9th Chianti Topics International Focus Workshop on Atmospheres

9-11 June 2026

FROM TITAN'S ATMOSPHERIC CHEMISTRY TO EXOPLANET BIOSIGNATURES: A PHYSICAL CHEMIST'S PERSPECTIVE

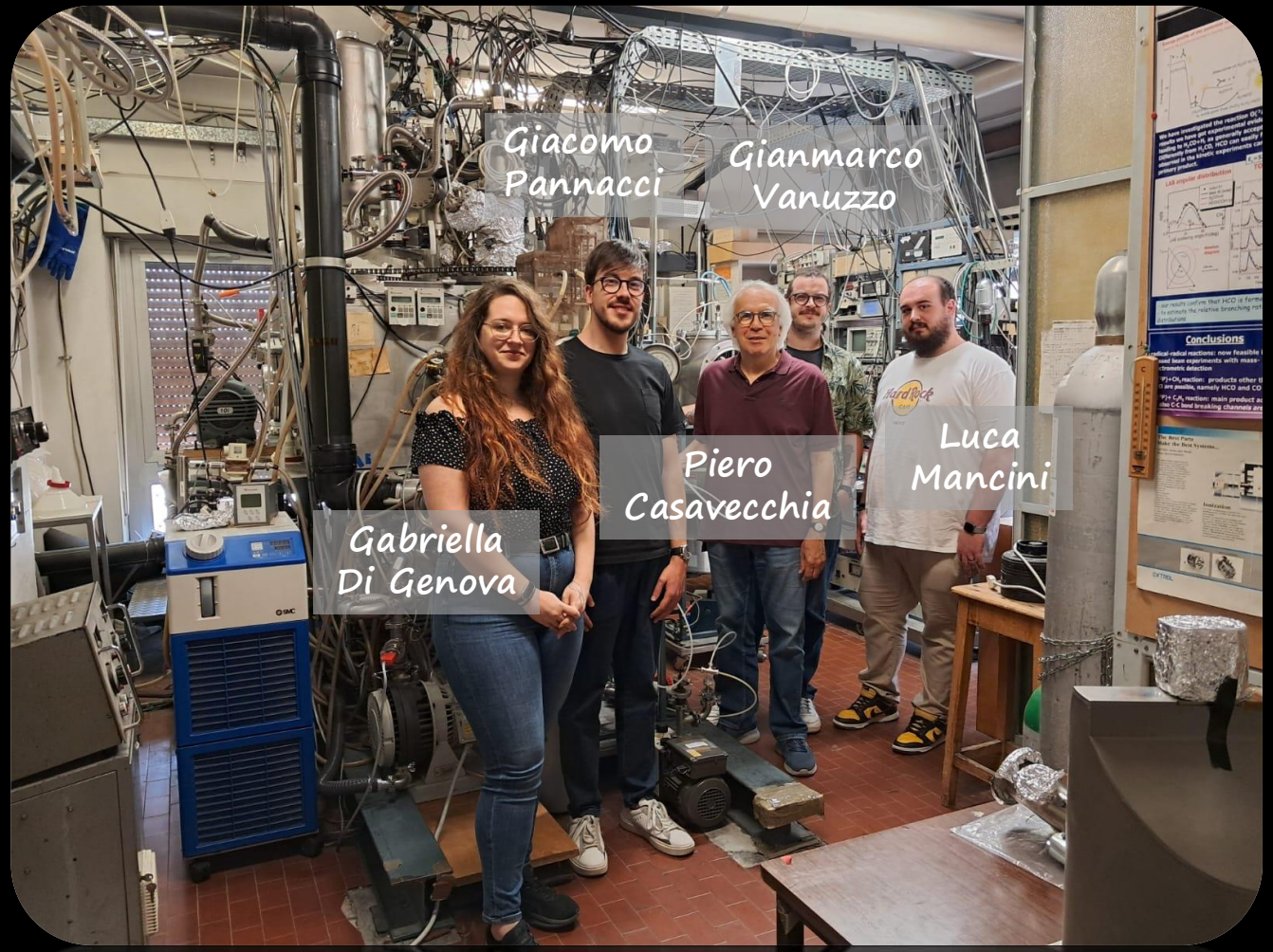
on reactivity

Nadia Balucani

Dipartimento di Chimica, Biologia e Biotecnologie

Università degli Studi di Perugia

In my group, we used a combined experimental and theoretical chemistry approach to investigate bimolecular reactions that are of relevance to astrochemistry and cosmochemistry toward prebiotic chemistry



Marzio Rosi

Dimitris Skouteris

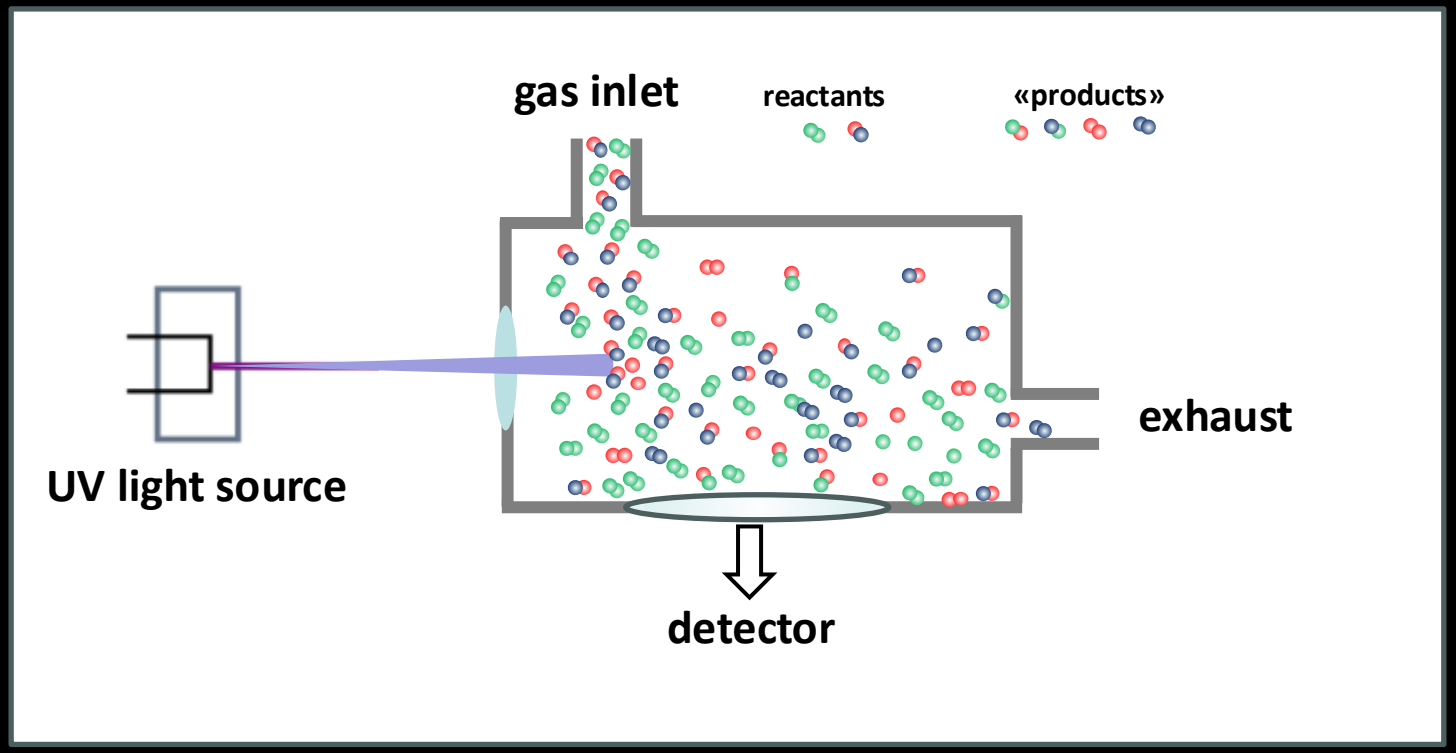
Dario Campisi

Andrea Giustini

Marco Parriani

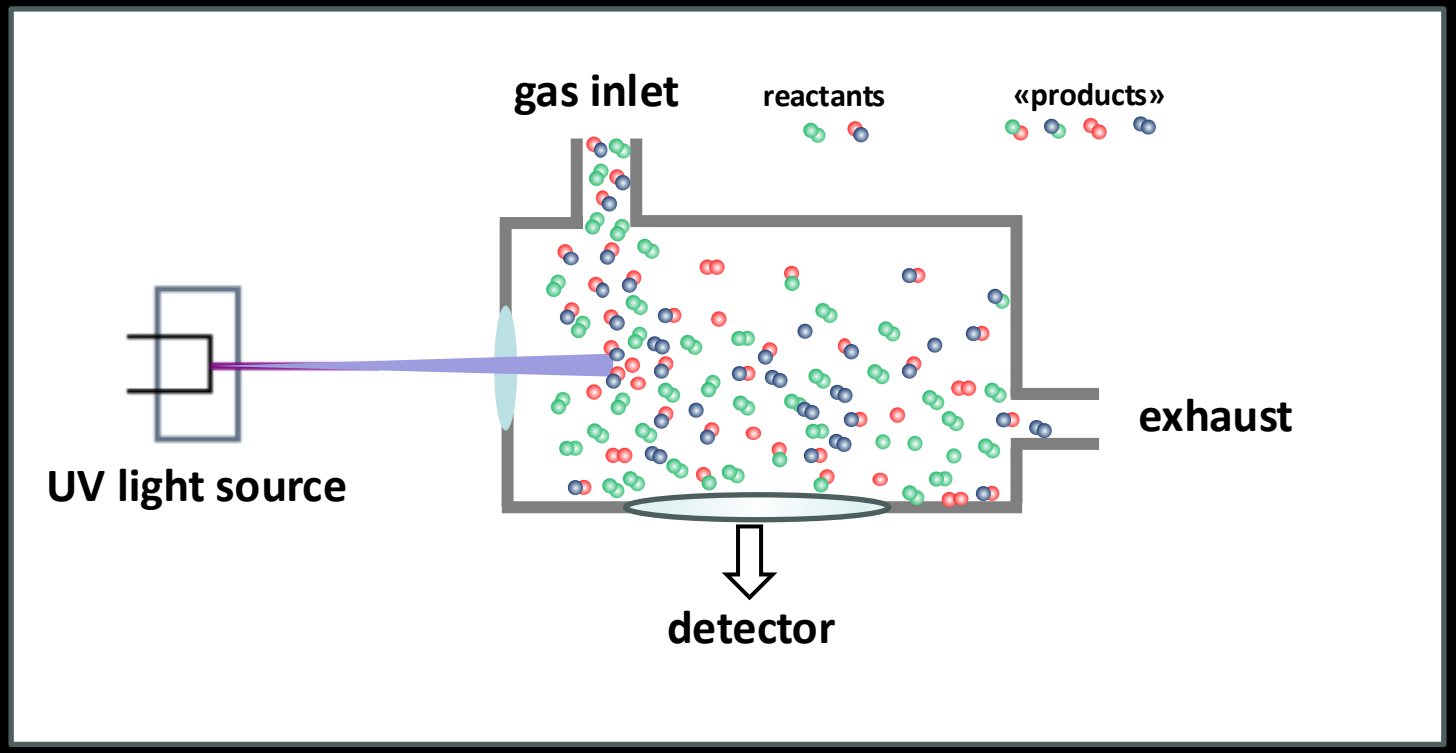
Jessica Perrero

Common approaches: bulk experiments
- very interesting insights into the global chemistry



