High accuracy in the calculation of energetic profiles for astrochemical reactions

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CEFET-MG

Outline

- Introduction
- Formation & destruction of SiS
- Formation of CH_2NH
- CNO (and HNCO?)
- Summary

Introduction

$$H\Psi = E\Psi$$

$$H = -\sum_{\mathrm{A}}^{M} \frac{1}{2M_{\mathrm{A}}}\nabla_{\mathrm{A}}^{2} - \sum_{i=1}^{N} \frac{1}{2}\nabla_{i}^{2} - \sum_{i=1}^{N}\sum_{\mathrm{A}=1}^{M} \frac{Z_{\mathrm{A}}}{r_{i\mathrm{A}}} + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{\mathrm{A}}^{M}\sum_{\mathrm{B}>\mathrm{A}}^{M} \frac{Z_{\mathrm{A}}Z_{\mathrm{B}}}{R_{\mathrm{AB}}}$$

M nuclei
N electrons

$$\Psi = \Psi(R_A, R_B, \ldots R_M, r_1, r_2, r_3, \ldots, r_N)$$

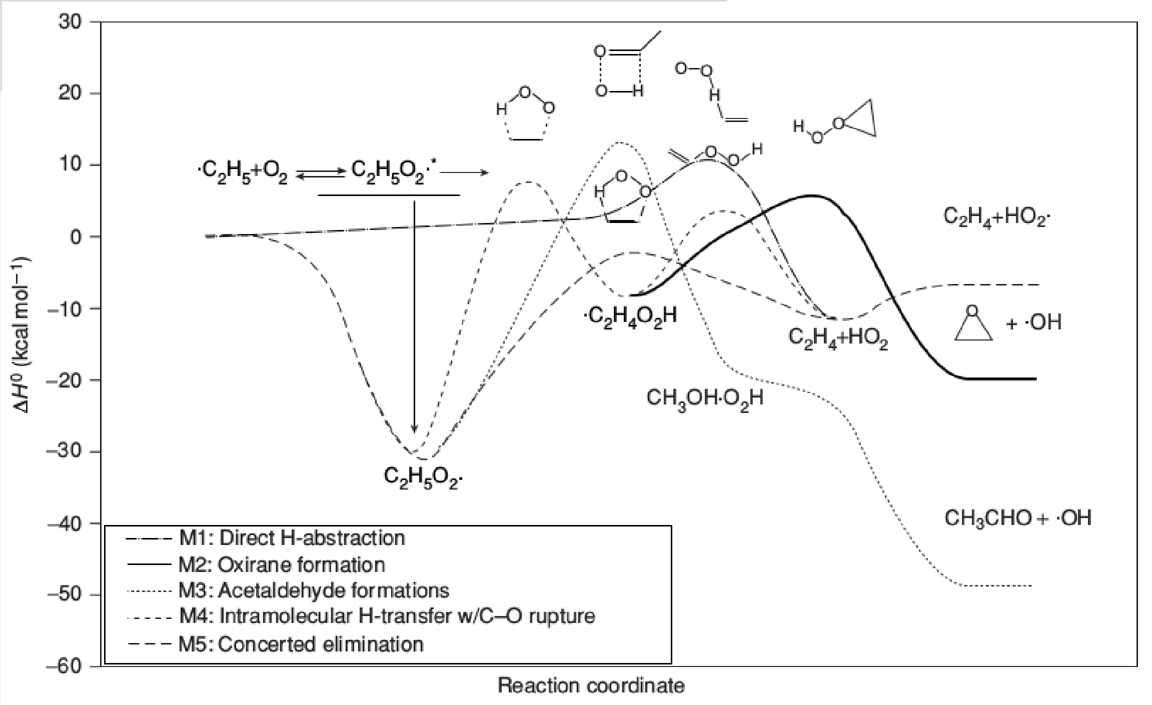
Introduction

Born-Oppenheimer approximation

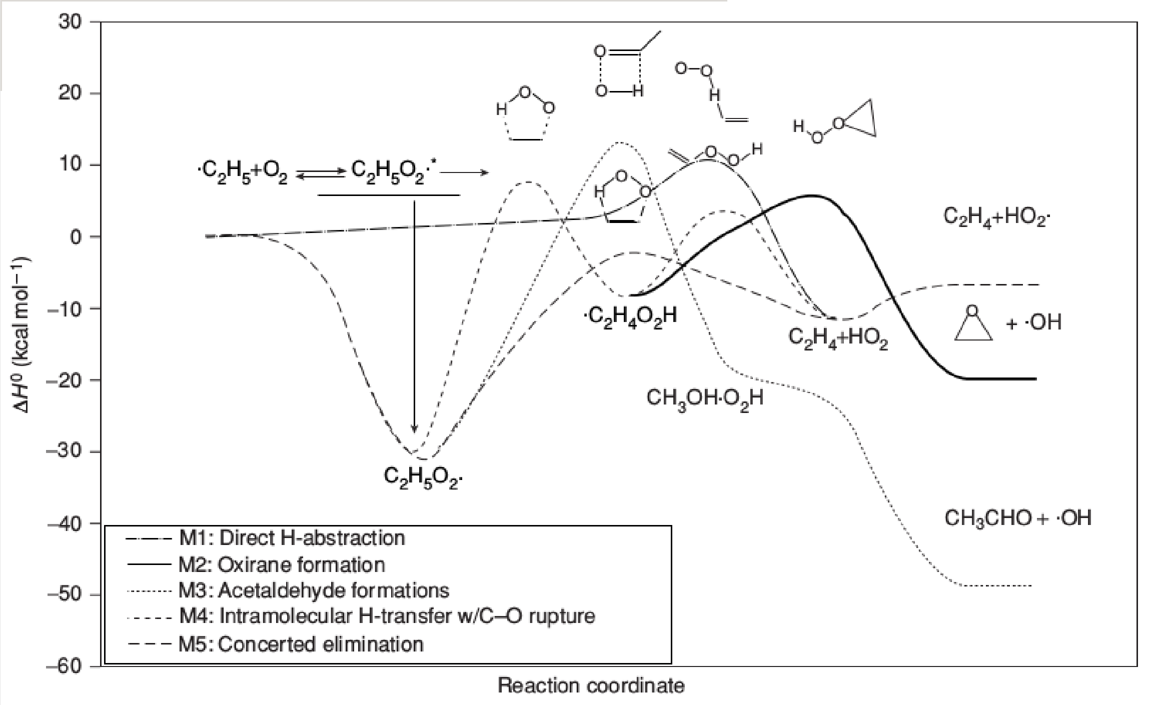
$$H = -\sum_{\mathrm{A}}^{M} \frac{1}{2M_{\mathrm{A}}}\nabla_{\mathrm{A}}^2 - \sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 - \sum_{i=1}^{N}\sum_{\mathrm{A}=1}^{M} \frac{Z_{\mathrm{A}}}{r_{i\mathrm{A}}} + \sum_{i=1}^{N}\sum_{j>i}^{N} \frac{1}{r_{ij}} + \sum_{\mathrm{A}}^{M}\sum_{\mathrm{B}>\mathrm{A}}^{M} \frac{Z_{\mathrm{A}}Z_{\mathrm{B}}}{R_{\mathrm{AB}}}$$

