

Flash pyrolysis mechanism of trimethylchlorosilane

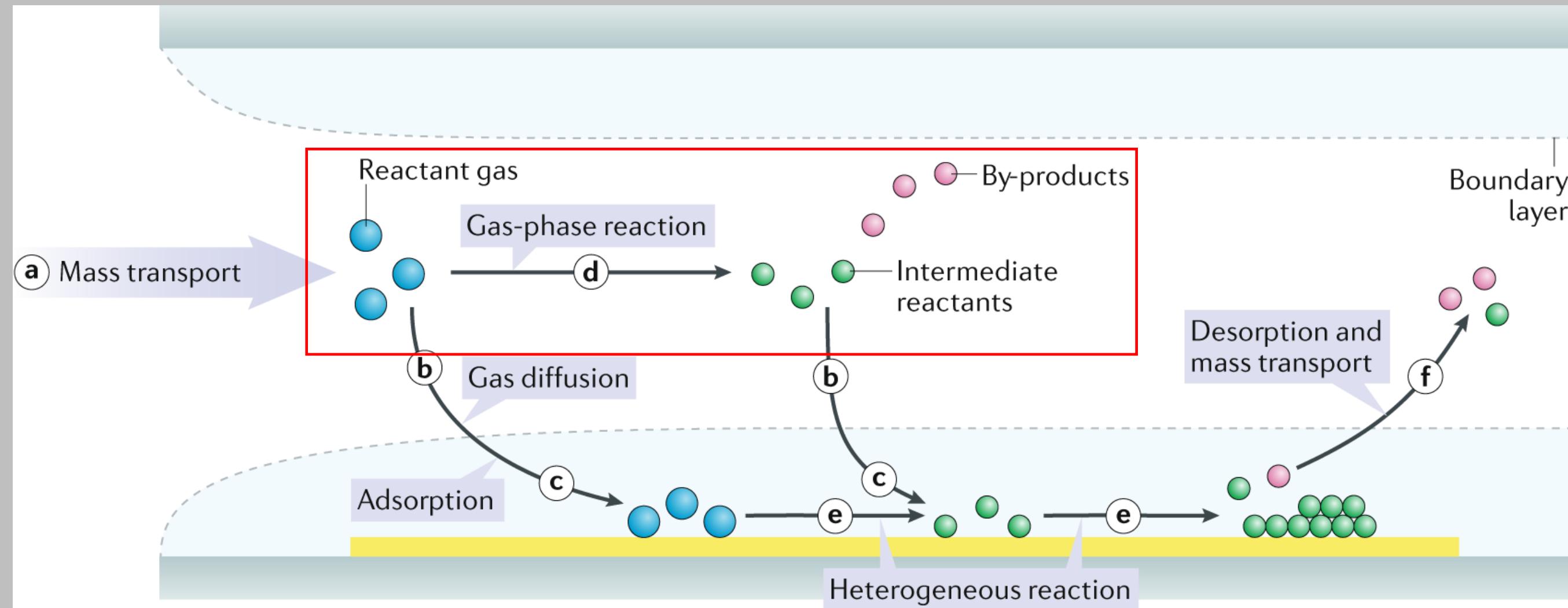
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Introduction

- Chemical vapor deposition (CVD) of SiC film and gas phase pyrolysis of silanes.



Pyrolyzing silanes was a critical step in the SiC film production

using CVD. Therefore, studying its gas phase pyrolysis mechanism is important.

2. Why trimethylchlorosilane?

(1) It can control the stoichiometry ratio of C/Si by controlling the number of chloride substitutes in the CVD production.

(2) The produced HCl could suppress the deposition of pure Si on Si substrates, therefore facilitated the production of pure SiC thin films.

