Silicon-Phosporus bonding: laboratory detection of $HPSiH_2$ employing high resolution spectroscopy

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Phosphorus-Silicon bonding

✓ Big literature focused on first-row element bondings

✓ Less extensive study on second-row

✓ In the past 10 years much progress has been made

(Cundari, Chem. Rev. 2000)

✓ Structure of second-row element bearing molecules can differs substantially comparing to first-row's

✓ Previously reported HPSi complex

(Lattanzi et al., Ang. Chem. 2010, in press)

✓ P and Si bearing compounds detected in circumstellar shells of evolved carbon-rich stars and other astronomical sources

(Tenenbaum & Ziurys, ApJ 2008)

Previous study on the [3H, P, Si] system

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A topographical study of bonding in the PP and SiP hydrides

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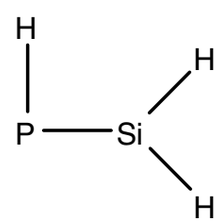
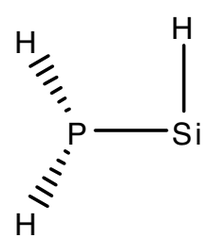
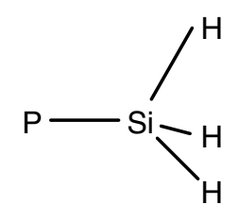
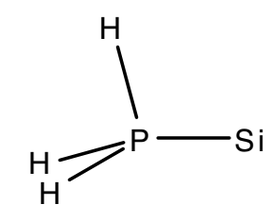






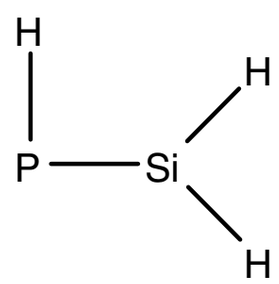


	$HPSiH_2$	H_2PSiH	$PSiH_3$	H_3PSi
r(PH) (Å)	1.426	1.4098 1.4096		1.424 (2) 1.412
r(SiH)	1.482 1.480	1.523	1.487 Å	
r(PSi)	2.087	2.228	2.257	2.260
E(rel)	0.0[b] kcal/mol	13.2	58.0	59.6

New Quantum Chemical Calculations

✓ Theoretical structure calculations performed at the CCSD(T)/cc-pwCVQZ level of theory

✓ Structure corrected for zero-point vibrational effects at the CCSD(T)/cc-pV(T+d)Z level.



