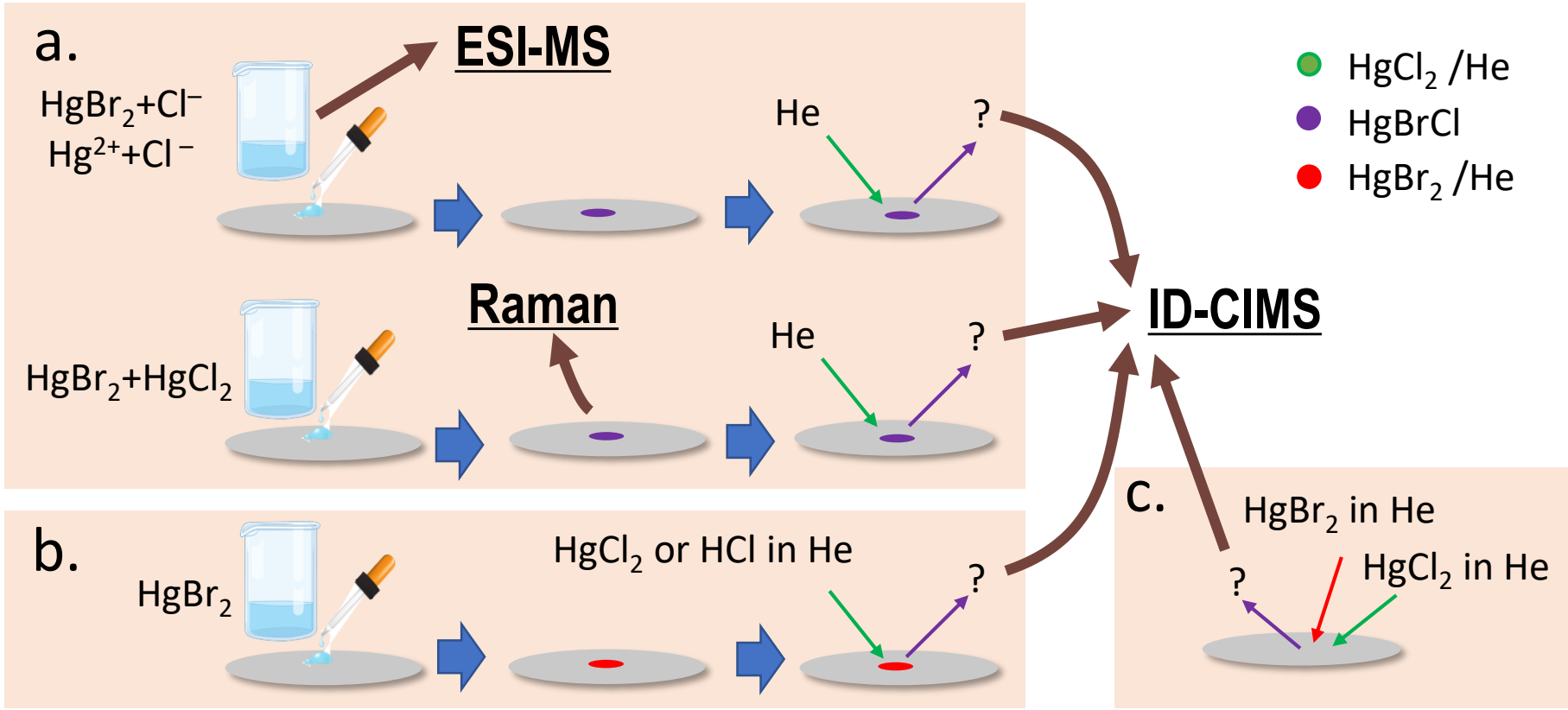
$$BrHgO + NO_2 \rightarrow \mathbf{BrHgONO_2}$$

(Lam et al., 2019; Jiao and Dibble, 2015&2017)

- Will such molecules maintain their chemical identities in condensed phase during sampling?
- Can they be re-volatilized by thermal desorption?