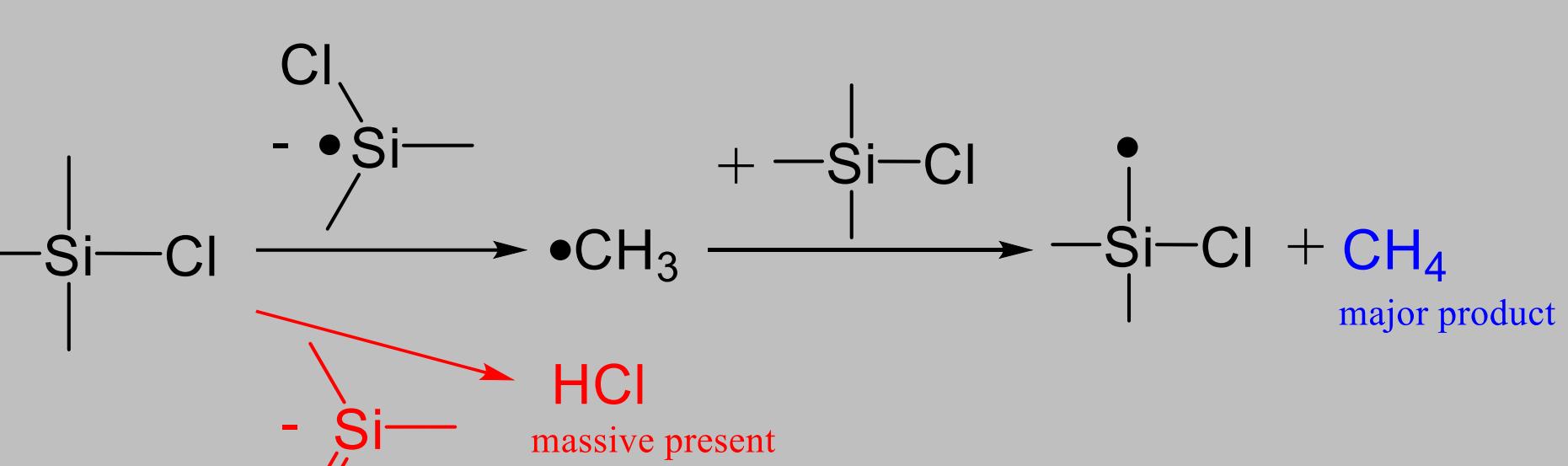
Question:

(1) Why there was a massive presence of HCl in the system?

(2) Is the proposed formation mechanism for CH₄ reasonable, any other possible reaction pathways?

Key:

Identify the key intermediate Me₂Si=CH₂ (m/z = 72) and •CH₂SiMe₂Cl (m/z = 107)



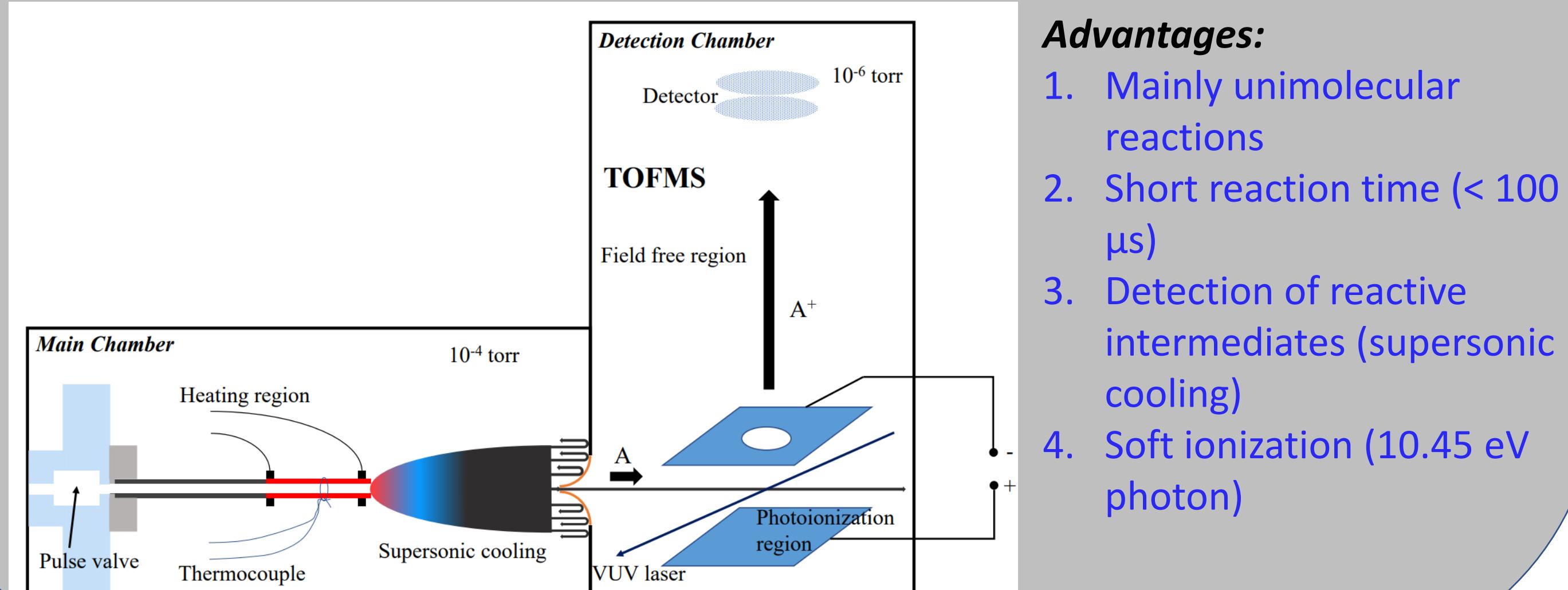
I.M.T. Davidson, C.E. Dean, *Organometallics*, 6 (1987) 966-969.