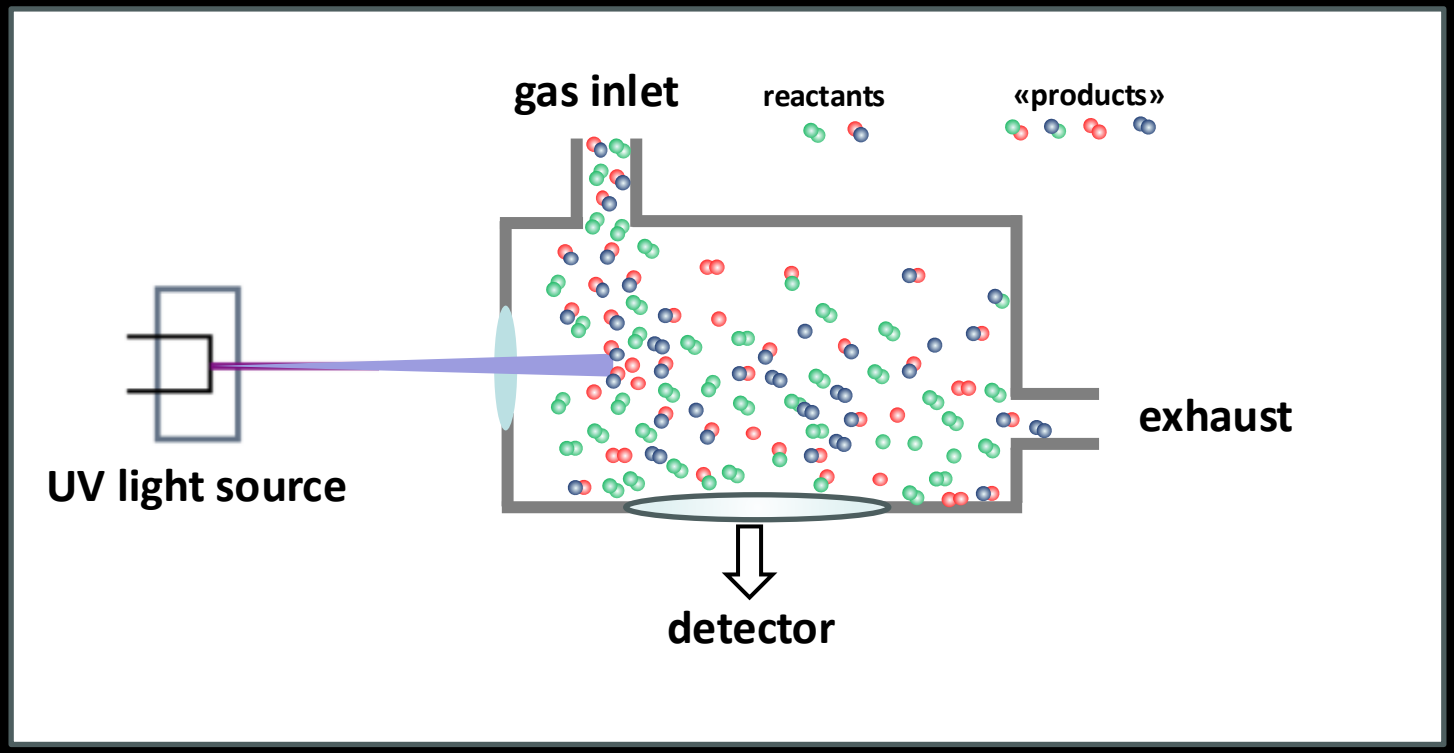
What we do not do:

- we do not try to simulate the atmosphere of a planet or a portion of it



What we do not do:

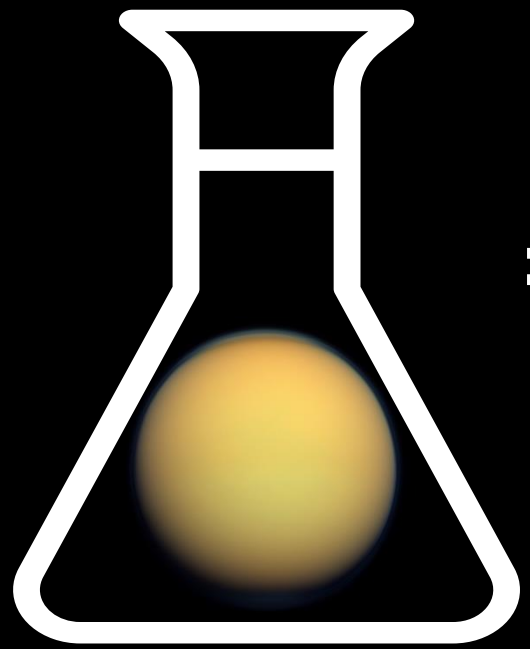
- we do not try to simulate the atmosphere of a planet or a portion of it



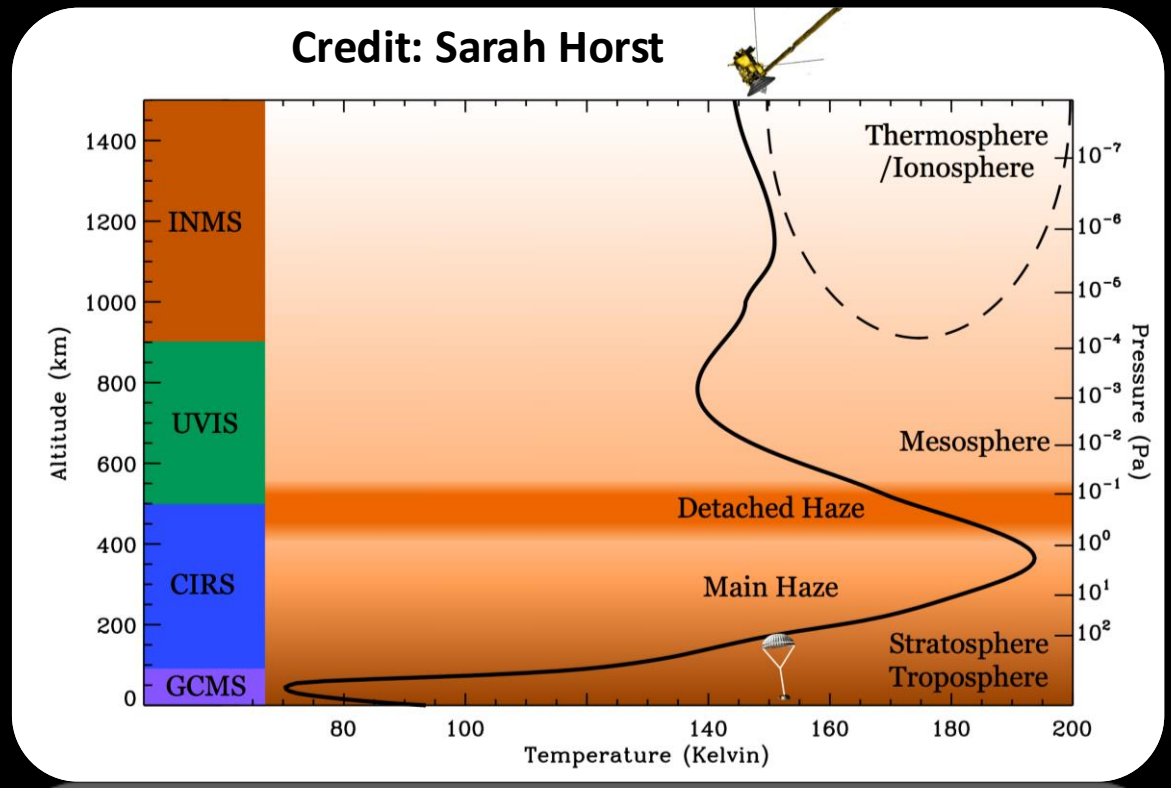
- wall collisions
- secondary collisions
- reactions of undissociated precursors

Other problems:

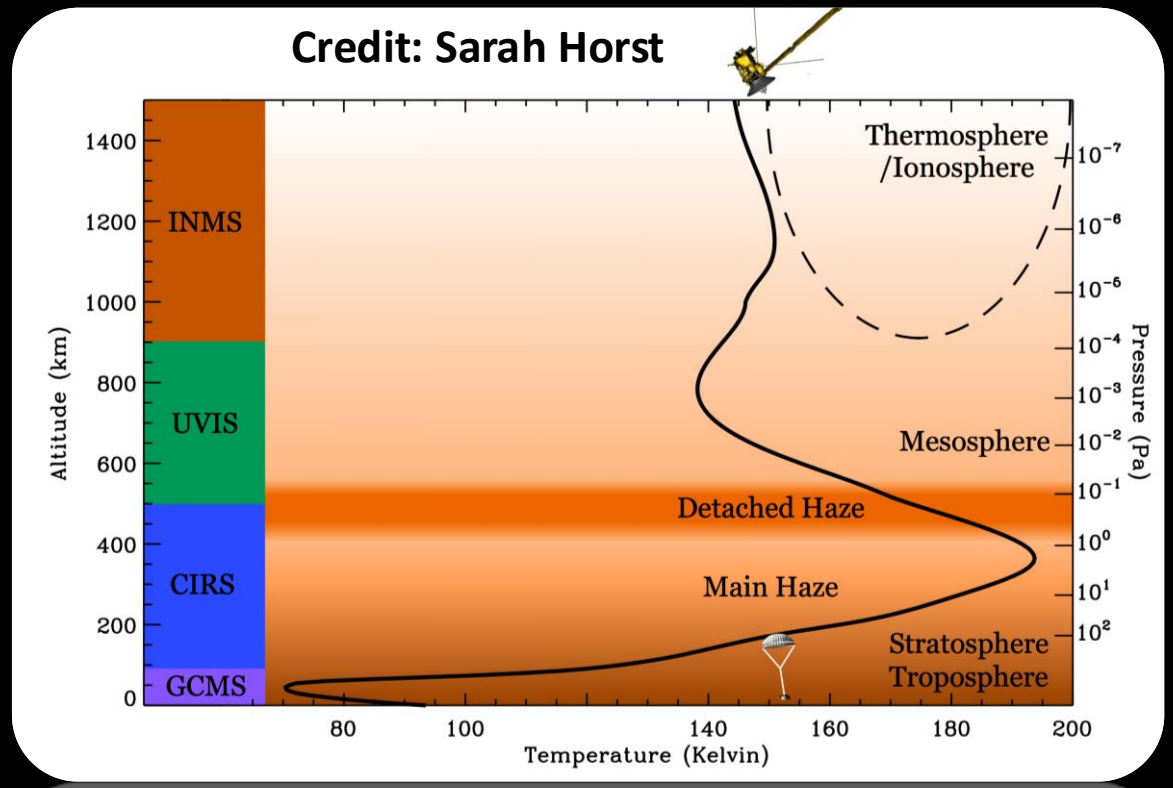
- realistic composition
- P and T gradient of a «real atmosphere»
- large-scale effects (transport, deposition etc)



≠


Credit: Sarah Horst
INMS
UVIS
CIRS
GCMS
Thermosphere
/Ionosphere
Mesosphere
Detached Haze
Main Haze
Stratosphere
Troposphere
Altitude (km)
Pressure (Pa)
Temperature (Kelvin)
0
200
400
600
800
1000
1200
1400
80
100
140
160
180
200
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
10^{1}
10^{2}

≠



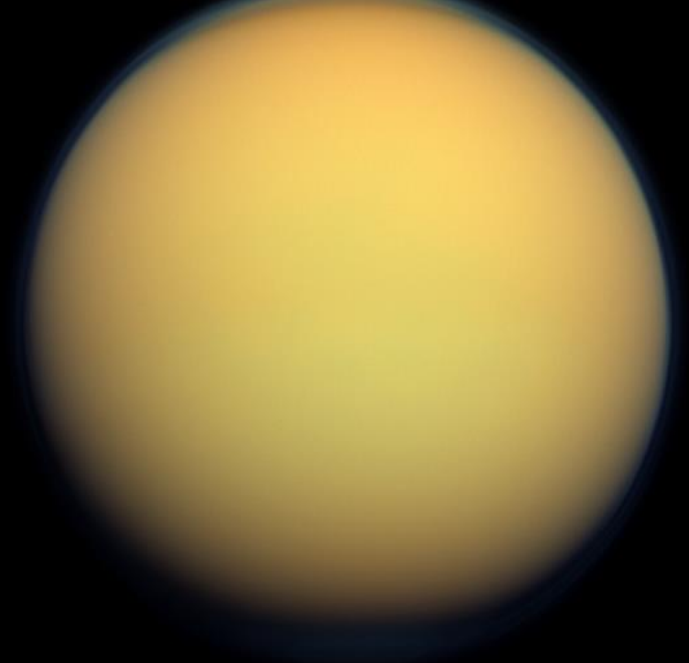
What we do:

- we investigate single bimolecular reactions to derive rate coefficients and product branching fractions to be included in photochemical models that explicitly consider both physical and chemical parameters

Vuitton et al., Icarus 2019 (Titan)