$$\Psi=\Psi(r_1,r_2,r_3,\ldots,r_N)$$

Introduction



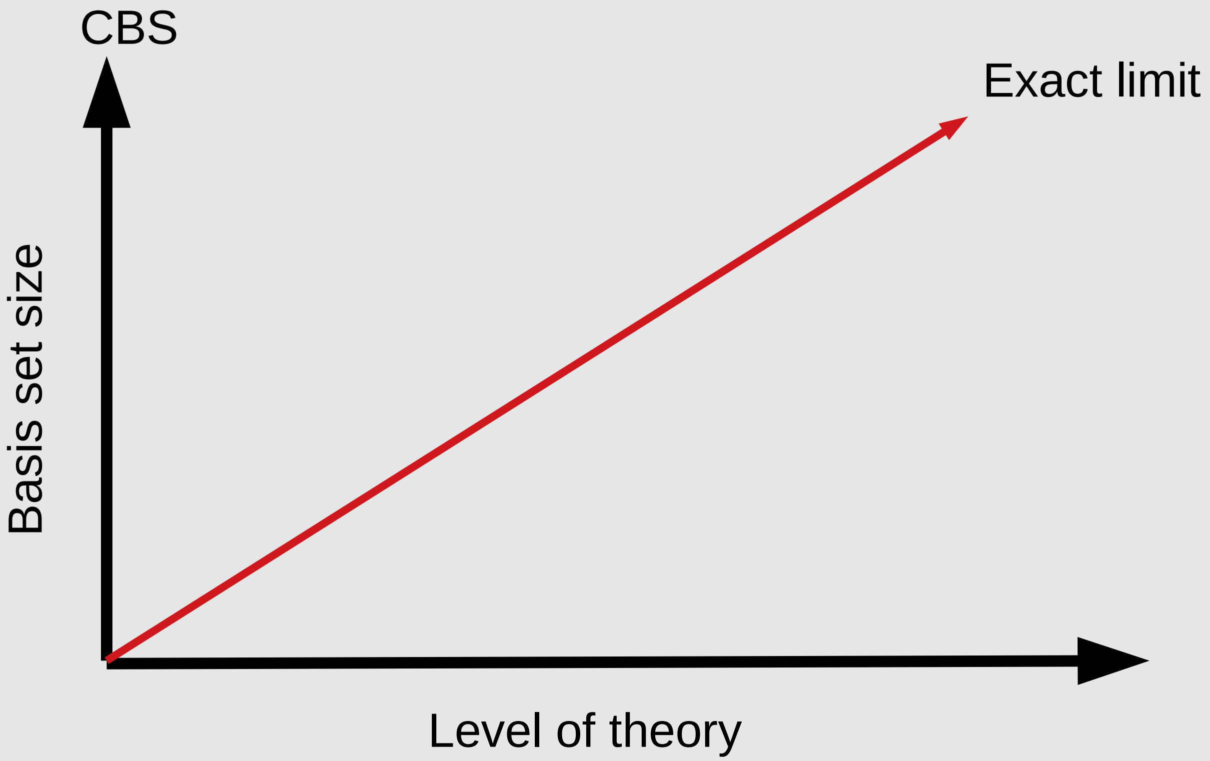
Introduction



Astrochemical reactions:

- **Small energy barriers (E_a)**
- **Small error in E_a → large errors in k**

Intro: Accurate potential energy



CCSD(T)

Gold-standard in quantum chemistry
Not suited for **bond-breaking** processes

MRCI(Q)

Accurate description
including **bond-breaking** barriers

Explicit correlation !
Extrapolation to the CBS limit !

Introduction

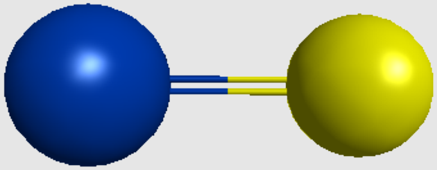
Calculation of the potential energy:

- Predict the viability of reactions
- Thermodynamical properties

For rate coefficients:

- Further methods: TST, QCT, QM...
- Small error in E_a → large errors in k

SiS: motivation

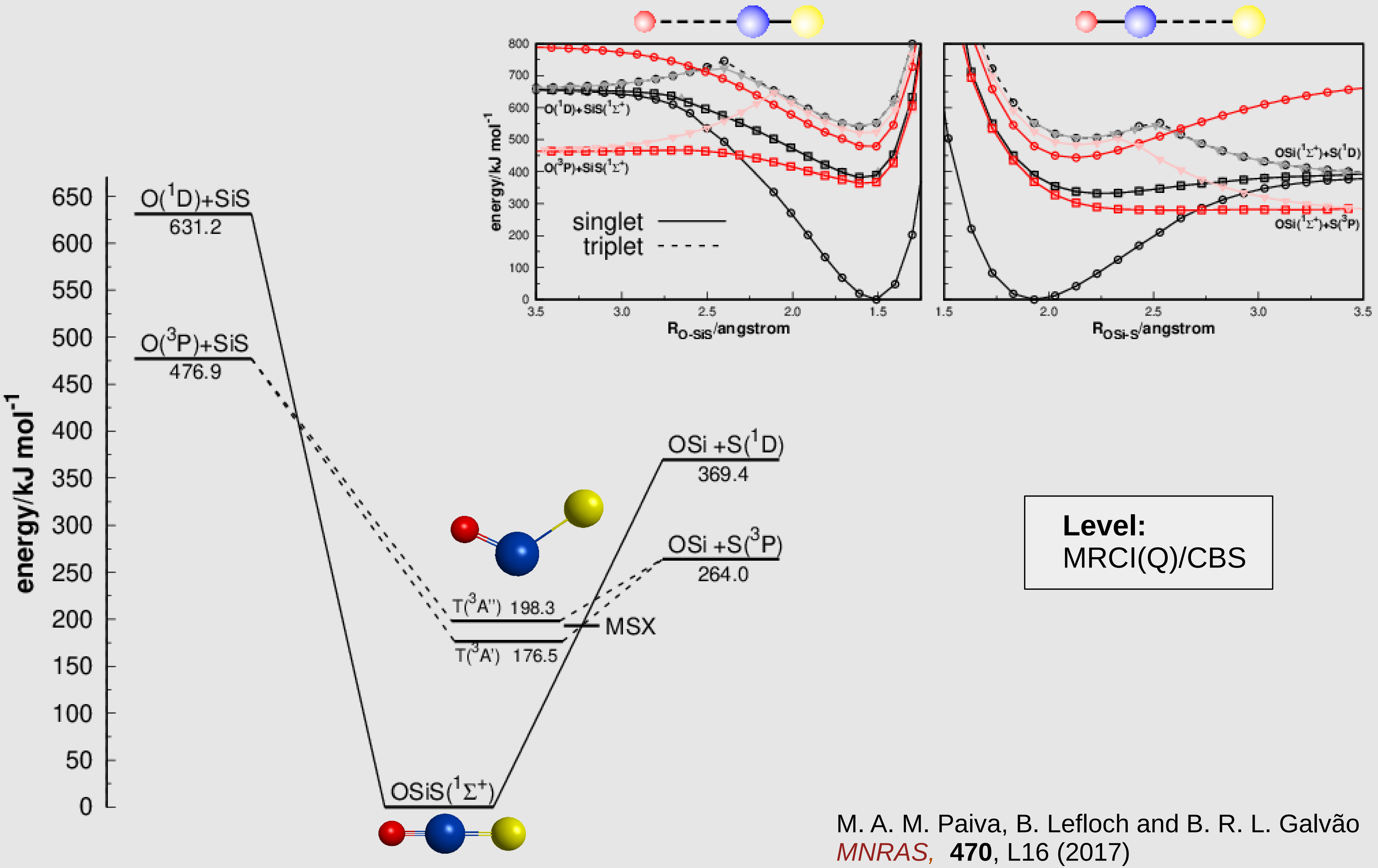


Observed:
- envelopes of evolved stars
- star-forming regions: Sgr B2, Orion KL, L1157-B1.
- 2017: Also in a solar type star