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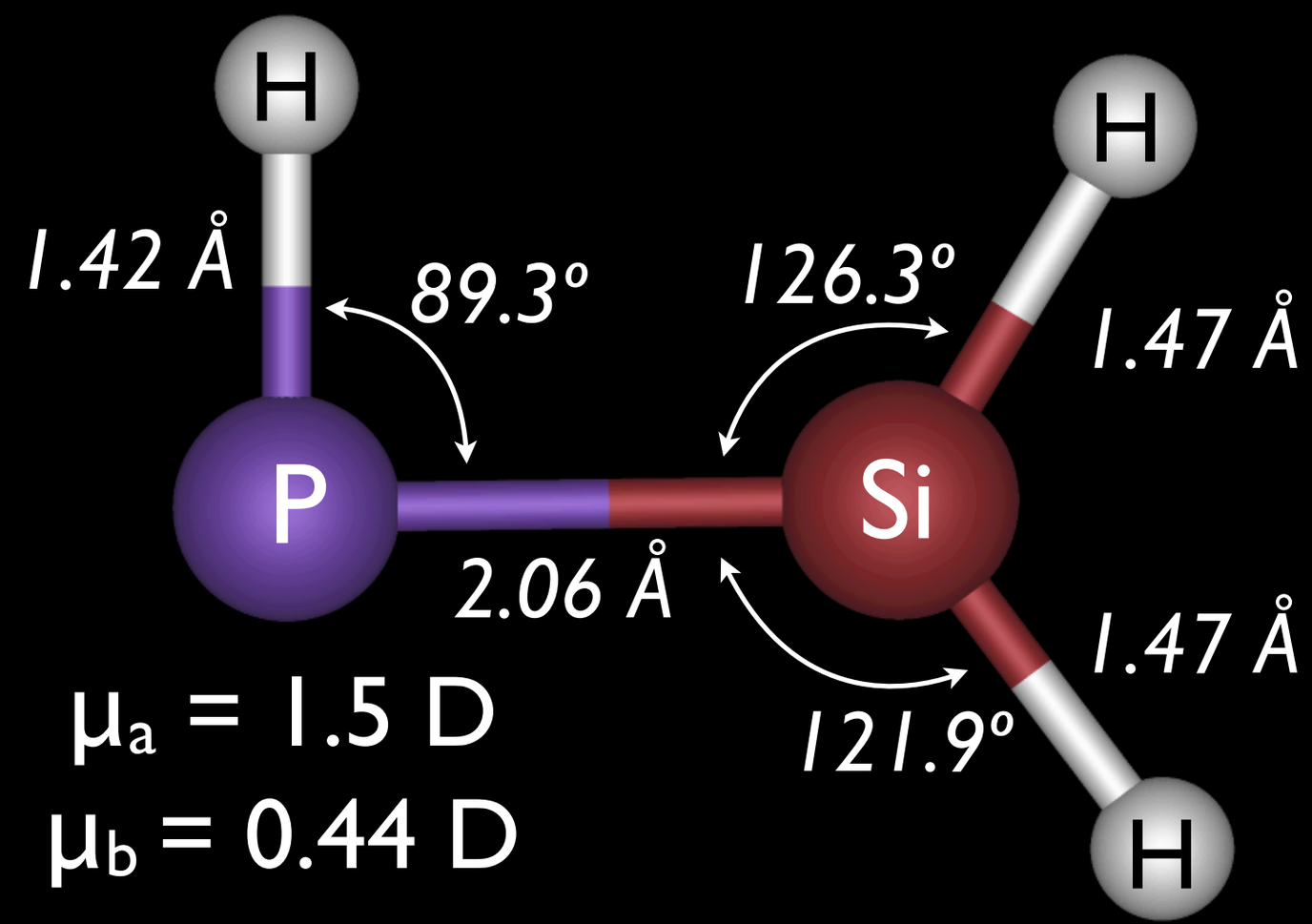


μ_a = 1.5 D

μ_b = 0.44 D

Experimental setup

- ✓ Detection of the rotational spectra by FTM spectroscopy
  - ✓ 5 - 42 GHz
  - ✓ 6 Hz pulsed nozzle to inject the supersonic molecular beam (~ Mach 2)
  - ✓ T_{rot} ~ 1-3 K
  - ✓ DC discharge of a mixture of Phosphine and Silane, heavily diluted in a Ne buffer

Analysis

✓ 3 lowest $K_a = 0$ lines measured

$J'_{K'a,K'c}$ — $J_{Ka,Kc}$	Freq (MHz)	O - C (kHz)
$1_{0,1}$ — $0_{0,0}$	13684.273	6
$2_{0,2}$ — $1_{0,1}$	27366.870	-5
$3_{0,3}$ — $2_{0,2}$	41046.170	1

✓ 2 rotational constants fitted

Const (MHz)	Exp.	Theor.
A	101157.025	101157.025
B	7064.298(206)	7105.729
C	6619.983(203)	6631.755

$\Delta \sim 0.5\ \%$

Isotopic confirmation

- ✓ Isotopic species detection provides crucial confirmation of the main molecule discovery !
- ✓ Theoretical rotational constants derived through structure calculation
- ✓ Scaling predicts frequencies better than 0.01 %

- ✓ The lowest 2 rotational transitions for $HP^{29}SiH_2$ and $HP^{30}SiH_2$ have been observed in natural abundance
- ✓ Using SiD_4 the 3 lowest rotational transitions of $DPSiD_2$