	Type	Reaction							k	F_c	T range	Ref.
R_n300	4	N	+	HC_2N	→	C_2N_2	+	H	8.00×10^{-11} 1.00×10^{-21} 2.00×10^{-11}	0.40	-	est.(Rad+Rad),est.(AtomNumber)
R_n301	4	N	+	C_3H_2N	→	$C_3H_2N_2$			8.00×10^{-11} 1.00×10^{-19} 8.00×10^{-11}	0.40	-	est.(Rad+Rad),est.(AtomNumber)
R_n302	4	N	+	C_3H_4N	→	$C_3H_4N_2$			8.00×10^{-11} 1.00×10^{-19} 8.00×10^{-11}	0.40	-	est.(Rad+Rad),est.(AtomNumber)
R_n303	1	$N(^2D)$			→	N	+	$h\nu$	2.30×10^{-05}		-	[111]
R_n304	2	$N(^2D)$	+	N_2	→	N	+	N_2	1.70×10^{-14}		298	[112]
R_n305	2	$N(^2D)$	+	$^{15}N^{14}N$	→	N	+	$^{15}N^{14}N$	1.70×10^{-14}		-	est.(N2D+N2)
R_n306	2	$N(^2D)$	+	H_2	→	NH	+	H	$4.20\times10^{-11}e^{-880./T}$		200-300	[112]
R_n307a	2	$N(^2D)$	+	CH_4	→	CH_2NH	+	H	$3.84\times10^{-11}e^{-750./T}$		223-292	[112]
R_n307b	2	$N(^2D)$	+	CH_4	→	NH	+	CH_3	$9.60\times10^{-12}e^{-750./T}$		223-292	[112]
R_n308	2	$N(^2D)$	+	C_2H_2	→	HC_2N	+	H	$1.60\times10^{-10}e^{-270./T}$		220-300	[112]
R_n309a	2	$N(^2D)$	+	C_2H_4	→	CH_3CN	+	H	$2.23\times10^{-10}e^{-500./T}$		230-292	[113],[114],[103]
R_n309b	2	$N(^2D)$	+	C_2H_4	→	CH_2CN	+	H_2	$1.96\times10^{-12}e^{-500./T}$		230-292	[113],[114],[103]
R_n309c	2	$N(^2D)$	+	C_2H_4	→	H_2CN	+	$^3CH_2$	$1.56\times10^{-12}e^{-500./T}$		230-292	[113],[114],[103]
R_n309d	2	$N(^2D)$	+	C_2H_4	→	HCN	+	CH_3	$2.71\times10^{-12}e^{-500./T}$		230-292	[113],[114],[103]
R_n309e	2	$N(^2D)$	+	C_2H_4	→	HNC	+	CH_3	$5.06\times10^{-13}e^{-500./T}$		230-292	[113],[114],[103]
R_n309f	2	$N(^2D)$	+	C_2H_4	→	NH	+	C_2H_3	$2.30\times10^{-14}e^{-500./T}$		230-292	[113],[114],[103]
R_n310a	2	$N(^2D)$	+	C_2H_6	→	CH_2NH	+	CH_3	1.52×10^{-11}		298,94-175	[112],[115]
R_n310b	2	$N(^2D)$	+	C_2H_6	→	C_2H_5N	+	H	2.72×10^{-12}		298,94-175	[112],[115]
R_n310c	2	$N(^2D)$	+	C_2H_6	→	NH	+	C_2H_5	1.05×10^{-12}		298,94-175	[112],[115]
R_n311	2	$N(^2D)$	+	CH_3CCH	→	C_3H_3N	+	H	$1.60\times10^{-10}e^{-270./T}$		-	est.(N2D+C2H2)
R_n312	2	$N(^2D)$	+	CH_2CCH_2	→	C_3H_3N	+	H	$2.30\times10^{-10}e^{-500./T}$		-	est.(N2D+C2H4)
R_n313	2	$N(^2D)$	+	C_3H_6	→	C_3H_5N	+	H	6.60×10^{-11}		298	[112]
R_n314a	2	$N(^2D)$	+	C_3H_8	→	CH_2NH	+	C_2H_5	9.67×10^{-12}		298	[112]
R_n314b	2	$N(^2D)$	+	C_3H_8	→	C_2H_5N	+	CH_3	9.67×10^{-12}		298	[112]
R_n314c	2	$N(^2D)$	+	C_3H_8	→	C_3H_7N	+	H	9.67×10^{-12}		298	[112]
R_n315	2	$N(^2D)$	+	C_4H_2	→	HC_4N	+	H	$1.60\times10^{-10}e^{-270./T}$		-	est.(N2D+C2H2)
R_n316	2	$N(^2D)$	+	C_4H_4	→	C_4H_3N	+	H	$1.60\times10^{-10}e^{-270./T}$		-	est.(N2D+C2H2)
R_n317	2	$N(^2D)$	+	C_4H_6	→	C_4H_5N	+	H	6.60×10^{-11}		-	est.(N2D+C3H6)
R_n318	2	$N(^2D)$	+	C_4H_8	→	C_4H_7N	+	H	6.60×10^{-11}		-	est.(N2D+C3H6)
R_n319a	2	$N(^2D)$	+	C_4H_{10}	→	CH_2NH	+	C_3H_7	7.75×10^{-12}		298	[112]
R_n319b	2	$N(^2D)$	+	C_4H_{10}	→	C_2H_5N	+	C_2H_5	7.75×10^{-12}		298	[112]
R_n319c	2	$N(^2D)$	+	C_4H_{10}	→	C_3H_7N	+	CH_3	7.75×10^{-12}		298	[112]
R_n319d	2	$N(^2D)$	+	C_4H_{10}	→	C_4H_9N	+	H	7.75×10^{-12}		298	[112]
R_n320	2	$N(^2D)$	+	C_6H_2	→	HC_6N	+	H	$1.60\times10^{-10}e^{-270./T}$		-	est.(N2D+C2H2)
R_n321	2	$N(^2D)$	+	HCN	→	N_2	+	CH	$1.07\times10^{-14}T^{1.82}e^{-149./T}$		50-300	ThisWork
R_n322	2	$N(^2D)$	+	HNC	→	CN_2	+	H	$1.61\times10^{-15}T^{1.60}e^{102./T}$		50-300	ThisWork
R_n323	2	$N(^2D)$	+	CH_2NH	→	CH_2N_2	+	H	$2.30\times10^{-10}e^{-500./T}$		-	est.(N2D+C2H4)
R_n324a	2	$N(^2D)$	+	CH_3CN	→	$C_2H_2N_2$	+	H	$3.84\times10^{-11}e^{-750./T}$		-	est.(N2D+CH4)
R_n324b	2	$N(^2D)$	+	CH_3CN	→	CH_2CN	+	NH	$9.60\times10^{-12}e^{-750./T}$		-	est.(N2D+CH4)
R_n325	2	$N(^2D)$	+	HC_3N	→	C_3N_2	+	H	$1.60\times10^{-10}e^{-270./T}$		-	est.(N2D+C2H2)
R_n326	2	$N(^2D)$	+	C_3H_3N	→	$C_3H_2N_2$	+	H	$2.30\times10^{-10}e^{-500./T}$		-	est.(N2D+C2H4)
R_n327a	2	$N(^2D)$	+	C_3H_5N	→	$C_3H_4N_2$	+	H	$3.84\times10^{-11}e^{-750./T}$		-	est.(N2D+CH4)
R_n327b	2	$N(^2D)$	+	C_3H_5N	→	C_3H_4N	+	NH	$9.60\times10^{-12}e^{-750./T}$		-	est.(N2D+CH4)
R_n328	2	$N(^2D)$	+	HC_5N	→	C_5N_2	+	H	$1.60\times10^{-10}e^{-270./T}$		-	est.(N2D+C2H2)

Continued on Next Page...



> 600 neutral-neutral reactions

> 1000 ion-molecule reactions

Photochemically produced SO_2 in the atmosphere of WASP-39b, Tsai et al. Nature (2023) 1100 K

```
S       + HS2     = S2      + SH                  6.925e-18  2.2    302.        ! Sendt+02; 873-1473 K (too fast at T > 200
S       + H2S2    = HS2     + SH                  4.733e-18  2.31 -606.         ! Sendt+02; also seems too fast at high T
S       + CS      + M       = CS2     + M         1.706e-24  -2.42   0.   5.0e-11  0.  0.      ! Glarborg+15 k0 and estimat
S       + CS2     = CS      + S2                  3.48e-18  0.7  -3623.         ! based on Gao & Marshall 11 and Woiki & Ro
S       + HCS     = CS2     + H                   3.32e-11   0.      0.         ! Alzueta+19
S       + SO      + M       = S2O     + M         1.00e-26  -2.      0.         ! estimate, Moses+02a
S       + SO3     = SO2     + SO                  1.00e-16   0.      0.         ! estimate, Moses+02a
S       + S2O     = S2      + SO                  3.00e-11   0.   -500.         ! estimate
S       + OCS     = S2      + CO                  1.43E-16  1.58  -1940.        ! Lu+06
S       + CL      + M       = CLS     + M         1.00e-29  -1.      0.         ! Moses+02b
S       + CL2     = CLS     + CL                  5.93E-14  0.1843  -689.2     ! Woon+21
S       + CLO     = SO      + CL                  4.00e-11   0.      0.         ! Moses+02b
S       + CLCO    = OCS     + CL                  3.00E-12   0.      0.         ! Mills1998estimate, Bierson+20
S       + CLCO    = OCS     + CL                  3.00E-12   0.      0.         ! Mills1998estimate, Bierson+20
S       + CLCO3   = CL      + SO      + CO2       3.00E-11   0.      0.         ! Mills1997estimate, Bierson+20
S       + CLS     = S2      + CL                  2.14e-11  0.1667   0.         ! Woon+21
S       + CLSH    = SH      + CLS                 1.70E-13   0.      0.         ! Bierson+20 -from krasnopolsky 2007, endot
S       + OSCL    = S2O     + CL                  5.00e-11   0.   -600.         ! Moses+02b
S       + OSCL    = SO      + CLS                 2.00e-11   0.   -600.         ! Moses+02b
S       + CLSO2   = SO2     + CLS                 1.00e-11   0.      0.         ! Moses+02b
S       + SO2CL2  = CLSO2   + CLS                 1.00E-12   0.      0.         ! Krasnopolsky 2007
S(1D)   + H2      = SH      + H                   2.10E-10   0.      0.         ! Black & Jusinski (1998)
S(1D)   + CH4     = CH3S    + H                   1.00E-10   0.      0.         ! based on Black & Jusinski (1998)
S(1D)   + CH4     = CH3     + SH                  7.00E-11   0.      0.         ! based on Black & Jusinski (1998)
S(1D)   + CO      = S       + CO                  1.00E-10   0.      0.         ! estimate
S(1D)   + CO2     = S       + CO2                 1.20E-10   0.      0.         ! based on Black & Jusinski (1998)
S(1D)   + CO2     = SO      + CO                  3.00E-11   0.      0.         ! based on Black & Jusinski (1998)
S(1D)   + N2      = S       + N2                  8.50E-11   0.      0.         ! Black & Jusinski (1998)
S(1D)   + OCS     = S2      + CO                  1.76E-10   0.      0.         ! based on Black & Jusinski 98, Yamushita+1
S(1D)   + OCS     = S       + OCS                 1.44E-10   0.      0.         ! based on Black & Jusinski 98, Yamushita+1
S2      + H       + M       = HS2     + M         3.171e-23  -2.84  838.        ! Sendt+02, near low pressure limit at 1 ba
S2      + C       = CS      + S                   1.05e-12   0.5     0.         ! estimate Tsai+21
S2      + CH      = CS2     + H                   1.00e-12   0.5     0.         ! estimate
S2      + O       = S       + SO                  2.20e-11   0.    -84.         ! Craven & Murrell (1987)
S2      + O       + M       = S2O     + M         5.184e-27  -2.8    0.         ! Zhou+13
S2      + O2      = S2O     + O                   2.84e-20  2.5 -17298.        ! Zhou+13  endothermic, reverse pretty slow
S2      + O2      =2SO                            3.82e-21  2.5 -15317.        ! Zhou+13
S2      + N       = NS      + S                   9.988e-13   0.5  -4000.      ! KIDA (Mitchell 1984) probably too slow?
2S2     + M       = S4      + M                   5.00e-17  -5.      0.         ! based on Fowles+67, Nicholas+79, Langford
S2      + HCS     = CS2     + SH                  5.00e-13   0.  -2013.         ! Alzueta+19
S2      + SO3     = S2O     + SO2                 1.00e-10   0.      0.         ! estimate, reverse slower than Zhou+13
S2      + S2O     = SO      + S3                  1.66e-10   0.  -9058.         ! Zhou+13; endothermic, reverse looks fine
S2      + CLO     = S2O     + CL                  2.80e-11   0.      0.         ! estimate Moses+02b
S2      + CLS     = S3      + CL                  1.00e-12   0.      0.         ! estimate, endothermic at high T
S2      + CLSO2   = CLS2    + SO2                 5.00e-11   0.   -800.         ! estimate Moses+02b
S3      + H       = S2      + SH                  5.00e-11   0.   -500.         ! estimate, Zahnle+16
```

> 1000 neutral-neutral reactions

Photochemically produced SO_2 in the atmosphere of WASP-39b, Tsai et al. Nature (2023) 1100 K