3. Approach:

- Vacuum ultraviolet photoionization mass spectrometry coupled with flash pyrolysis: (**Unimolecular reactions were predominant!**)
- Perform quantum chemistry calculations on the energetics of the decomposition pathways.

Experimental and computational method

- Vacuum ultraviolet mass spectrometry (VUV-MS) coupled with flash pyrolysis microreactor:



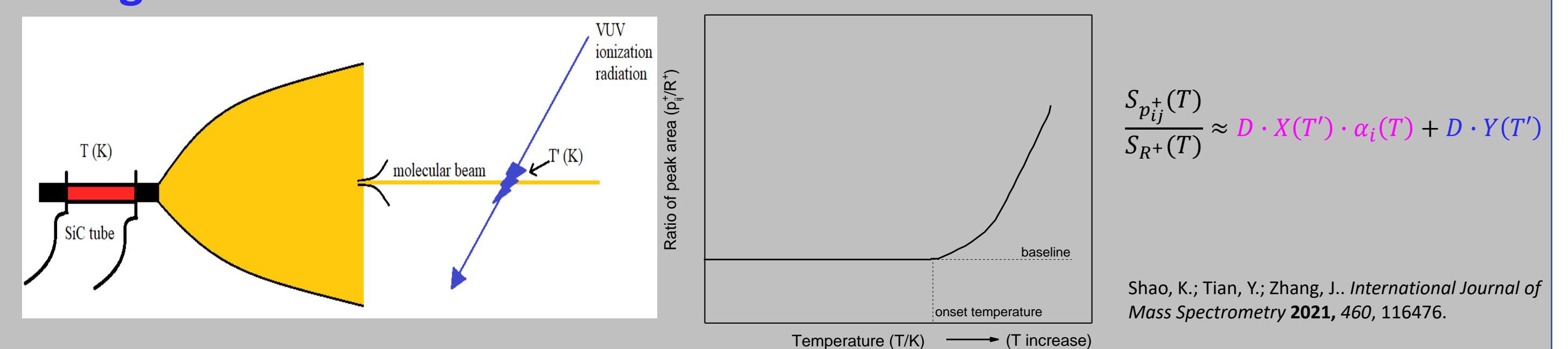
2. Reaction energetics calculations.

- Geometry optimization and frequency calculations: UM05-2X/aug-cc-pVDZ.

- Single point energy calculation: UCCSD(T)/cc-pVTZ.