> *“The strong gradient of the [SiO/SiS] abundance ratio across the shock (from ≥180 to ∼25) points to a different chemical origin of the two species”*
>
> Podio L. et al.
> *MNRAS,* **470**, L16 (2017)

UMIST: no neutral-neutral formation or destruction route

SiS: destruction

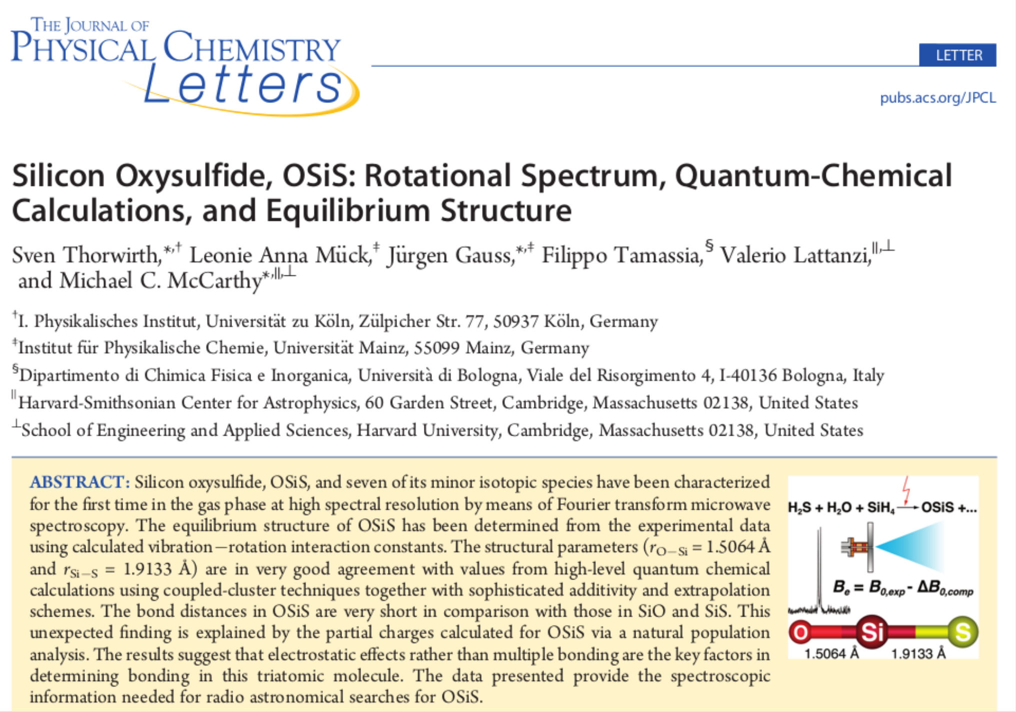


Level:
MRCI(Q)/CBS

M. A. M. Paiva, B. Lefloch and B. R. L. Galvão
MNRAS, **470**, L16 (2017)

OSiS?

OSiS: Experimentally produced (2011), but not observed in ISM yet



THE JOURNAL OF PHYSICAL CHEMISTRY Letters

LETTER

pubs.acs.org/JPCL

Silicon Oxysulfide, OSiS: Rotational Spectrum, Quantum-Chemical Calculations, and Equilibrium Structure

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ABSTRACT: Silicon oxysulfide, OSiS, and seven of its minor isotopic species have been characterized for the first time in the gas phase at high spectral resolution by means of Fourier transform microwave spectroscopy. The equilibrium structure of OSiS has been determined from the experimental data using calculated vibration−rotation interaction constants. The structural parameters (r_{O-Si} = 1.5064 Å and r_{Si-S} = 1.9133 Å) are in very good agreement with values from high-level quantum chemical calculations using coupled-cluster techniques together with sophisticated additivity and extrapolation schemes. The bond distances in OSiS are very short in comparison with those in SiO and SiS. This unexpected finding is explained by the partial charges calculated for OSiS via a natural population analysis. The results suggest that electrostatic effects rather than multiple bonding are the key factors in determining bonding in this triatomic molecule. The data presented provide the spectroscopic information needed for radio astronomical searches for OSiS.

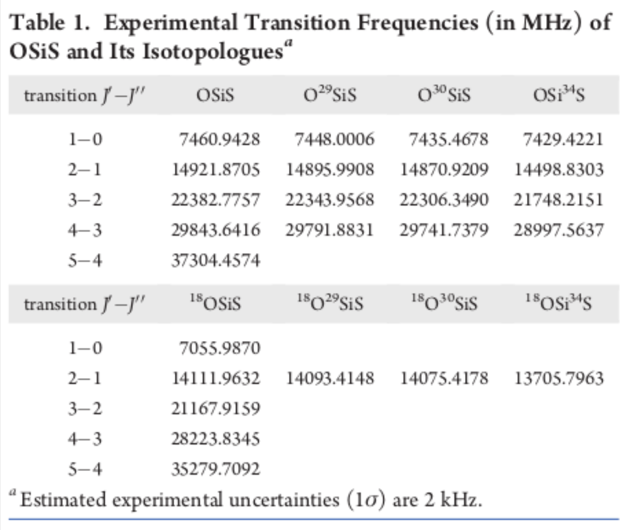


Table 1. Experimental Transition Frequencies (in MHz) of OSiS and Its Isotopologues[a]

transition $J'-J''$	OSiS	$O^{29}SiS$	$O^{30}SiS$	$OSi^{34}S$
1−0	7460.9428	7448.0006	7435.4678	7429.4221
2−1	14921.8705	14895.9908	14870.9209	14498.8303
3−2	22382.7757	22343.9568	22306.3490	21748.2151
4−3	29843.6416	29791.8831	29741.7379	28997.5637
5−4	37304.4574			

transition $J'-J''$	$^{18}OSiS$	$^{18}O^{29}SiS$	$^{18}O^{30}SiS$	$^{18}OSi^{34}S$
1−0	7055.9870			
2−1	14111.9632	14093.4148	14075.4178	13705.7963
3−2	21167.9159			
4−3	28223.8345			
5−4	35279.7092			

[a] Estimated experimental uncertainties (1σ) are 2 kHz.