S	+ HS2	= S2	+ SH		6.925e-18	2.2	302.	! Sendt+02; 873-1473 K (
S	+ H2S2	= HS2	+ SH		4.733e-18	2.31	-606.	! Sendt+02; also seems t
S	+ CS	+ M	= CS2	+ M	1.706e-24	-2.42	0.	5.0e-11 0. 0. ! Glarbor
S	+ CS2	= CS	+ S2		3.48e-18	0.7	-3623.	! based on Gao & Marshal
S	+ HCS	= CS2	+ H		3.32e-11	0.	0.	! Alzueta+19
S	+ SO	+ M	= S2O	+ M	1.00e-26	-2.	0.	! estimate, Moses+02a
S	+ SO3	= SO2	+ SO		1.00e-16	0.	0.	! estimate, Moses+02a
S	+ S2O	= S2	+ SO		3.00e-11	0.	-500.	! estimate
S	+ OCS	= S2	+ CO		1.43E-16	1.58	-1940.	! Lu+06
S	+ CL	+ M	= CLS	+ M	1.00e-29	-1.	0.	! Moses+02b
S	+ CL2	= CLS	+ CL		5.93E-14	0.1843	-689.2	! Woon+21
S	+ CLO	= SO	+ CL		4.00e-11	0.	0.	! Moses+02b
S	+ CLCO	= OCS	+ CL		3.00E-12	0.	0.	! Mills1998estimate, Bi
S	+ CLCO	= OCS	+ CL		3.00E-12	0.	0.	! Mills1998estimate,
S	+ CLCO3	= CL	+ SO	+ CO2	3.00E-11	0.	0.	! Mills1997estimate,
S	+ CLS	= S2	+ CL		2.14e-11	0.1667	0.	! Woon+21
S	+ CLSH	= SH	+ CLS		1.70E-13	0.	0.	! Bierson+20 -from
S	+ OSCL	= S2O	+ CL		5.00e-11	0.	-600.	! Moses+02b
S	+ OSCL	= SO	+ CLS		2.00e-11	0.	-600.	! Moses+02b
S	+ CLSO2	= SO2	+ CLS		1.00e-11	0.	0.	! Moses+02b
S	+ SO2CL2	= CLSO2	+ CLS		1.00E-12	0.	0.	! Krasnopolsky 2007
S(1D)	+ H2	= SH	+ H		2.10E-10	0.	0.	! Black & Jusinski
S(1D)	+ CH4	= CH3S	+ H		1.00E-10	0.	0.	! based on Black &
S(1D)	+ CH4	= CH3	+ SH		7.00E-11	0.	0.	! based on Black &
S(1D)	+ CO	= S	+ CO		1.00E-10	0.	0.	! estimate
S(1D)	+ CO2	= S	+ CO2		1.20E-10	0.	0.	! based on Black &
S(1D)	+ CO2	= SO	+ CO		3.00E-11	0.	0.	! based on Black &
S(1D)	+ N2	= S	+ N2		8.50E-11	0.	0.	! Black & Jusinski
S(1D)	+ OCS	= S2	+ CO		1.76E-10	0.	0.	! based on Black &
S(1D)	+ OCS	= S	+ OCS		1.44E-10	0.	0.	! based on Black &
S2	+ H	+ M	= HS2	+ M	3.171e-23	-2.84	838.	! Sendt+02, near lo
S2	+ C	= CS	+ S		1.05e-12	0.5	0.	! estimate Tsai+21
S2	+ CH	= CS2	+ H		1.00e-12	0.5	0.	! estimate
S2	+ O	= S	+ SO		2.20e-11	0.	-84.	! Craven & Murrell
S2	+ O	+ M	= S2O	+ M	5.184e-27	-2.8	0.	! Zhou+13
S2	+ O2	= S2O	+ O		2.84e-20	2.5	-17298.	! Zhou+13 endother
S2	+ O2	=2SO			3.82e-21	2.5	-15317.	! Zhou+13
S2	+ N	= NS	+ S		9.988e-13	0.5	-4000.	! KIDA (Mitchell 19
2S2	+ M	= S4	+ M		5.00e-17	-5.	0.	! based on Fowles+6
S2	+ HCS	= CS2	+ SH		5.00e-13	0.	-2013.	! Alzueta+19
S2	+ SO3	= S2O	+ SO2		1.00e-10	0.	0.	! estimate, reverse
S2	+ S2O	= SO	+ S3		1.66e-10	0.	-9058.	! Zhou+13; endother
S2	+ CLO	= S2O	+ CL		2.80e-11	0.	0.	! estimate Moses+02b
S2	+ CLS	= S3	+ CL		1.00e-12	0.	0.	! estimate, endotherm
S2	+ CLSO2	= CLS2	+ SO2		5.00e-11	0.	-800.	! estimate Moses+02b
S3	+ H	= S2	+ SH		5.00e-11	0.	-500.	! estimate, Zahnle+16

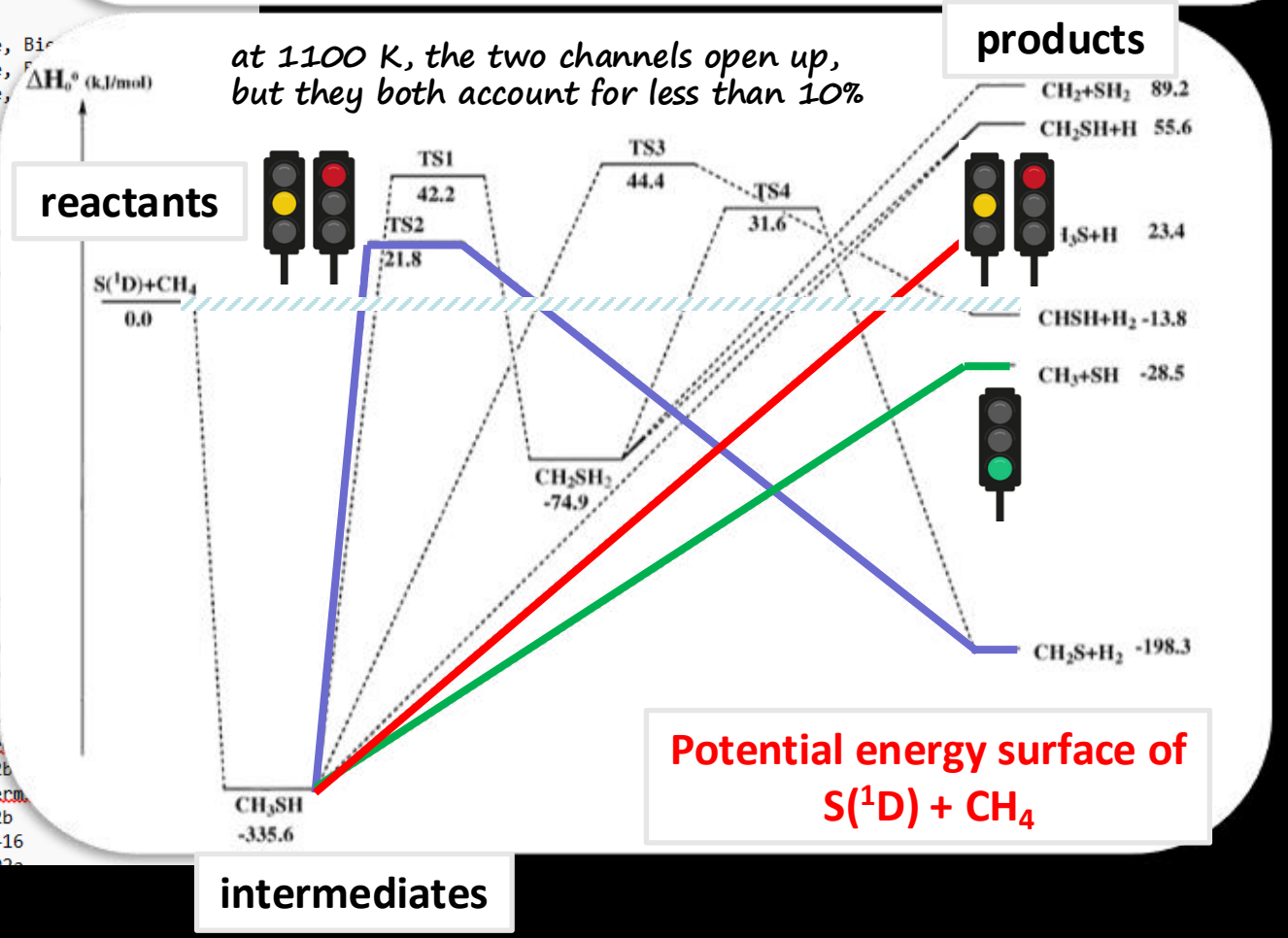
> 1000 neutral-neutral reactions

Cite this: *Phys. Chem. Chem. Phys.*, 2011, **13**, 8485–8501

www.rsc.org/pccp **PAPER**

Low temperature kinetics, crossed beam dynamics and theoretical studies of the reaction $S(^1D) + CH_4$ and low temperature kinetics of $S(^1D) + C_2H_2$

Coralie Berteloite,[a] Sébastien D. Le Picard,*[a] Ian R. Sims,[a] Marzio Rosi,[b] Francesca Leonori,[c] Raffaele Petrucci,[c] Nadia Balucani,[c] Xingan Wang†[c] and Piergiorgio Casavecchia*[c]



Photochemically produced SO_2 in the atmosphere of WASP-39b, Tsai et al. Nature (2023) 1100 K

```
S       + HS2     = S2      + SH                    6.925e-18  2.2    302.        ! Sendt+02; 873-1473 K (
S       + H2S2    = HS2     + SH                    4.733e-18  2.31 -606.         ! Sendt+02; also seems t
S       + CS      + M       = CS2     + M           1.706e-24  -2.42   0.   5.0e-11  0.  0.      ! Glarbor
S       + CS2     = CS      + S2                    3.48e-18  0.7   -3623.        ! based on Gao & Marshal
S       + HCS     = CS2     + H                     3.32e-11   0.      0.         ! Alzueta+19
S       + SO      + M       = S2O     + M           1.00e-26  -2.      0.         ! estimate, Moses+02a
S       + SO3     = SO2     + SO                    1.00e-16   0.      0.         ! estimate, Moses+02a
S       + S2O     = S2      + SO                    3.00e-11   0.    -500.        ! estimate
S       + OCS     = S2      + CO                    1.43E-16  1.58  -1940.        ! Lu+06
S       + CL      + M       = CLS     + M           1.00e-29  -1.      0.         ! Moses+02b
S       + CL2     = CLS     + CL                    5.93E-14  0.1843  -689.2     ! Woon+21
S       + CLO     = SO      + CL                    4.00e-11   0.      0.         ! Moses+02b
S       + CLCO    = OCS     + CL                    3.00E-12   0.      0.         ! Mills1998estimate, Bi
S       + CLCO    = OCS     + CL                    3.00E-12   0.      0.         ! Mills1998estimate,
S       + CLCO3   = CL      + SO      + CO2         3.00E-11   0.      0.         ! Mills1997estimate,
S       + CLS     = S2      + CL                    2.14e-11  0.1667   0.         ! Woon+21
S       + CLSH    = SH      + CLS                   1.70E-13   0.      0.         ! Bierson+20 -from
S       + OSCL    = S2O     + CL                    5.00e-11   0.    -600.        ! Moses+02b
S       + OSCL    = SO      + CLS                   2.00e-11   0.    -600.        ! Moses+02b
S       + CLSO2   = SO2     + CLS                   1.00e-11   0.      0.         ! Moses+02b
S       + SO2CL2  = CLSO2   + CLS                   1.00E-12   0.      0.         ! Krasnopolsky 2007
S(1D)   + H2      = SH      + H                     2.10E-10   0.      0.         ! Black & Jusinski
S(1D)   + CH4     = CH3S    + H                     1.00E-10   0.      0.         ! based on Black &
S(1D)   + CH4     = CH3     + SH                    7.00E-11   0.      0.         ! based on Black &
S(1D)   + CO      = S       + CO                    1.00E-10   0.      0.         ! estimate
S(1D)   + CO2     = S       + CO2                   1.20E-10   0.      0.         ! based on Black &
S(1D)   + CO2     = SO      + CO                    3.00E-11   0.      0.         ! based on Black &
S(1D)   + N2      = S       + N2
S(1D)   + OCS     = S2      + CO
S(1D)   + OCS     = S       + OCS
S2      + H       + M       = HS2     + M
S2      + C       = CS      + S
S2      + CH      = CS2     + H
S2      + O       = S       + SO
S2      + O       + M       = S2O     + M
S2      + O2      = S2O     + O
S2      + O2      =2SO
S2      + N       = NS      + S
2S2     + M       = S4      + M
S2      + HCS     = CS2     + SH
S2      + SO3     = S2O     + SO2
S2      + S2O     = SO      + S3
S2      + CLO     = S2O     + CL
S2      + CLS     = S3      + CL
S2      + CLSO2   = CLS2    + SO2                   ! estimate Moses+02b
S3      + H       = S2      + SH                    5.00e-11   0.    -500.        ! estimate, Zahnle+16
```