- What will happen to these molecules after their uptake by atmospheric aerosols?

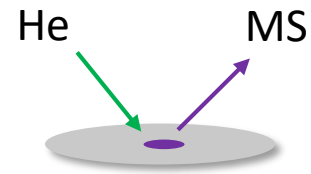
Experimental matrix



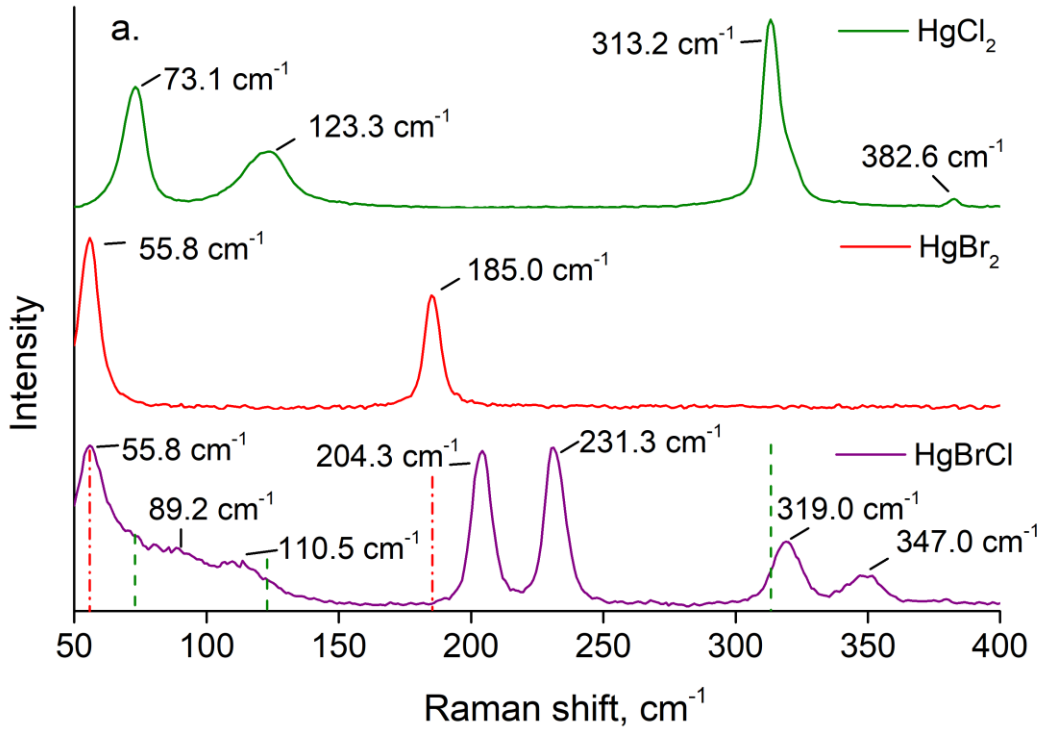
Na Mao and Alexei Khalizov, Exchange Reactions May Bias Molecular Speciation of Gaseous Oxidized Mercury, *ACS Earth and Space Chemistry*, 2021, 5, 8, 1842