Upper limit in Orion KL:

N(OSiS)≤$6.3\times10^{13}cm^{-2}$

N(SiS)/N(OSiS) ≥ 22

G. Esplugues *et al.*
A&A, **556**, A143 (2013)

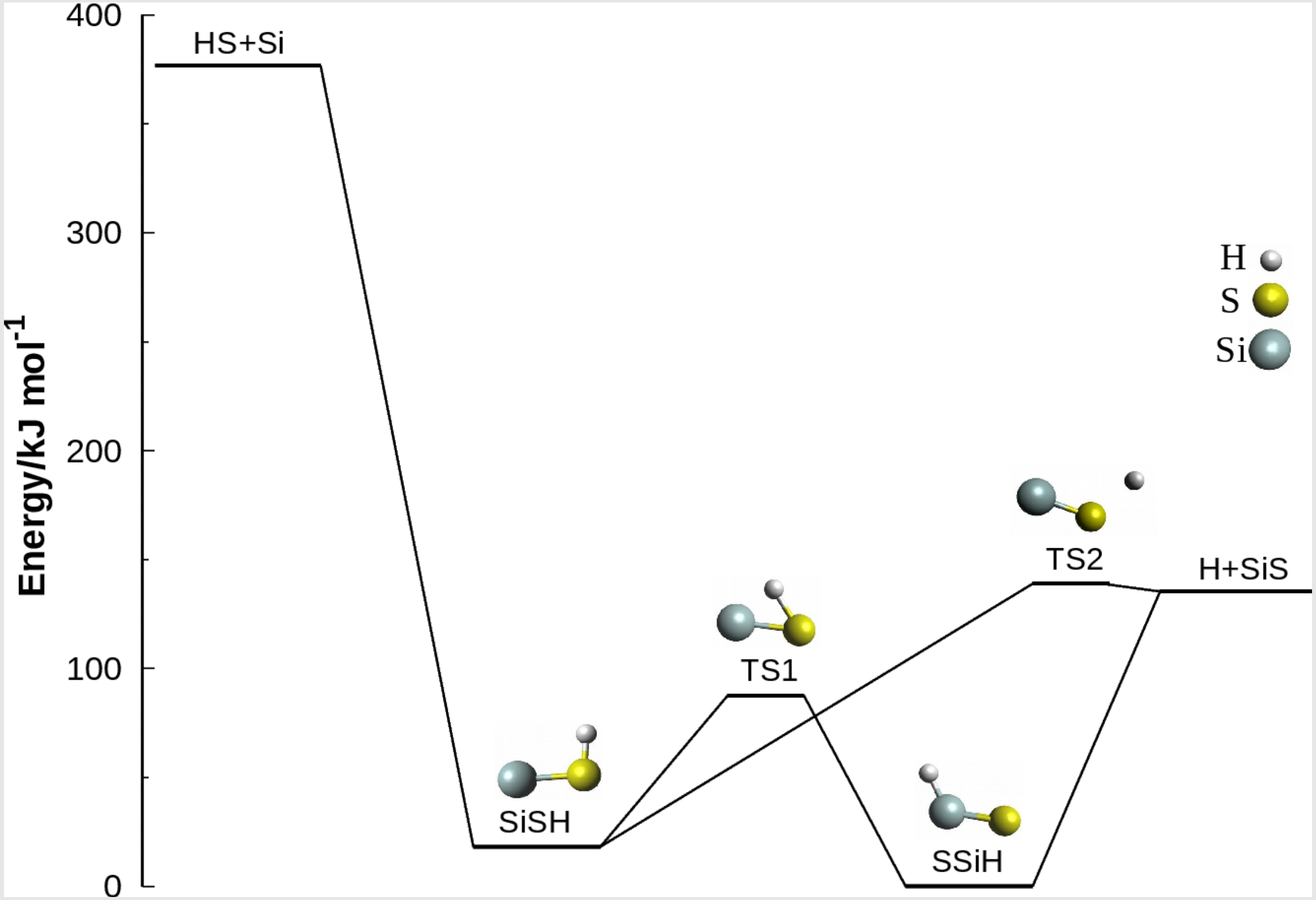
SiS formation

> *“This suggests that **SiS** is not directly released from the grain cores but instead **should be formed through slow gas-phase** processes using part of the released silicon.”*
>
> Podio L. et al.
> *MNRAS*, **470**, L16 (2017)

→ Recent models suggest that the **main reservoir of sulfur** on dust grains would be **HS** and **H_2S**, which are released in grain sputtering.

→ Could **Si+SH** or **Si+H_2S** collisions be potential sources for SiS?

SiS formation: Si+SH?



Highly reactive!

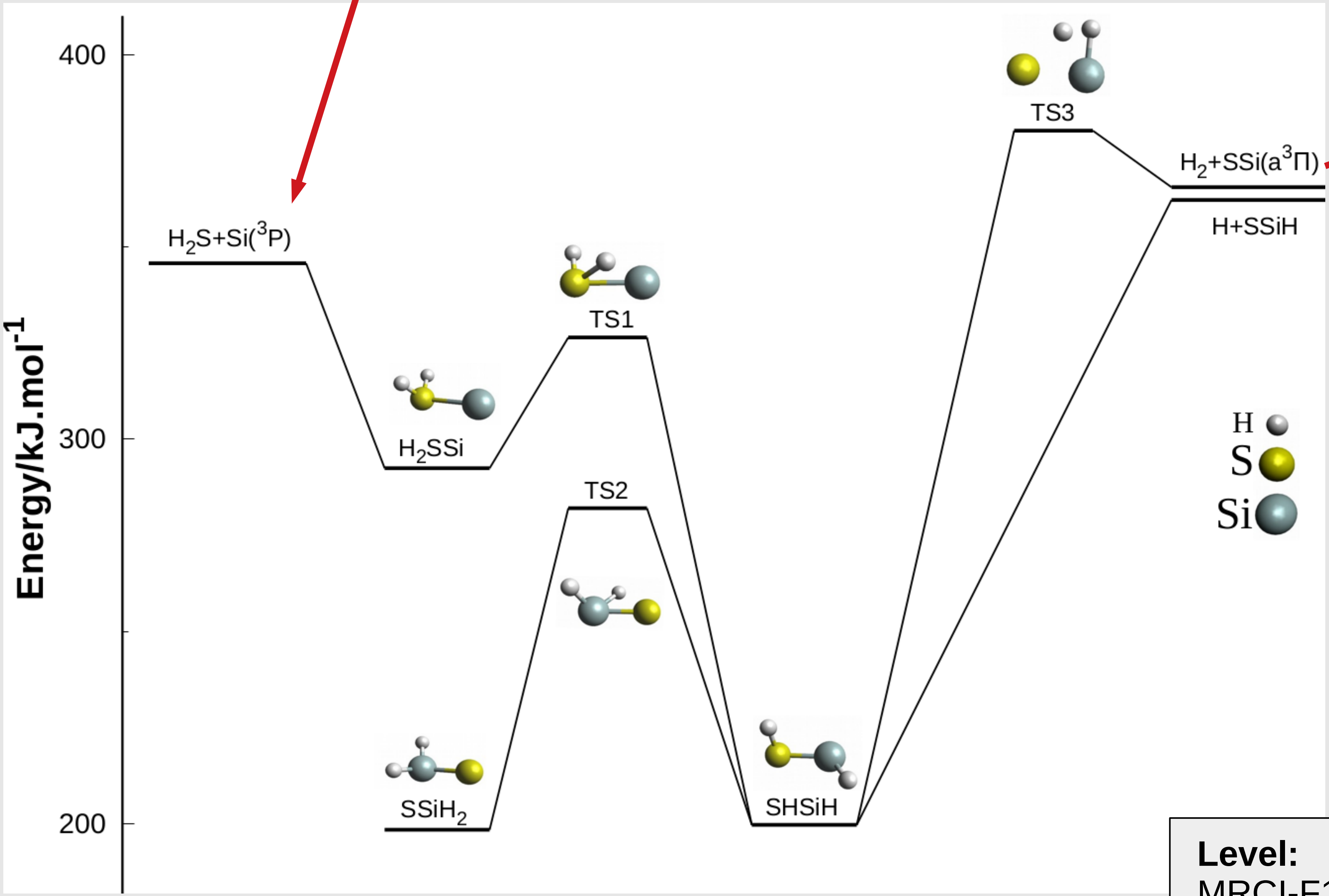
Current work: calculate accurate rate coefficients

Level:
MRCI-F12/cc-pVQZ-F12

Is there HSiS?
$HSiS^+$ is in UMIST

SiS formation: Si+SH$_2$?