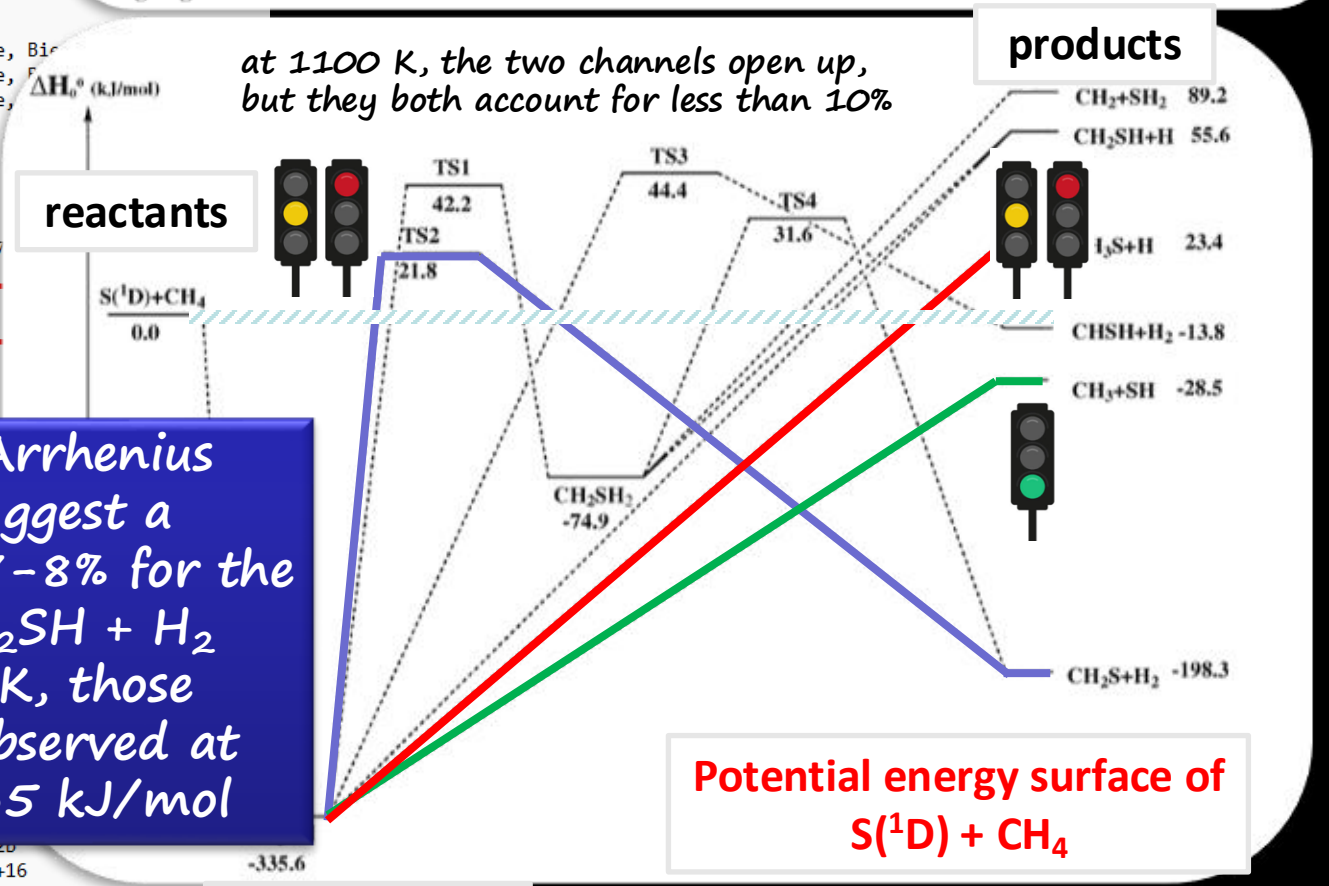
> 1000 neutral-neutral reactions

Cite this: *Phys. Chem. Chem. Phys.*, 2011, **13**, 8485–8501

www.rsc.org/pccp **PAPER**

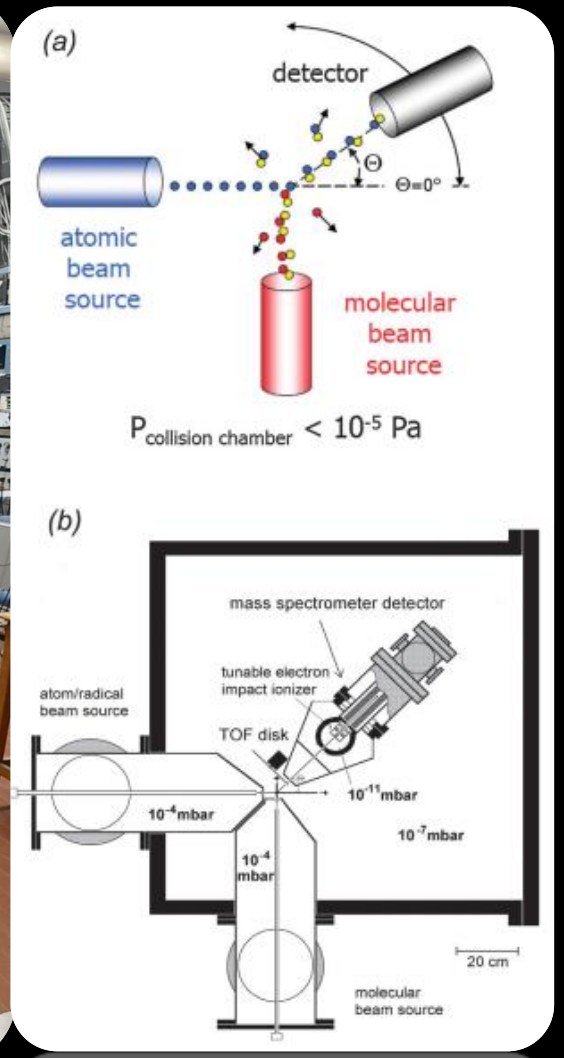
Low temperature kinetics, crossed beam dynamics and theoretical studies of the reaction $S(^1D) + CH_4$ and low temperature kinetics of $S(^1D) + C_2H_2$

Coralie Berteloite,[a] Sébastien D. Le Picard,*[a] Ian R. Sims,[a] Marzio Rosi,[b] Francesca Leonori,[c] Raffaele Petrucci,[c] Nadia Balucani,[c] Xingan Wang†[c] and Piergiorgio Casavecchia*[c]

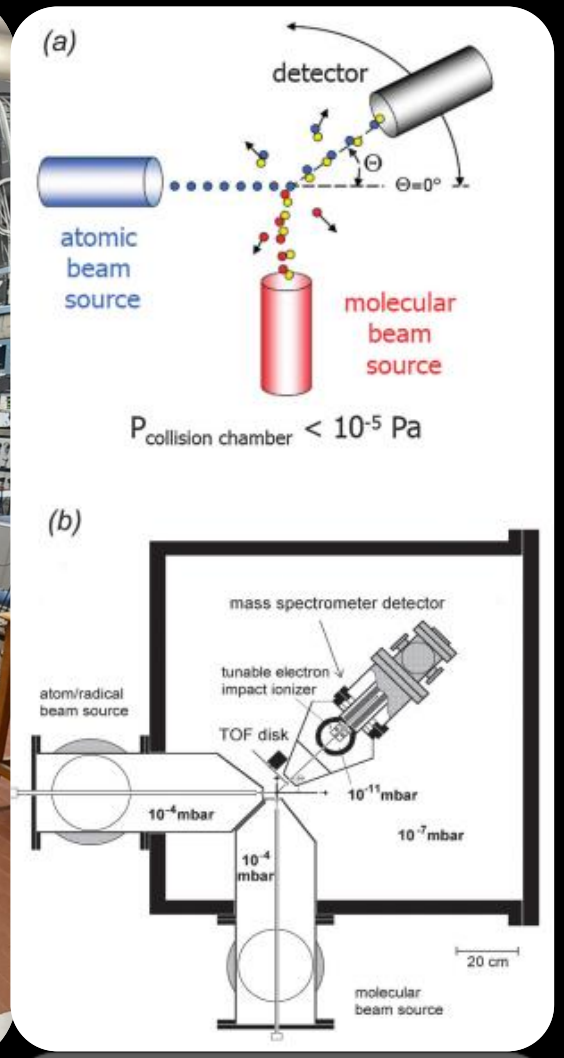


Although a simple Arrhenius estimate would suggest a branching fraction of 7–8% for the $CH_3SH + H$ and $CH_2SH + H_2$ channels at 1100 K, those products were not observed at collision energies > 35 kJ/mol

Potential energy surface of $S(^1D) + CH_4$

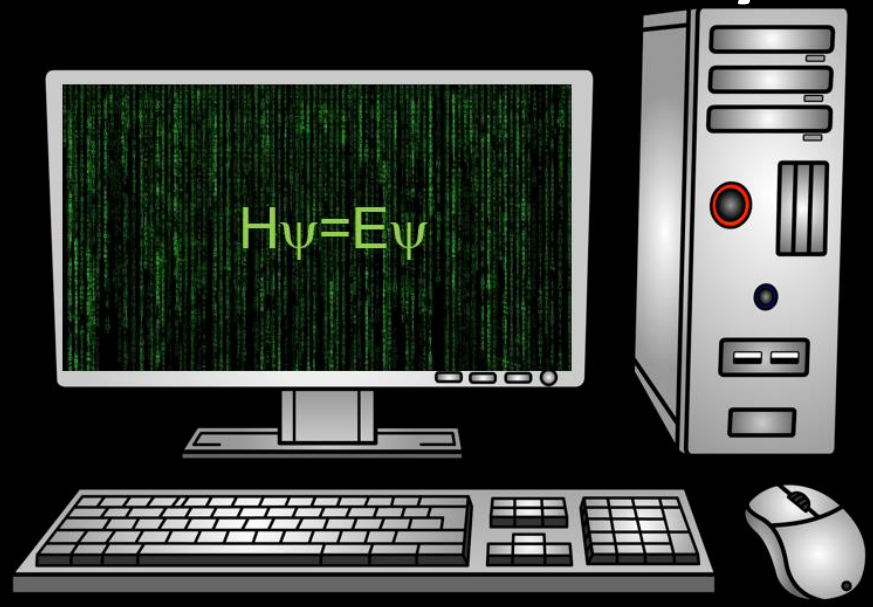


The characteristics of our experimental technique make it unique to study bimolecular reactions in extremely rarefied conditions



The characteristics of our experimental technique make it unique to study bimolecular reactions in extremely rarefied conditions

Computational and theoretical chemistry



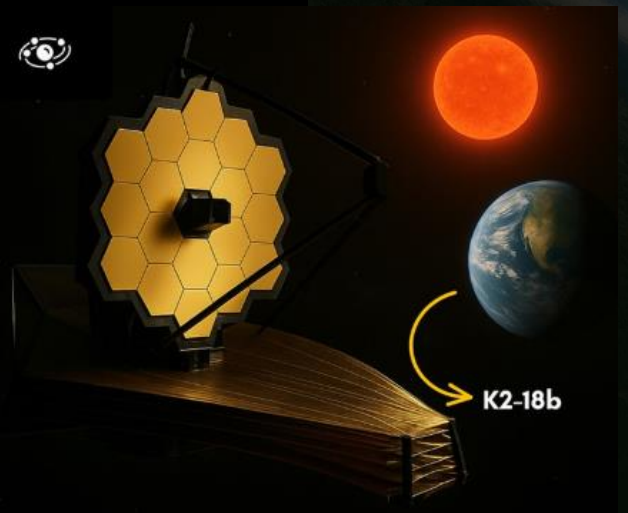
Our computational methods have been validated by the comparison with experimental results for almost two decades

A couple of examples:

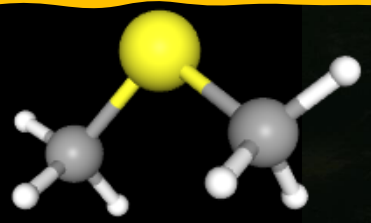
1) Dimethyl sulfide in the atmosphere of K2-18b