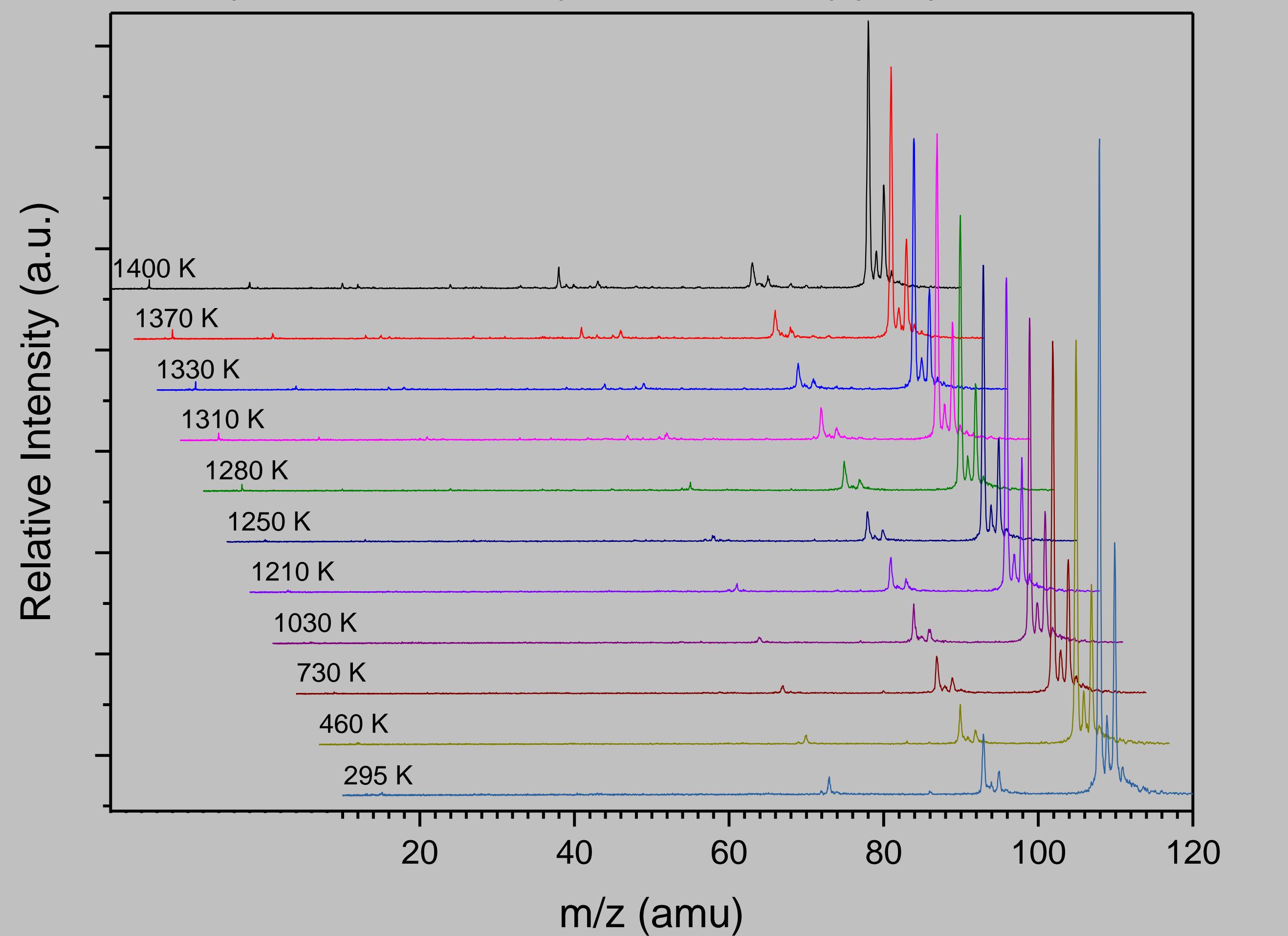
- Gaussian 16 package.

3. Ratio of peak area: distinguish the contributions from **ionization fragmentation** and **thermal dissociation**.



Results and Discussions

1. Mass spectra of trimethylchlorosilane pyrolysis.



Shao, K.; Brunson, J.; Tian, Y.; Zhang, J., *International Journal of Mass Spectrometry* (Submitted)

Relative Intensity (a.u.)

m/z (amu)

20 40 60 80 100 120

1400 K
1370 K
1330 K
1310 K
1280 K
1250 K
1210 K
1030 K
730 K
460 K
295 K

Relative Intensity (a.u.)

20 40 60 80 100 120

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