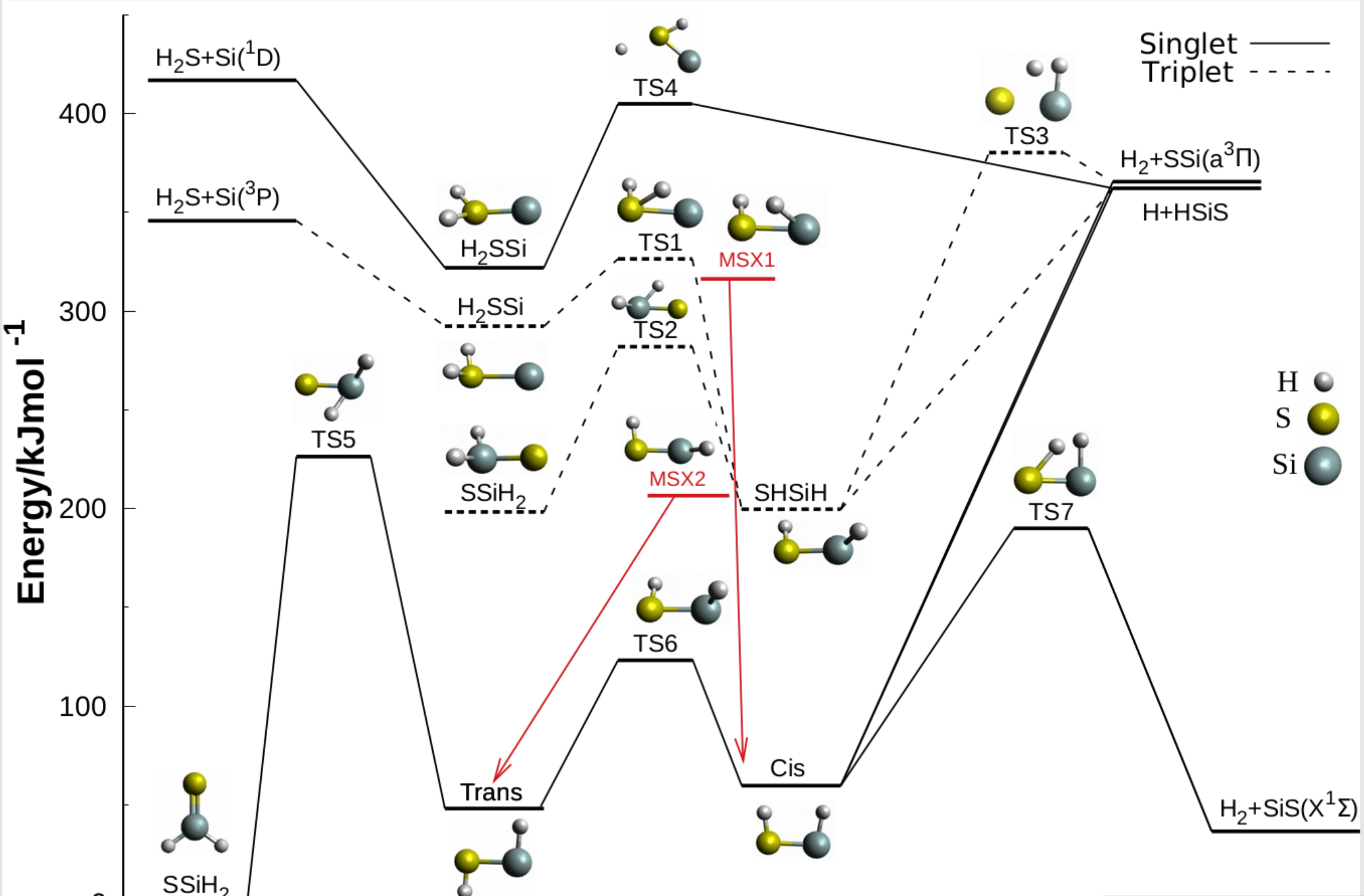
Singlet-Triplet collisions



Excited SiS*

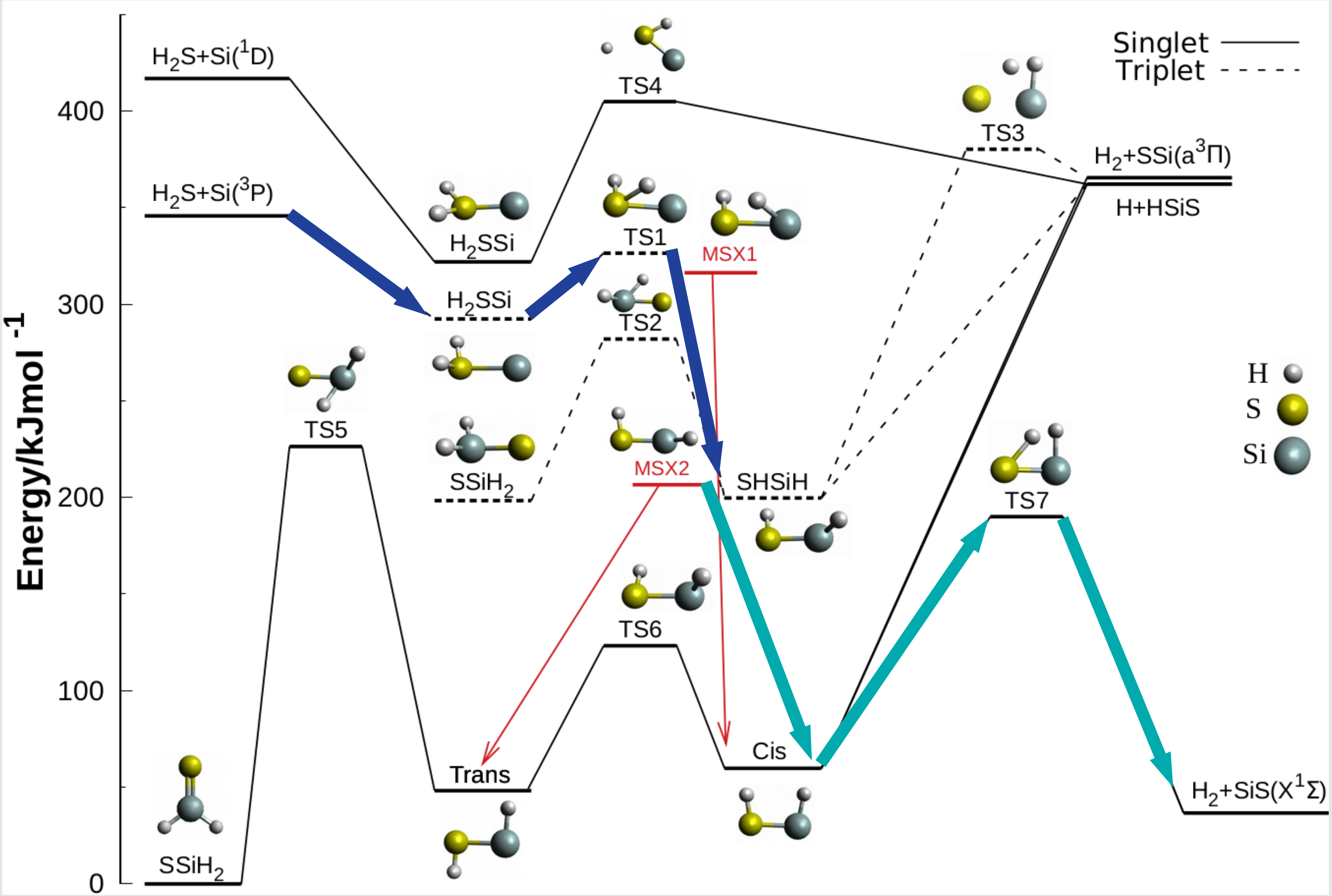
Level:
MRCI-F12/cc-pVQZ-F12

SiS formation: Si+SH$_2$?



Level:
MRCI-F12/cc-pVQZ-F12