2) Pyridine in the atmosphere of Titan

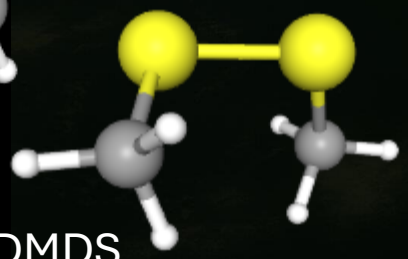
Habitable-zone Exoplanet **K2-18 b**



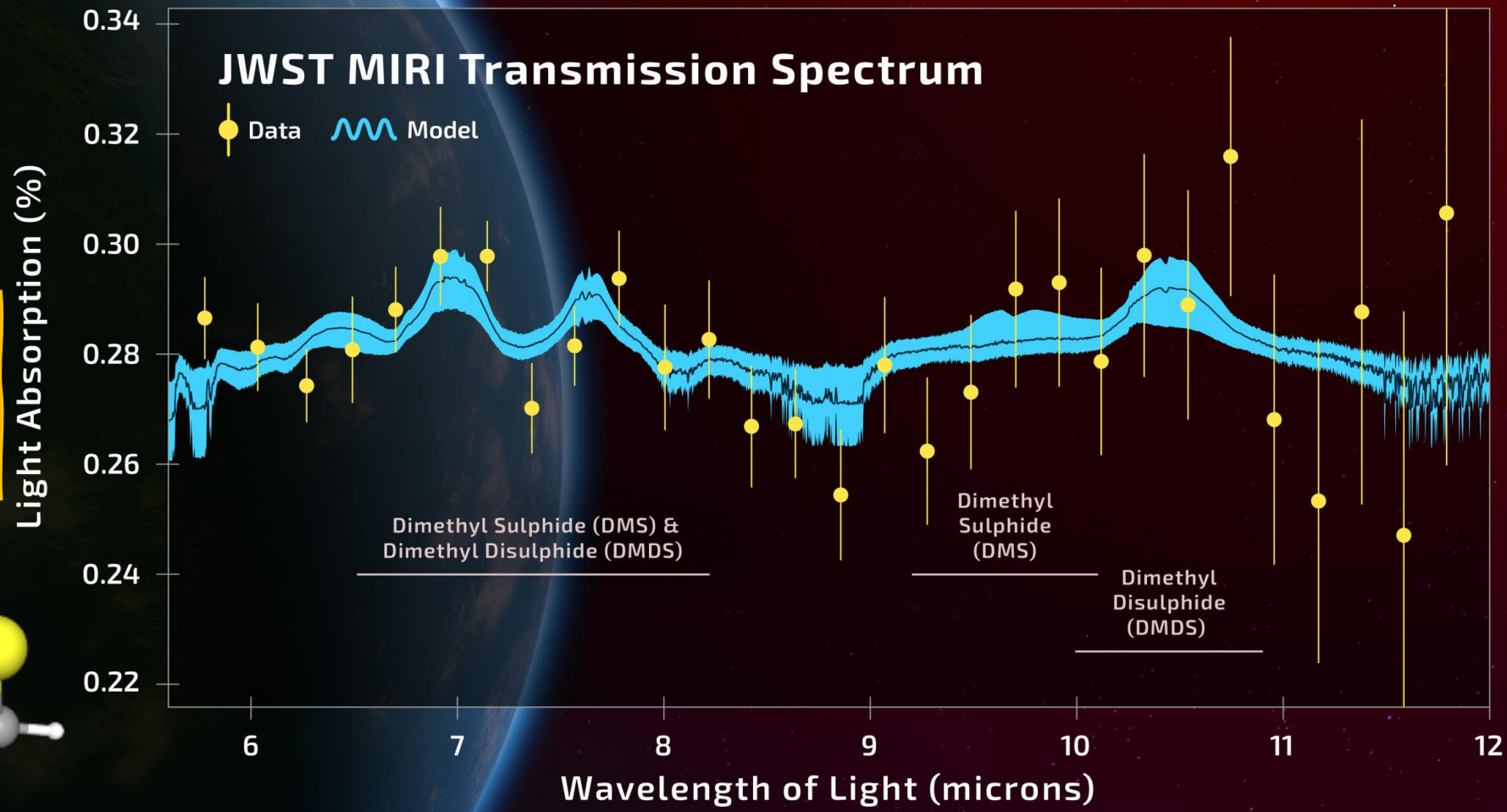
The JWST has potentially detected a molecule called **dimethyl sulfide** on an **alien world**. On Earth, this molecule is only produced by **living organisms**



DMS



DMDS



Credit: A. Smith, N. Madhusudhan (University of Cambridge)

The Astrophysical Journal, 976:74 (8pp), 2024 November 20 https://doi.org/10.3847/1538-4357/ad8565

Evidence for Abiotic Dimethyl Sulfide in Cometary Matter

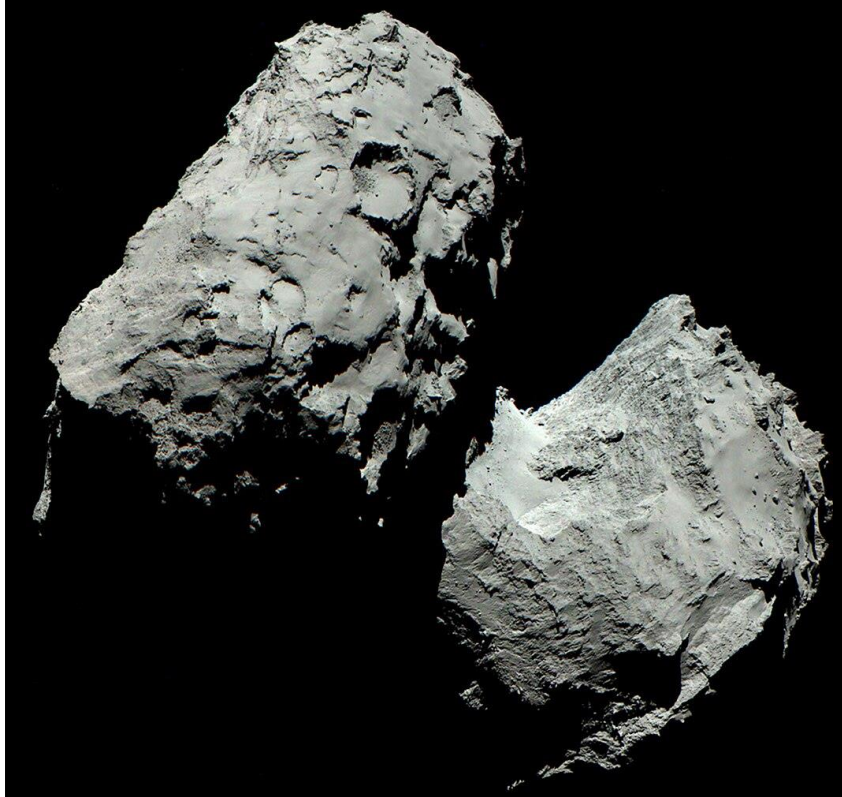
Nora Hänni[1], Kathrin Altwegg[1], Michael Combi[2], Stephen A. Fuselier[3,4], Johan De Keyser[5], Niels F. W. Ligterink[1,6], Martin Rubin[1], and Susanne F. Wampfler[7]

[1] Physics Institute, Space Research & Planetary Sciences, University of Bern, Sidlerstrasse 5, CH-3012 Bern, Switzerland; nora.haenni@unibe.ch
[2] Department of Climate and Space Sciences and Engineering, University of Michigan, Ann Arbor, MI, USA
[3] Space Science Division, Southwest Research Institute, San Antonio, TX, USA
[4] Department of Physics and Astronomy, The University of Texas at San Antonio, San Antonio, TX, USA
[5] Royal Belgian Institute for Space Aeronomy, BIRA-IASB, Brussels, Belgium
[6] Faculty of Aerospace Engineering, Delft University of Technology, Delft, The Netherlands
[7] Center for Space and Habitability, University of Bern, Gesellschaftsstrasse 6, CH-3012 Bern, Switzerland
Received 2024 April 25; revised 2024 October 5; accepted 2024 October 8; published 2024 November 14

Abstract

Technological progress related to astronomical observatories such as the recently launched James Webb Space Telescope (JWST) allows searching for signs of life beyond our solar system, namely, in the form of unambiguous biosignature gases in exoplanetary atmospheres. The tentative assignment of a 1σ–2.4σ spectral feature observed with JWST in the atmosphere of exoplanet K2-18b to the biosignature gas dimethyl sulfide (DMS; sum formula C_2H_6S) raised hopes that, although controversial, a second genesis had been found. Terrestrial atmospheric DMS is exclusively stemming from marine biological activity, and no natural abiotic source has been identified—neither on Earth nor in space. Therefore, DMS is considered a robust biosignature. Since comets possess a pristine inventory of complex organic molecules of abiotic origin, we have searched high-resolution mass spectra collected at comet 67P/Churyumov–Gerasimenko, target of the European Space Agency's Rosetta mission, for the signatures of DMS. Previous work reported the presence of a C_2H_6S signal when the comet was near its equinox, but distinction of DMS from its structural isomer ethanethiol remained elusive. Here we reassess these and evaluate additional data. Based on differences in the electron ionization-induced fragmentation pattern of the two isomers, we show that DMS is significantly better compatible with the observations. Deviations between expected and observed signal intensities for DMS are $<1\sigma$, while for ethanethiol they are 2σ–4σ. The local abundance of DMS relative to methanol deduced from these data is $(0.13 \pm 0.04)\%$. Our results provide the first evidence for the existence of an abiotic synthetic pathway to DMS in pristine cometary matter and hence motivate more detailed studies of the sulfur chemistry in such matter and its analogs. Future studies need to investigate whether or not the present inference of cometary DMS could provide an abiotic source of DMS in a planetary atmosphere.

Unified Astronomy Thesaurus concepts: Comet volatiles (2162); Biosignatures (2018); Mass spectrometry (2094)

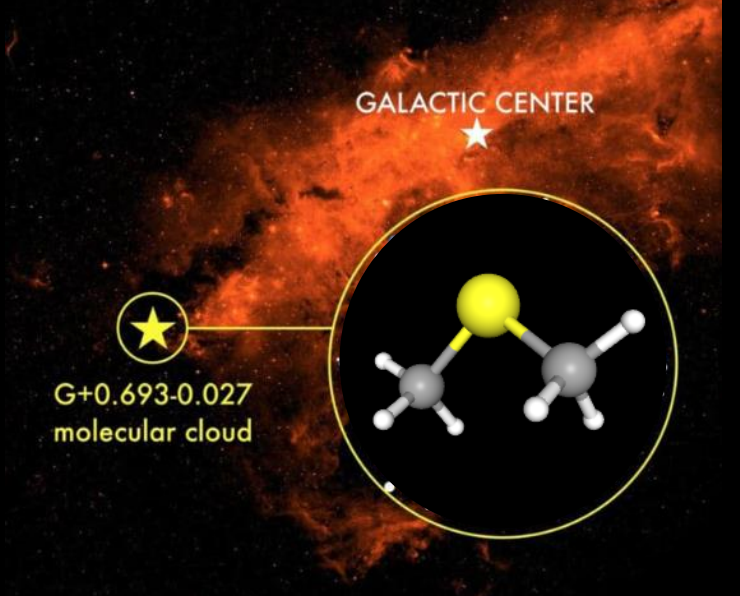


The Astrophysical Journal Letters, 980:L37 (11pp), 2025 February 20 https://doi.org/10.3847/2041-8213/adafa7

On the Abiotic Origin of Dimethyl Sulfide: Discovery of Dimethyl Sulfide in the Interstellar Medium

Miguel Sanz-Novo[1], Víctor M. Rivilla[1], Christian P. Endres[2], Valerio Lattanzi[2], Izaskun Jiménez-Serra[1], Laura Colzi[1], Shaoshan Zeng[3], Andrés Megías[1], Álvaro López-Gallifa[1], Antonio Martínez-Henares[1], David San Andrés[1], Belén Tercero[4], Pablo de Vicente[5], Sergio Martín[6,7], Miguel A. Requena-Torres[8], Paola Caselli[2], and Jesús Martín-Pintado[1]

[1] Centro de Astrobiología (CAB), INTA-CSIC, Carretera de Ajalvir, km 4, Torrejón de Ardoz, 28850 Madrid, Spain
[2] Center for Astrochemical Studies, Max-Planck-Institut für Extraterrestrische Physik, Gießenbachstraße 1, 85748 Garching, Germany
[3] Star and Planet Formation Laboratory, Cluster for Pioneering Research, RIKEN, 2-1 Hirosawa, Wako, Saitama, 351-0198, Japan
[4] Observatorio Astronómico Nacional (OAN-IGN), Calle Alfonso XII, 3, 28014 Madrid, Spain
[5] Observatorio de Yebes (OY-IGN), Cerro de la Palera SN, Yebes, Guadalajara, Spain
[6] European Southern Observatory, Alonso de Córdova 3107, Vitacura 763 0355, Santiago, Chile
[7] Joint ALMA Observatory, Alonso de Córdova 3107, Vitacura 763 0355, Santiago, Chile
[8] Department of Physics, Astronomy and Geosciences, Towson University, Towson, MD 21252, USA
Received 2024 November 26; revised 2025 January 27; accepted 2025 January 29; published 2025 February 18



Abstract

Following the discovery of dimethyl sulfide (DMS; CH_3SCH_3) signatures in comet 67P/Churyumov–Gerasimenko, we report the first detection of this organosulfur species in the interstellar medium during the exploration of an ultradeep molecular line survey performed toward the Galactic center molecular cloud G+0.693-0.027 with the Yebes 40 m and IRAM 30 m telescopes. We derive a molecular column density of $N = (2.6 \pm 0.3) \times 10^{13}$ cm^{-2}, yielding a fractional abundance relative to H_2 of $\sim 1.9 \times 10^{-10}$. This implies that DMS is a factor of $\sim$1.6 times less abundant than its structural isomer CH_3CH_2SH and $\sim$30 times less abundant than its O-analog dimethyl ether (CH_3OCH_3) toward this cloud, in excellent agreement with previous results on various O/S pairs. Furthermore, we find a remarkable resemblance between the relative abundance of DMS/CH_3OH in G+0.693-0.027 ($\sim 1.7 \times 10^{-3}$) and in the comet ($\sim 1.3 \times 10^{-3}$). Although the chemistry of DMS beyond Earth has yet to be fully disclosed, this discovery provides conclusive observational evidence on its efficient abiotic production in the interstellar medium, casting doubt on using DMS as a reliable biomarker in exoplanet science.