Reaction in solution: **covalent** mercuric species

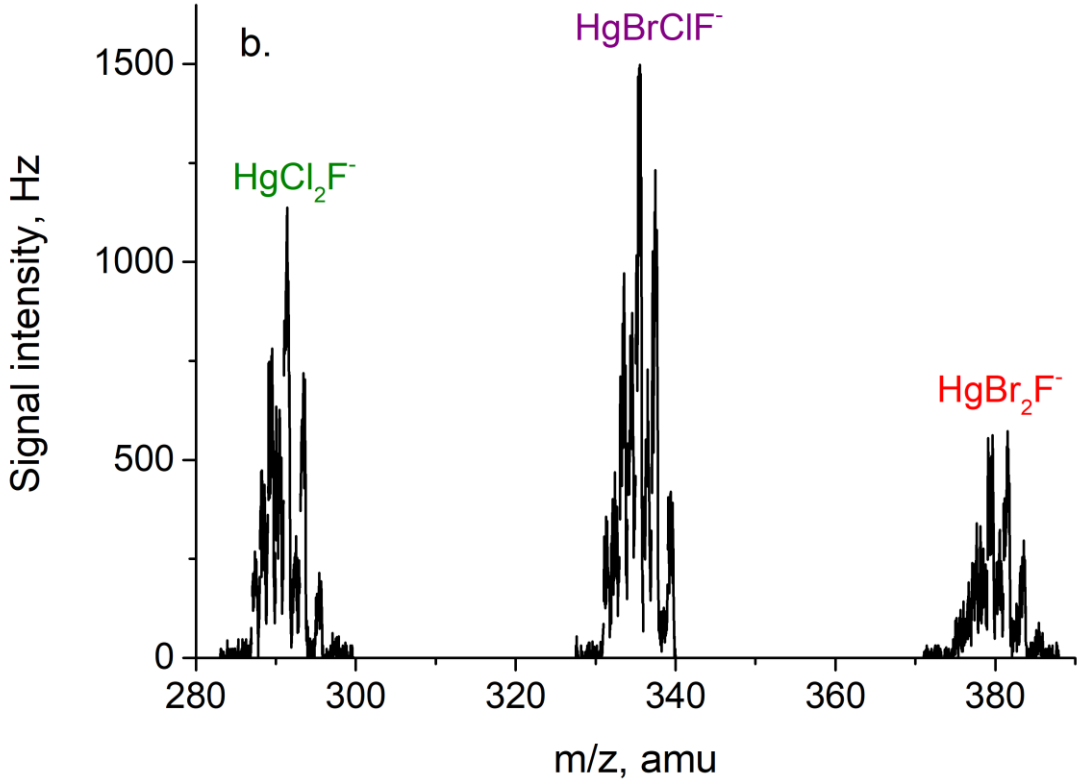
$$HgCl_2 + HgBr_2 \rightarrow 2HgClBr$$



Raman analysis of the dry product



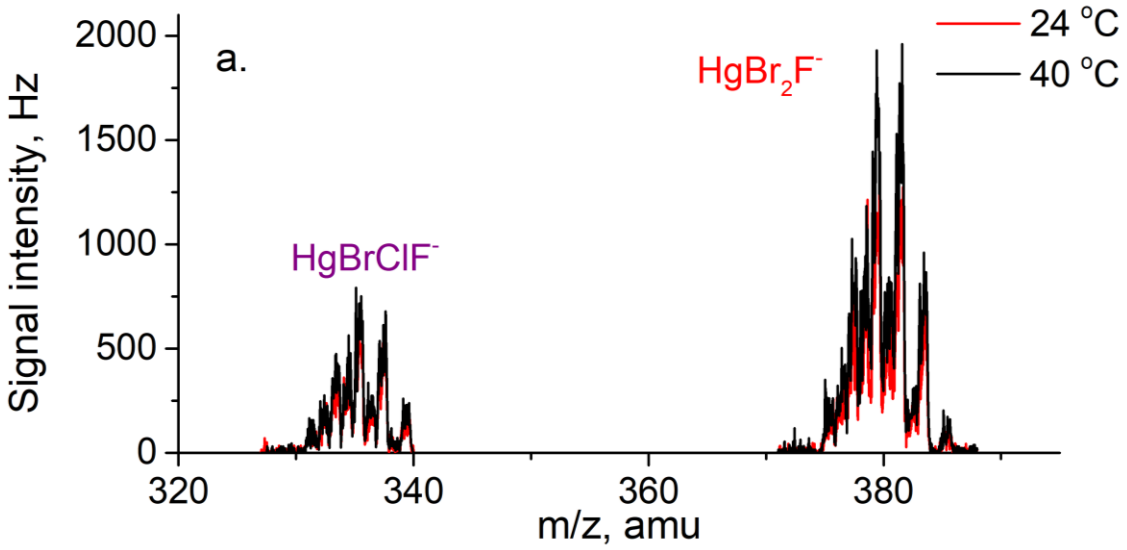
MS analysis of vapor above the dry product