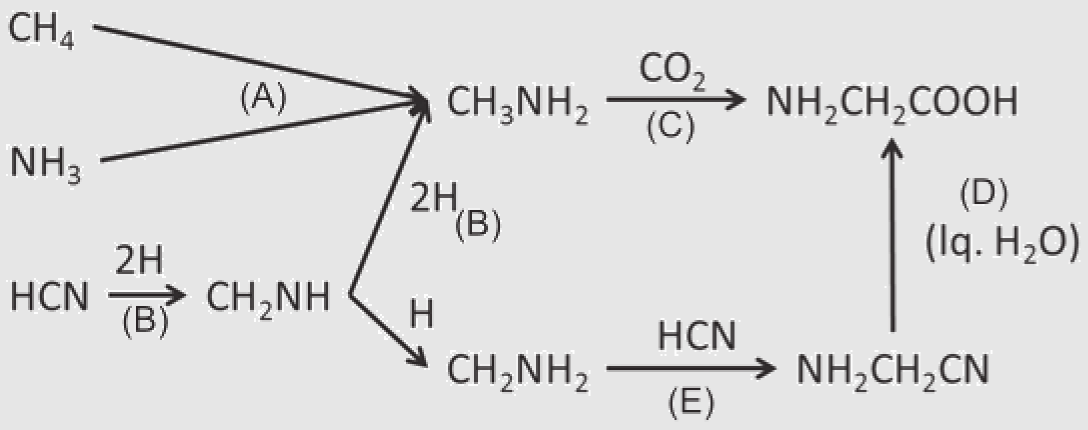
SiS formation: Si+SH$_2$?



Formation of CH_2NH

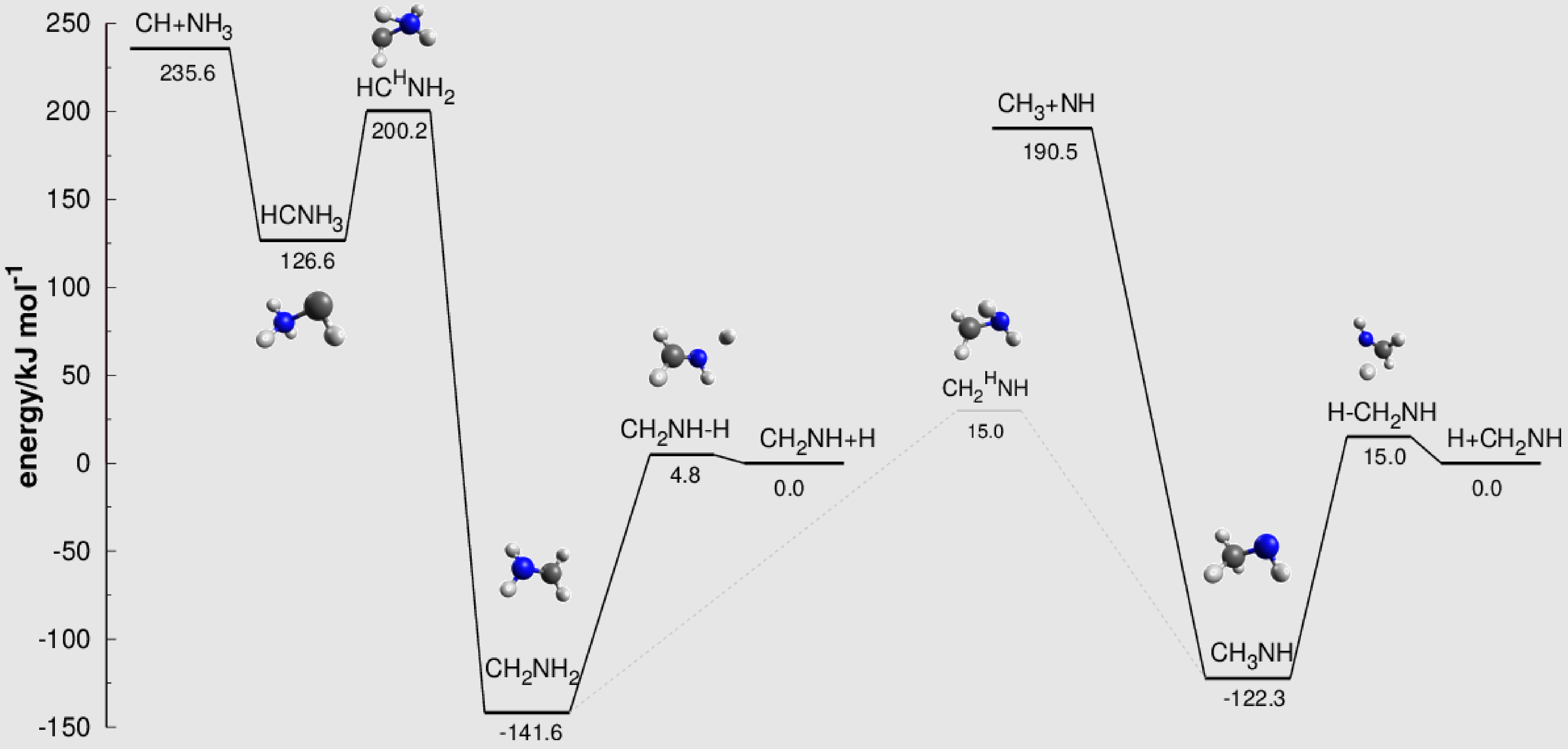
Work in collaboration with IAG
(Edgar Mendoza)
Detected at G331.512-0.103

glycine precursor??