Unified Astronomy Thesaurus concepts: Interstellar molecules (849); Interstellar clouds (834); Galactic center (565); Spectral line identification (2073); Astrochemistry (75)

DOI: 10.1051/0004-6361/202555216

A&A, 704, A305 (2025)
https://doi.org/10.1051/0004-6361/202555216

Astronomy & Astrophysics

Gas-phase formation routes of dimethyl sulfide in the interstellar medium

Gabriella Di Genova[1], Nadia Balucani[1,*], Luca Mancini[1], Andrea Giustini[2], Marzio Rosi[2], Dimitrios Skouteris[3], and Cecilia Ceccarelli[4]

[1] Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, Via Elce di Sotto, 8, 06123 Perugia, Italy
[2] Dipartimento di Ingegneria Civile ed Ambientale, Università degli Studi di Perugia, via G. Duranti, Perugia, Italy
[3] Master-Tec, Via Gerardo Dottori 94, 06132 Perugia, Italy
[4] Univ. Grenoble Alpes, CNRS, Institut de Planétologie et d'Astrophysique de Grenoble (IPAG), 38000 Grenoble, France

Received 18 April 2025 / Accepted 22 October 2025

Suggested by Sanz-Novo:

$CH_{3(ice)} + CH_3S_{(ice)} \rightarrow CH_3SCH_{3(ice)}$

$CH_3SH_{(gas)} + CH_3SH_2^+{}_{(gas)}$

$CH_3OH_{(gas)} + CH_3SH_2^+{}_{(gas)}$

What we have done:

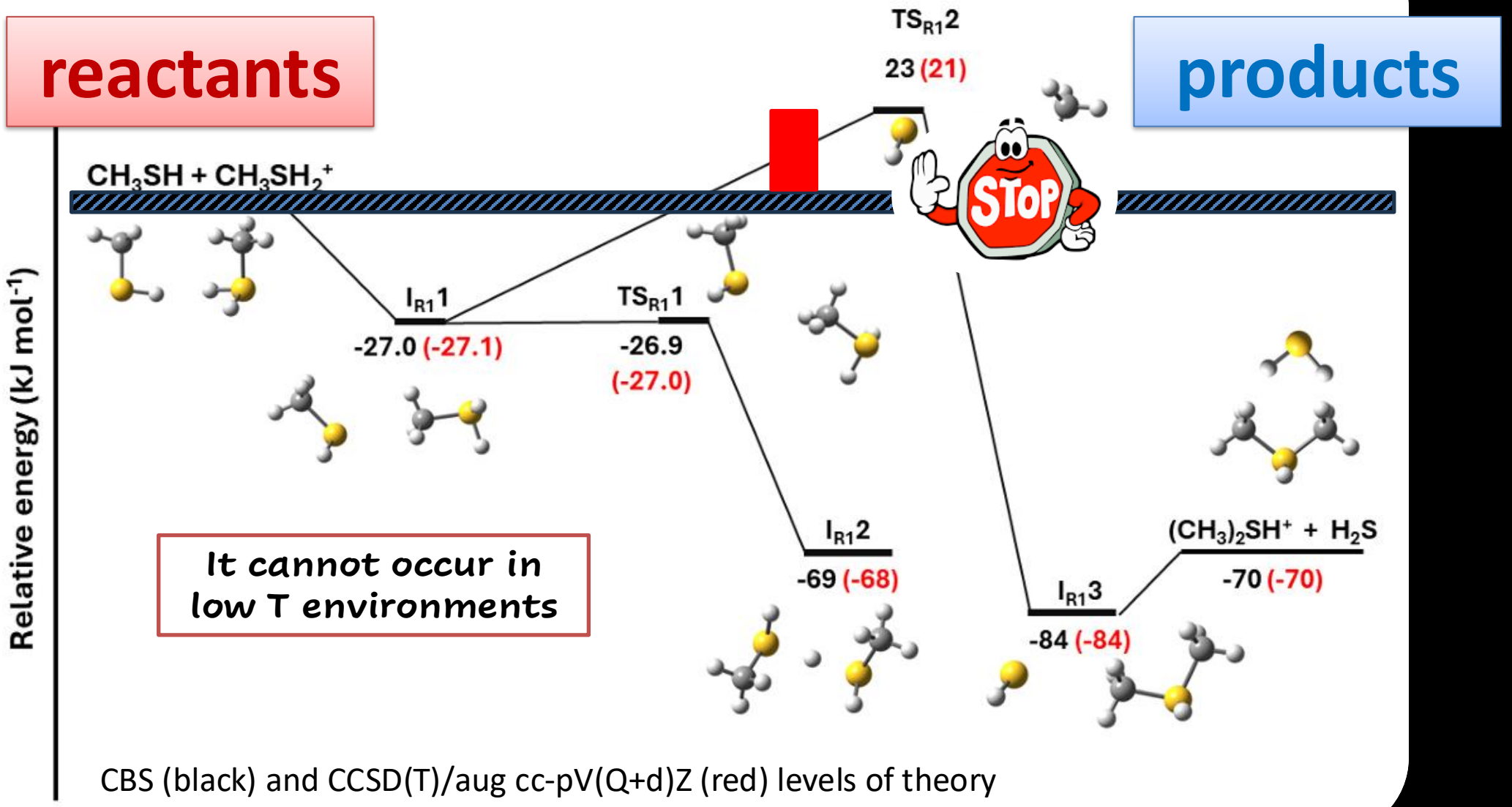
$CH_{3(gas)} + CH_3S_{(gas)} \rightarrow CH_3SCH_{3(gas)} + h\nu$

$CH_3SH_{(gas)} + CH_3SH_2^+{}_{(gas)}$

$CH_3OH_{(gas)} + CH_3SH_2^+{}_{(gas)}$

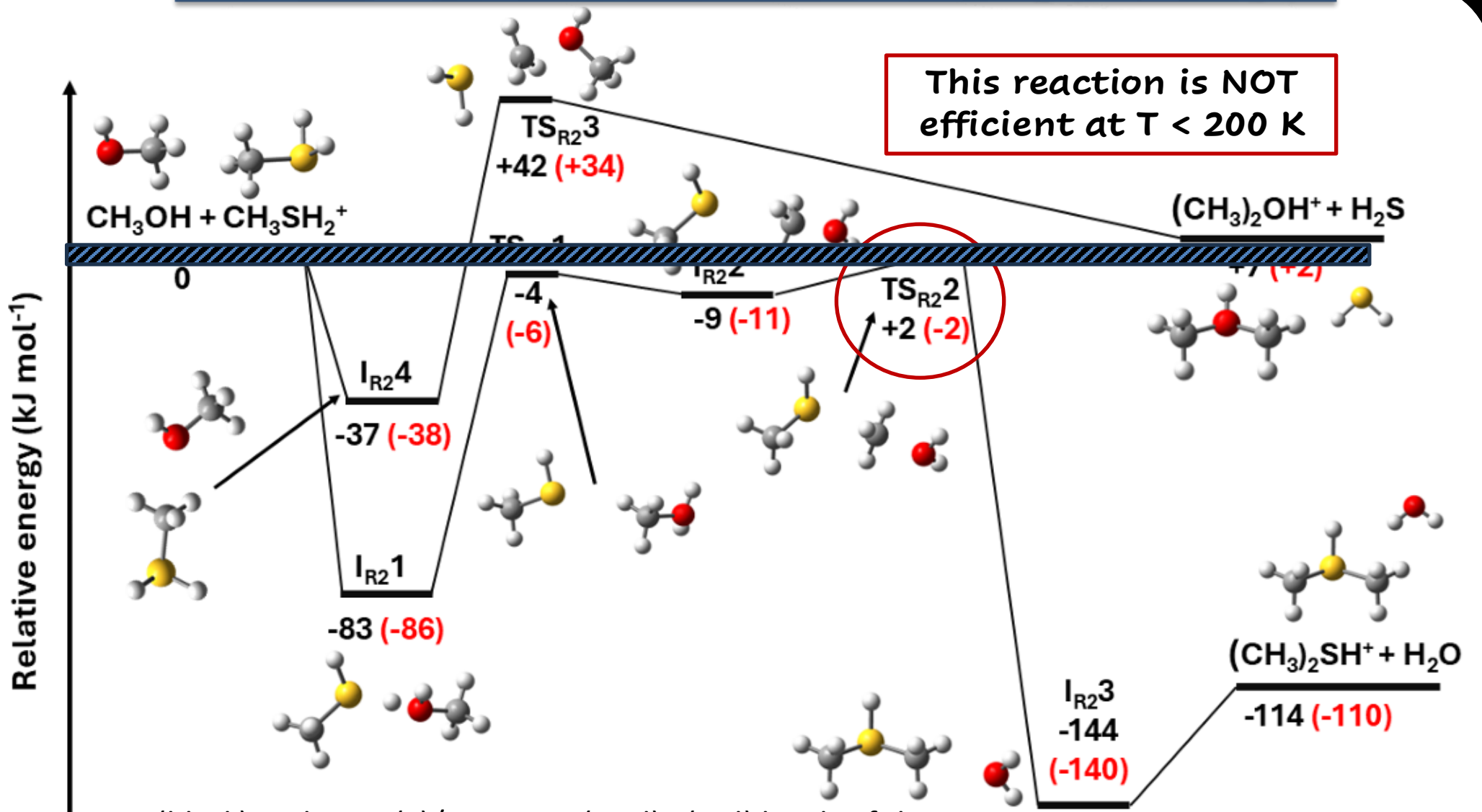
$CH_3SH_{(gas)} + CH_3OH_2^+{}_{(gas)}$

The potential energy surface of the reaction $CH_3SH_{(gas)} + CH_3SH_2^+{}_{(gas)}$