Conclusion

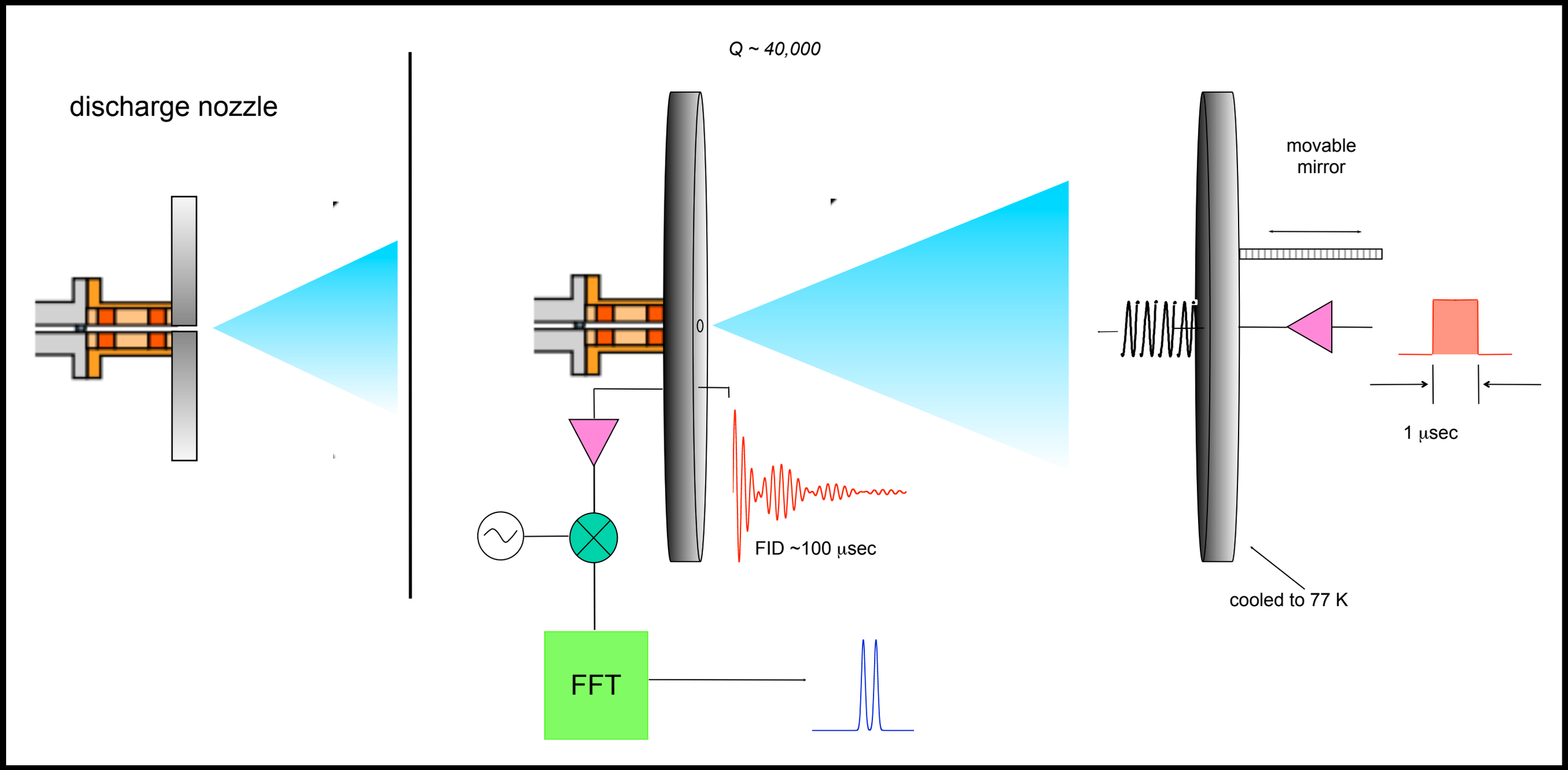
- ✓ High resolution spectroscopy of second-row element compounds
- ✓ Spectrometer high sensitivity allowed to detect isotopic species, providing key confirmation

- ✓ Possible extension to higher frequency (< 60 GHz) through MW-MW Double Resonance experiment
- ✓ Other P- or Si- complexes highly favorable to study in our FTMW
- ✓ The H_2P_2 system: *trans* and *cis* isomer almost isoenergetic

Acknowledgments

- ✓ Harvard-Smithsonian Center for Astrophysics
- ✓ NSF - NASA
- ✓ Silvia Spezzano

FTM spectrometer



credit M. C. McCarthy