Reaction in solution: **covalent** + **ionic** species

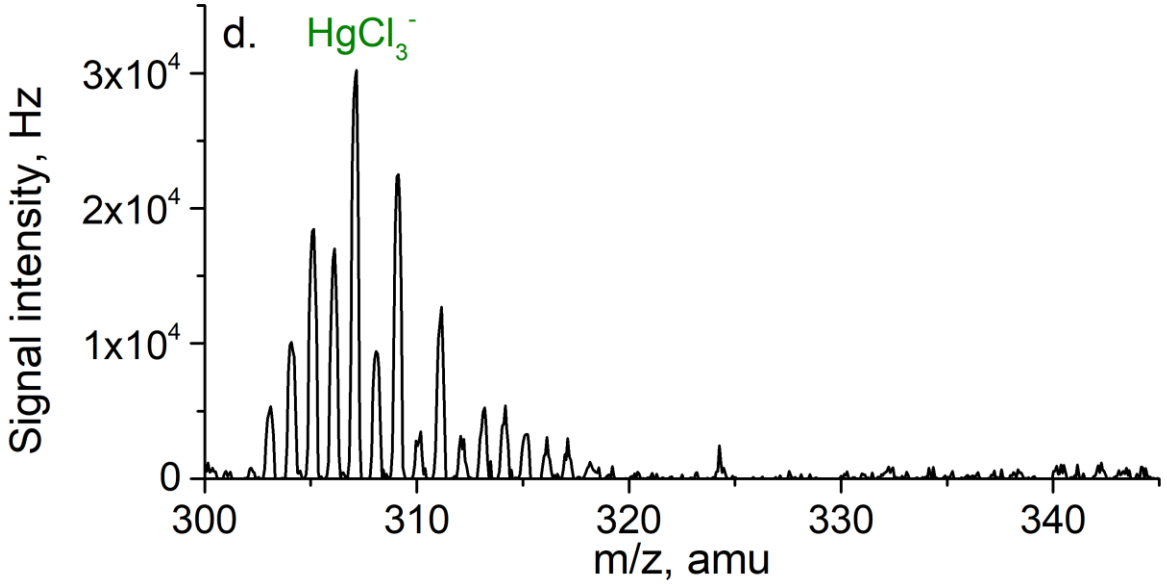
Analysis in gas phase

$$HgBr_2 + Cl^- \rightarrow HgBrCl + Br^-$$



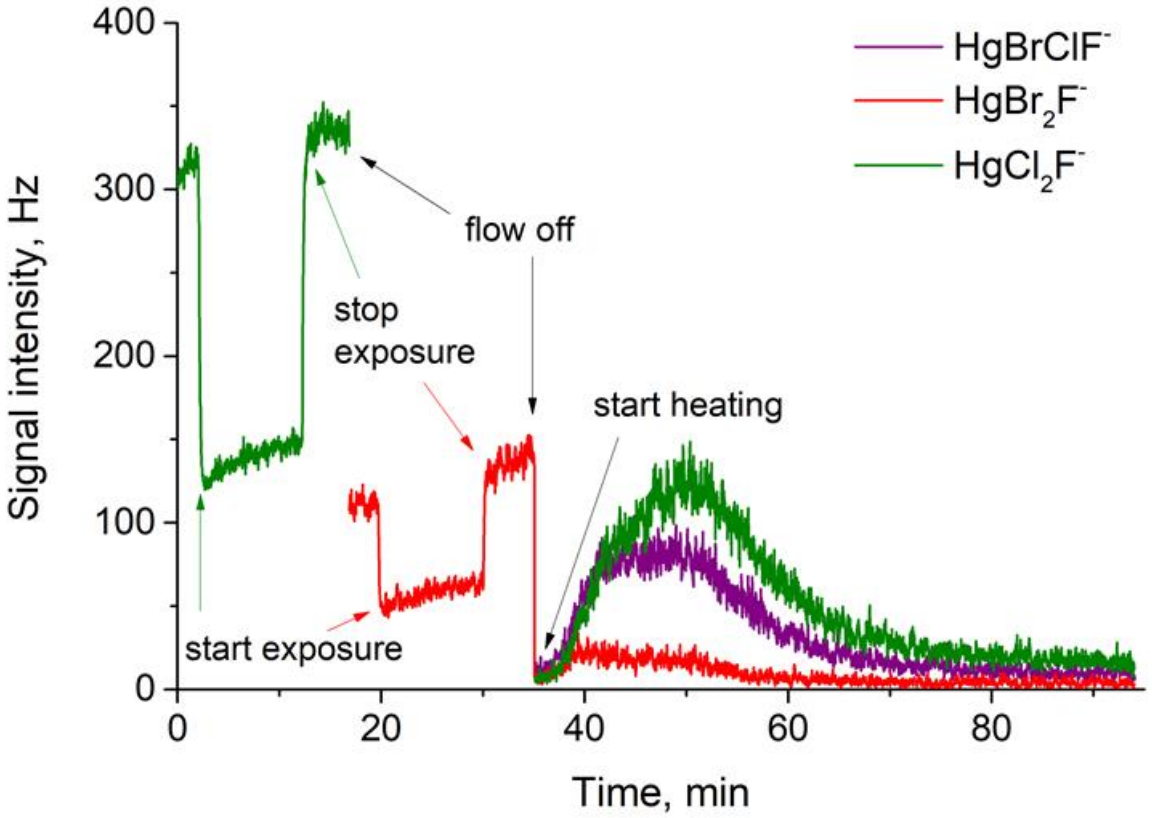
Analysis in solution

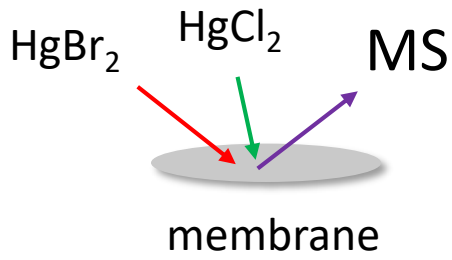
$$Hg^{2+} + 2Cl^- \rightarrow HgCl_2$$



Gaseous $HgCl_2$ and $HgBr_2$ on a membrane

$$HgCl_2 + HgBr_2 \rightarrow 2HgClBr$$

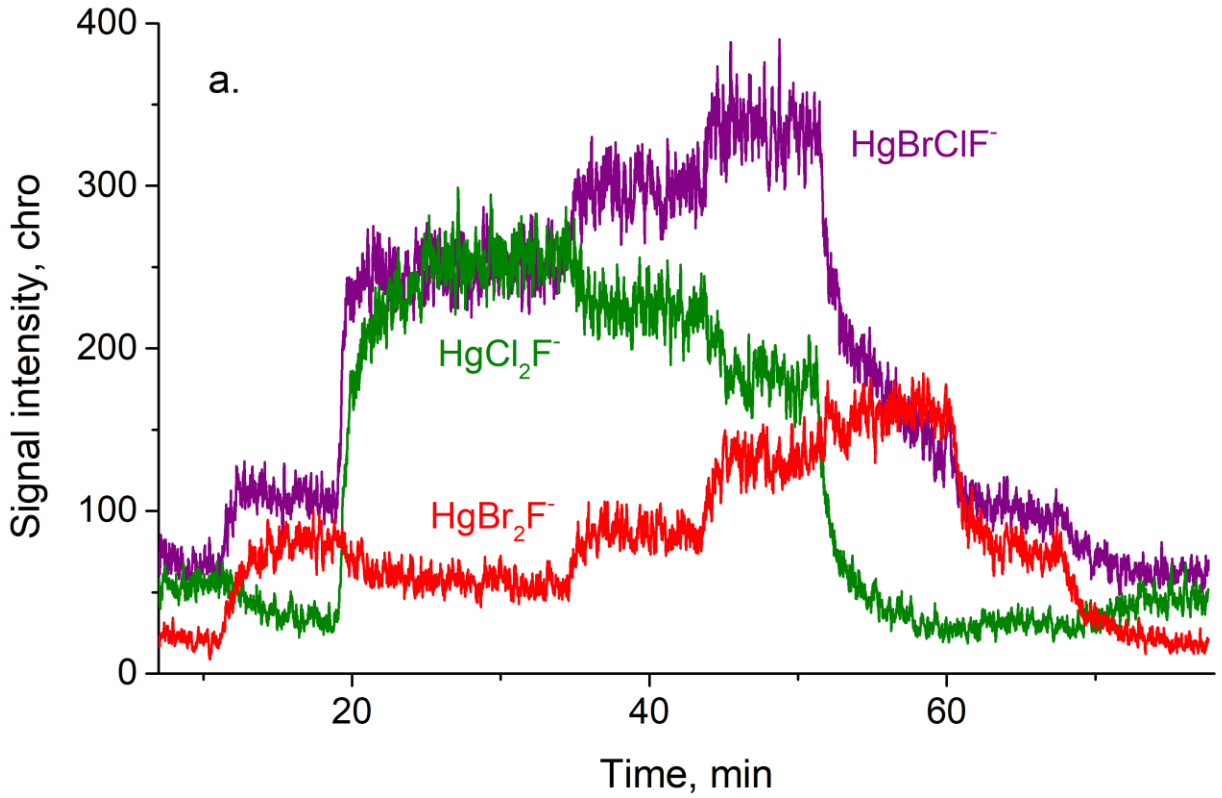


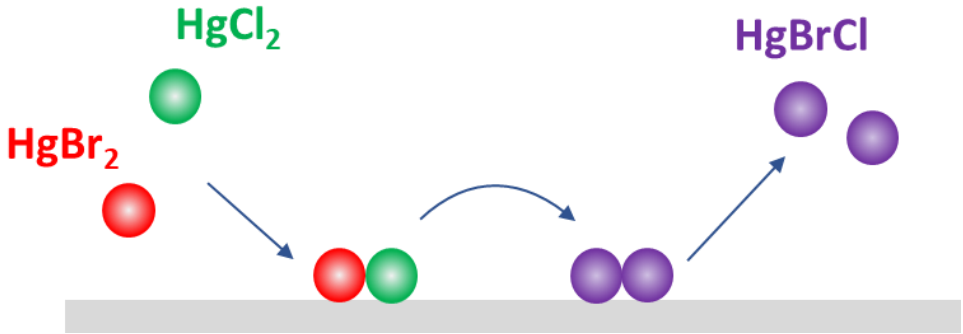


Rapid exchange of individual GOM compounds on a membrane to form a mixed product

Gaseous $HgCl_2$ and $HgBr_2$ on deactivated Pyrex

$$HgCl_2 + HgBr_2 \rightarrow 2HgClBr$$





Extrapolation to atmospheric conditions

- Atmospheric concentrations are lower (e.g., 10^5, not 10^{10} molecules cm^{-3})
- But correct metrics are surface coverages and contact times!

Surface coverage (molecules cm^{-2})

	Field sampling	Experiment
Hg(II)	8×10^{10}	8×10^{14} (membrane)
		4×10^{11} (deactivated Pyrex)
HCl	3×10^{16}	4×10^{17} (membrane)

- In the field, humid air is sampled over 1-2 weeks, giving plenty of reaction time
- No water in our experiments and contact times ranged from milliseconds to minutes

Conclusions

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- Pre-concentrating GOM on sorbents leads to rapid exchange that can scramble its molecular speciation
- Atmospheric aerosols are a significant sink for GOM and a similar scrambling can occur via exchange-revolatilization on aerosols
- A direct analysis method that does not involve pre-concentration is required for obtaining true molecular speciation