Suzuki T. et al.
ApJ, **859**, 79 (2016)

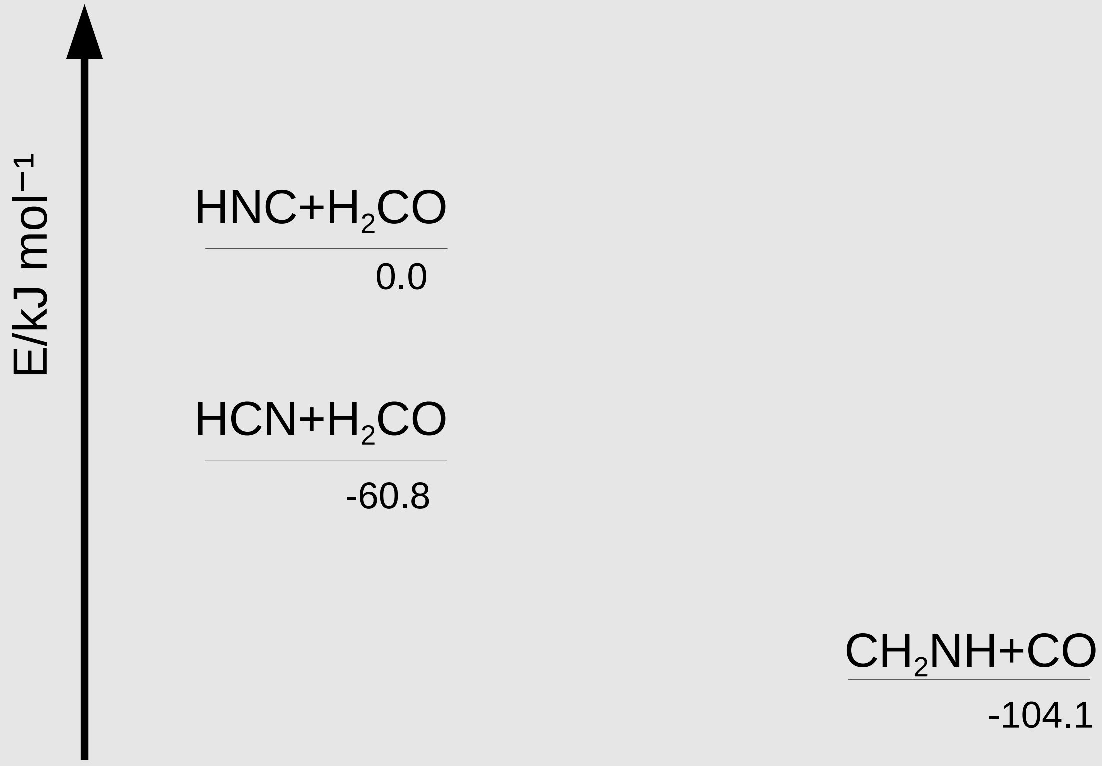
Formation of CH_2NH



Level:
MRCI(Q)/CBS

Formation of CH_2NH

Other formation reactions?



E/kJ mol⁻¹

$HNC+H_2CO$

0.0

$HCN+H_2CO$

-60.8

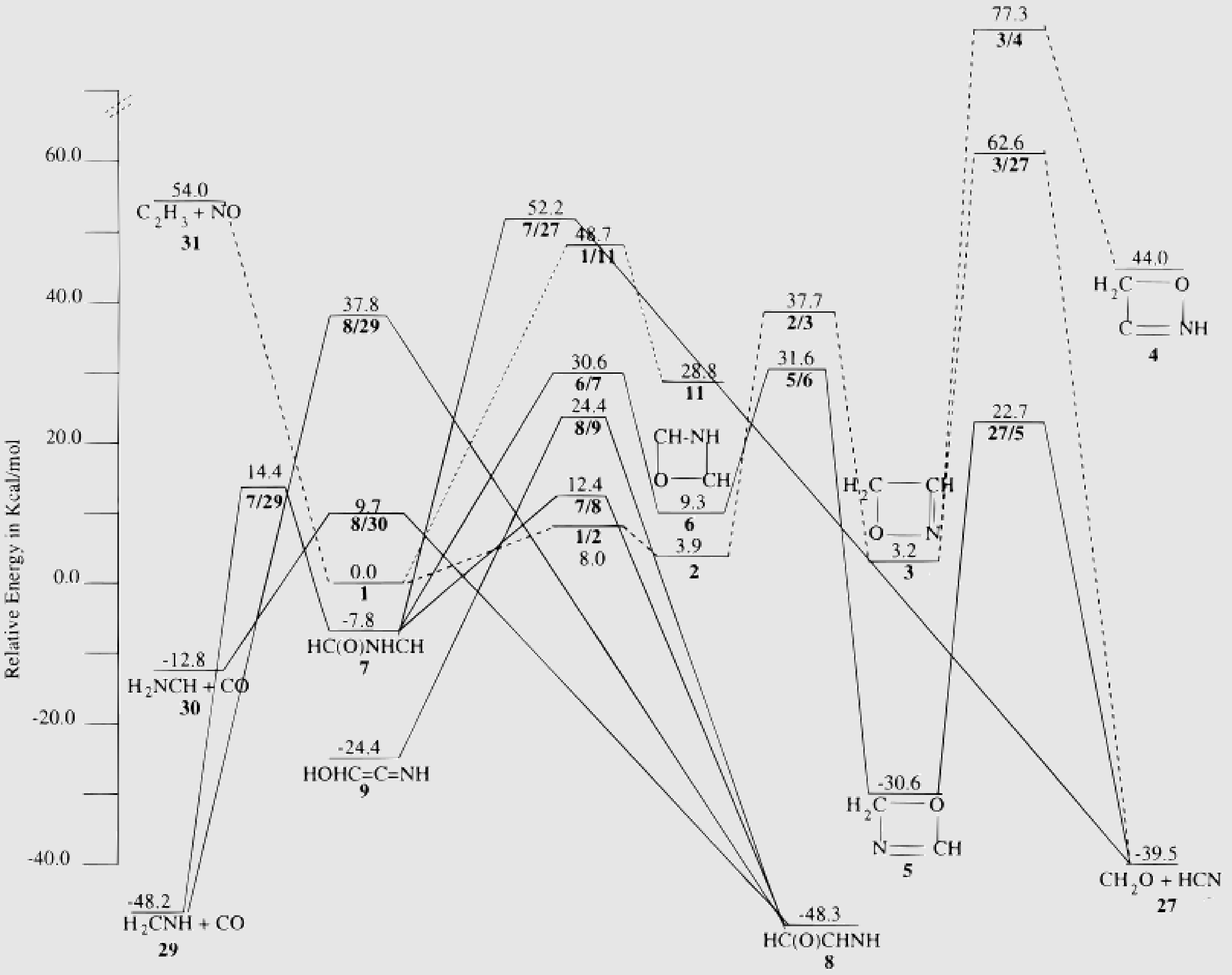
CH_2NH+CO

-104.1

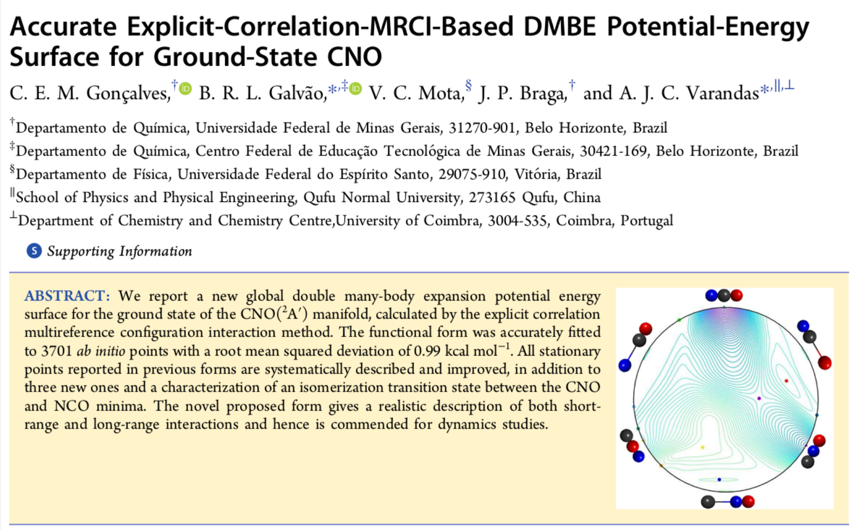
Thermodynamically favorable!!!
Kinetics?

Formation of CH_2NH

Previous: Electronic Structure calculations on the Reaction of Vinyl Radical with Nitric Oxide
Sumathi R. *et al.*
J. Phys. Chem. A, **104**, 1905 (2000)



NCO and HNCO?



Accurate Explicit-Correlation-MRCI-Based DMBE Potential-Energy Surface for Ground-State CNO

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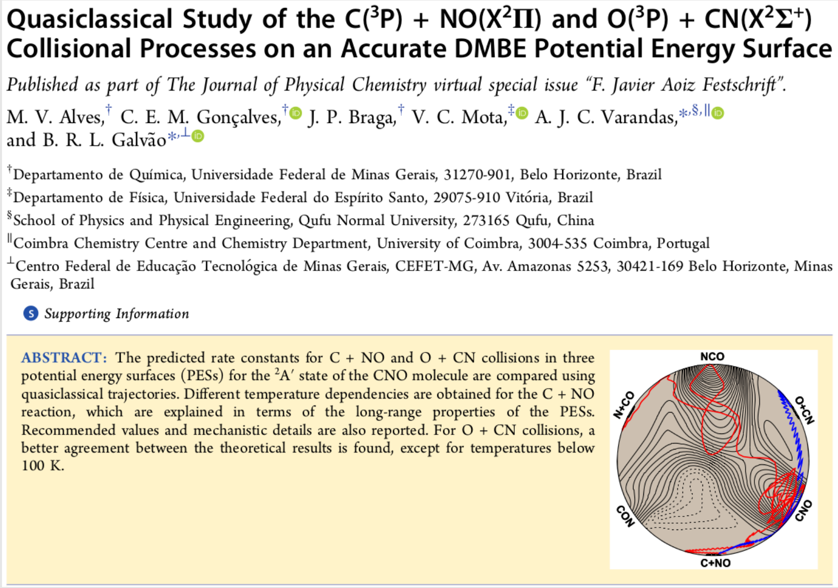
Supporting Information

ABSTRACT: We report a new global double many-body expansion potential energy surface for the ground state of the $CNO(^2A')$ manifold, calculated by the explicit correlation multireference configuration interaction method. The functional form was accurately fitted to 3701 *ab initio* points with a root mean squared deviation of 0.99 kcal mol^{-1}. All stationary points reported in previous forms are systematically described and improved, in addition to three new ones and a characterization of an isomerization transition state between the CNO and NCO minima. The novel proposed form gives a realistic description of both short-range and long-range interactions and hence is commended for dynamics studies.

J. Phys. Chem. A,
122, 4198 (2018)



Quasiclassical Study of the $C(^3P) + NO(X^2\Pi)$ and $O(^3P) + CN(X^2\Sigma^+)$ Collisional Processes on an Accurate DMBE Potential Energy Surface

Published as part of The Journal of Physical Chemistry virtual special issue "F. Javier Aoiz Festschrift".

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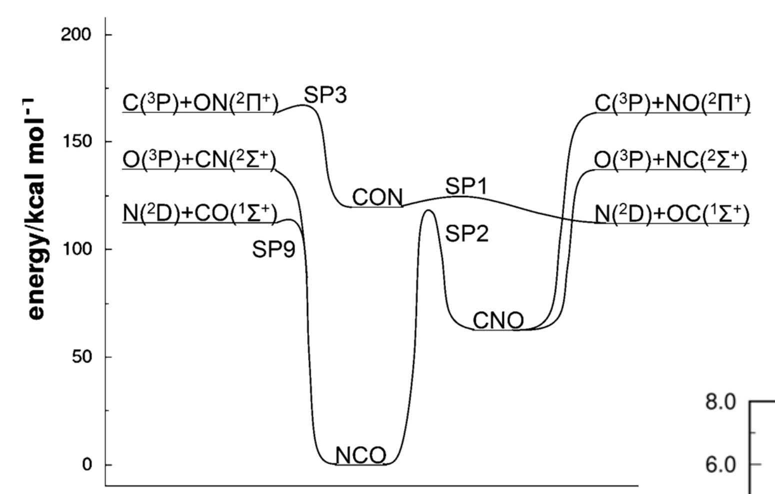
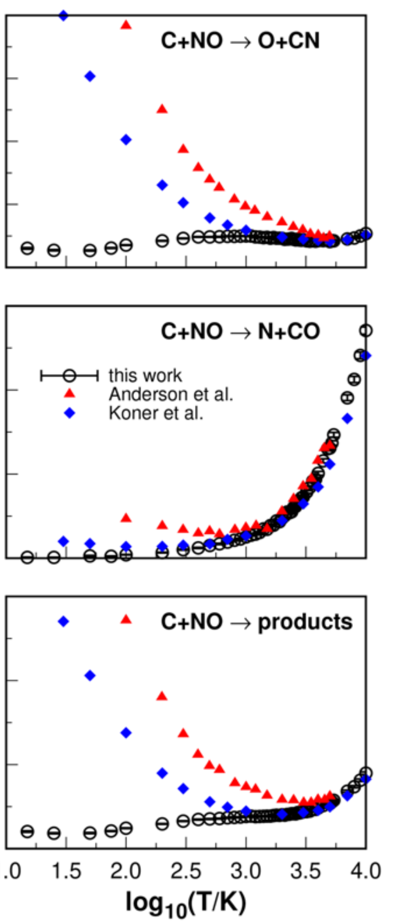
Supporting Information

ABSTRACT: The predicted rate constants for C + NO and O + CN collisions in three potential energy surfaces (PESs) for the $^2A'$ state of the CNO molecule are compared using quasiclassical trajectories. Different temperature dependencies are obtained for the C + NO reaction, which are explained in terms of the long-range properties of the PESs. Recommended values and mechanistic details are also reported. For O + CN collisions, a better agreement between the theoretical results is found, except for temperatures below 100 K.

J. Phys. Chem. A, (2019)
DOI:10.1021/acs.jpca.9b03860





UMIST:
H_3^+ + CNO → $HCNO^+$+H_2
→ $HONC^+$+H_2

NCO? H_2?

Summary

- **Accurate potential energies:**
  - Assess the viability of proposed reactions as sources/sinks of chemical species
  - First step towards obtaining rate coefficients

Summary

- **SiS:**
  - Quickly destructed by collisions with atomic O
  - Si+SH: potential source
  - $Si+SH_2$: thermodinamically favorable, spin forbidden

- **CH_2NH:**
  - Main formation reactions: $CH+NH_3$ and $NH+CH_3$
  - Observed in G331.512-0.103
  - Potential glycine precursor

Acknowledgments

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Conselho Nacional de Desenvolvimento
Científico e Tecnológico

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Thank you for your attention!