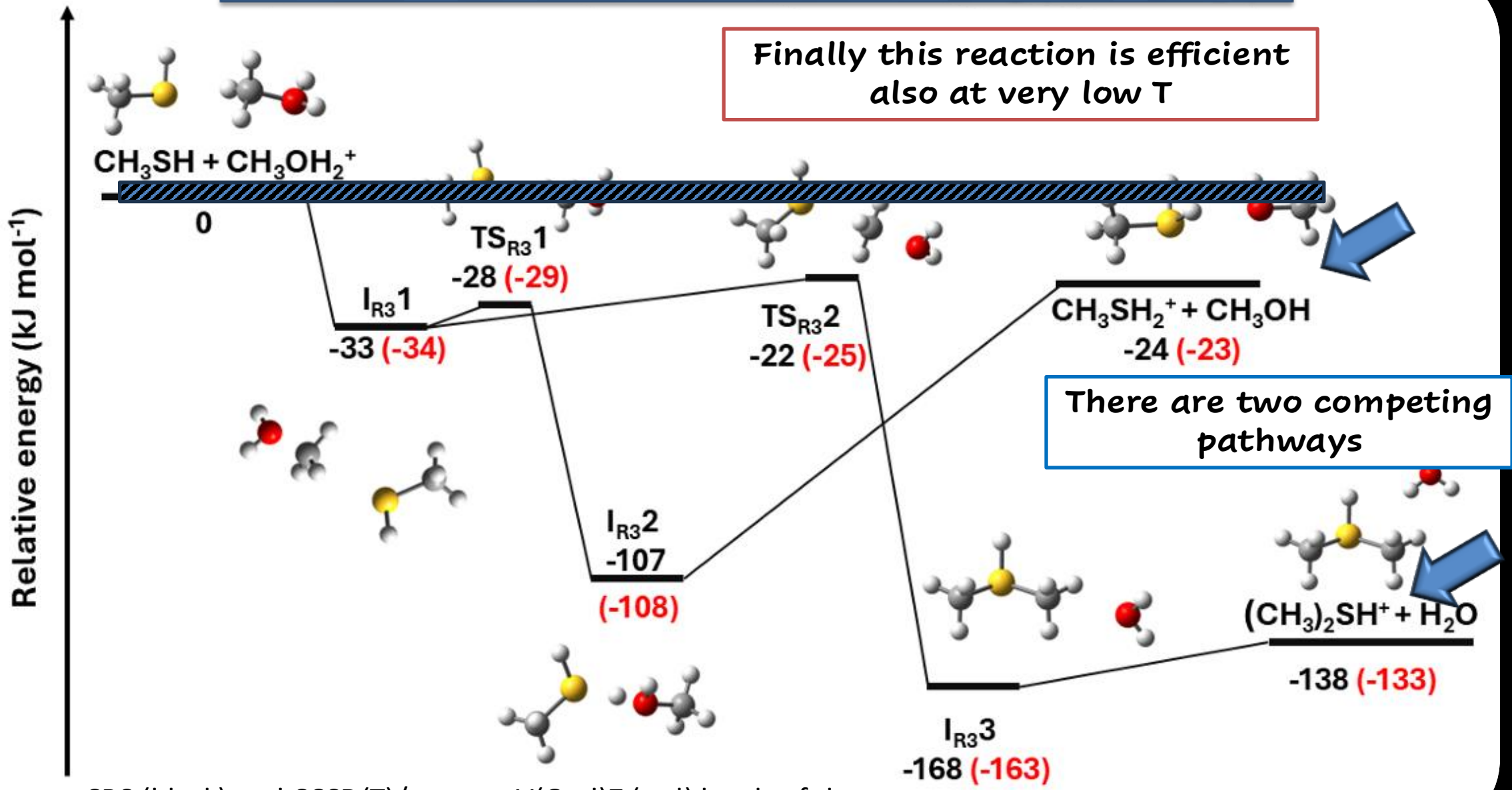
CBS (black) and CCSD(T)/aug cc-pV(Q+d)Z (red) levels of theory

The potential energy surface of the reaction $CH_3OH_{(gas)} + CH_3SH_2^+{}_{(gas)}$



CBS (black) and CCSD(T)/aug cc-pV(Q+d)Z (red) levels of theory

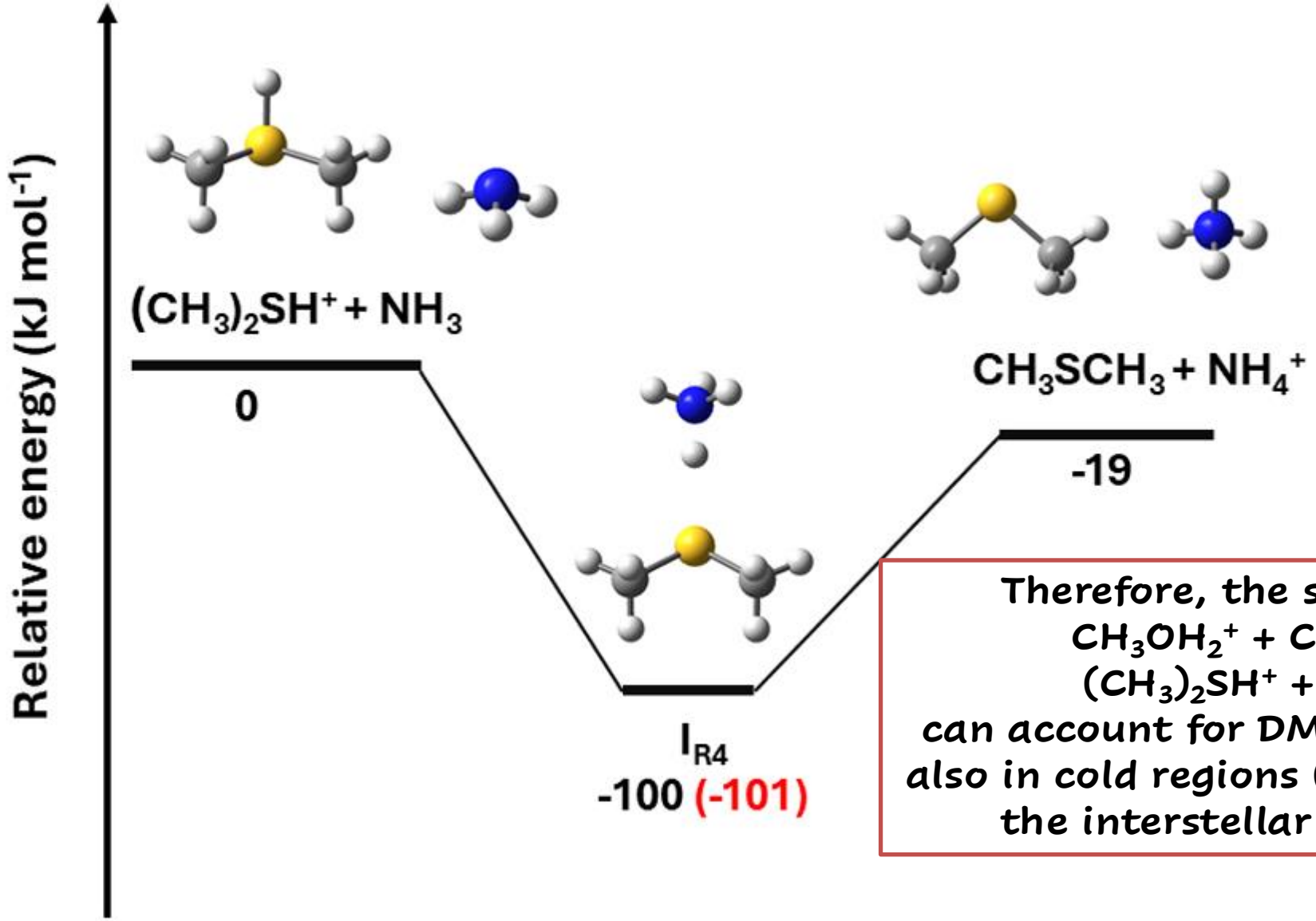
The potential energy surface of the reaction $CH_3SH_{(gas)} + CH_3OH_2^+{}_{(gas)}$



CBS (black) and CCSD(T)/aug cc-pV(Q+d)Z (red) levels of theory

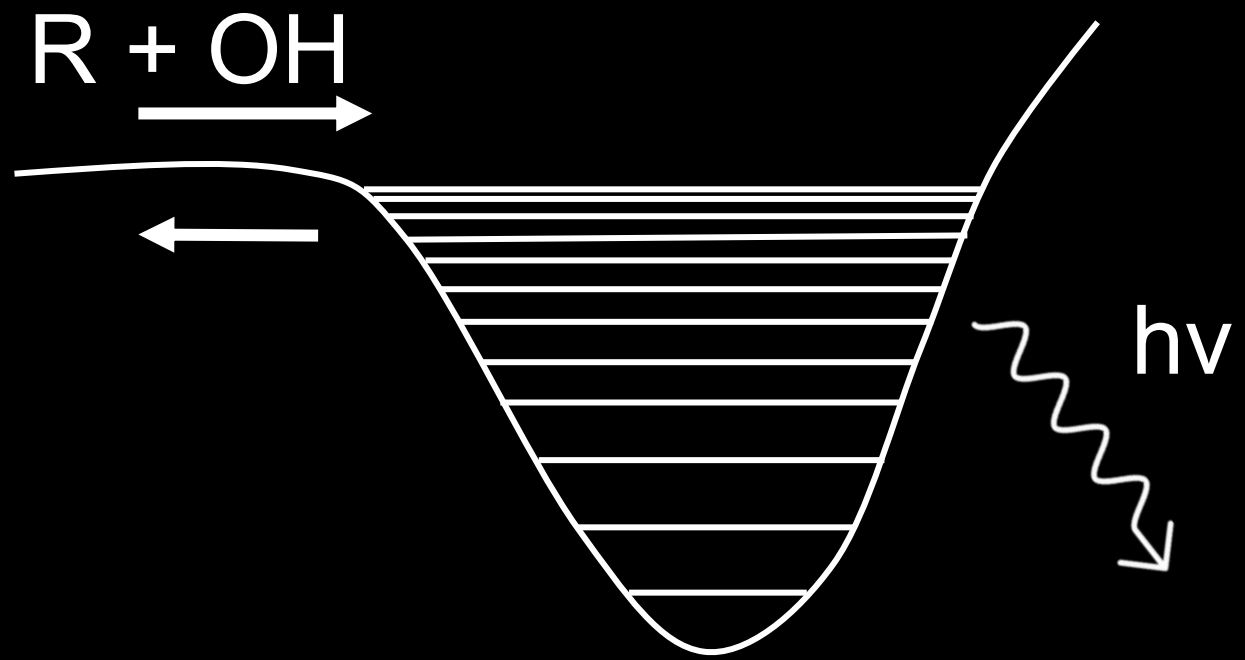
The potential energy surface of the reaction $(CH_3S)_2H^+_{(gas)} + NH_3\ _{(gas)}$

an alternative to dissociative electron-ion recombination

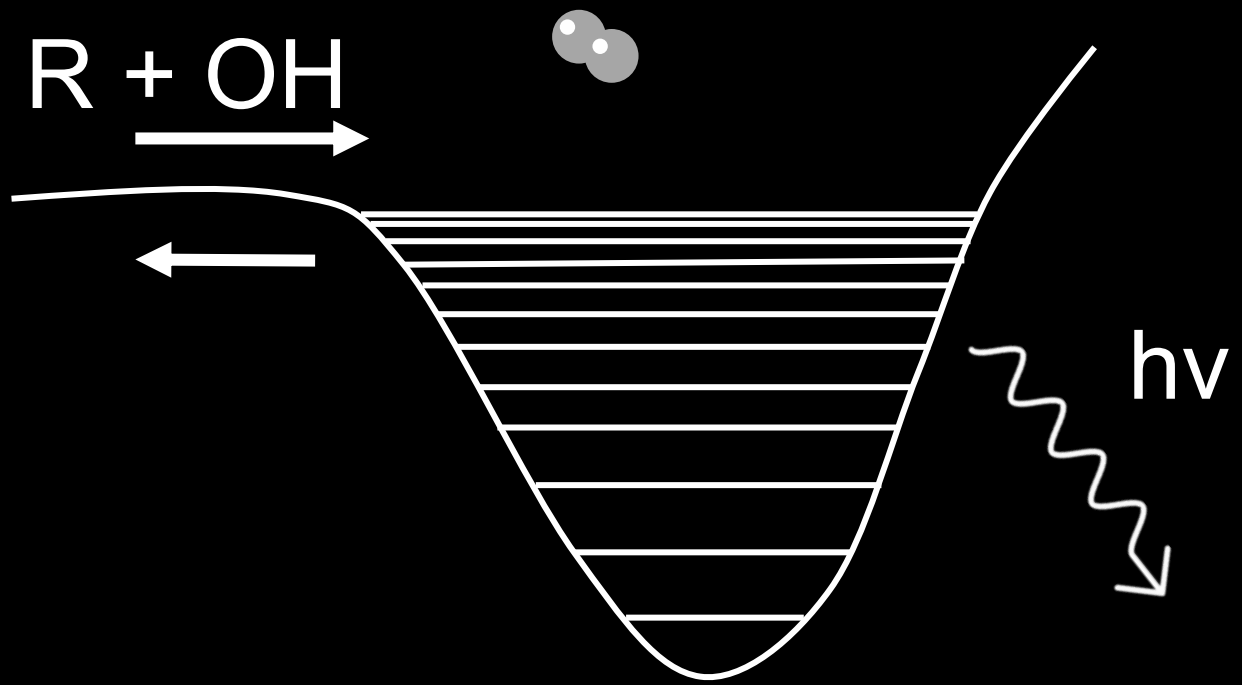


Therefore, the sequence
$CH_3OH_2^+ + CH_3SH$
$(CH_3)_2SH^+ + NH_3$
can account for DMS formation also in cold regions (T < 100 K) of the interstellar medium

Radiative association reactions

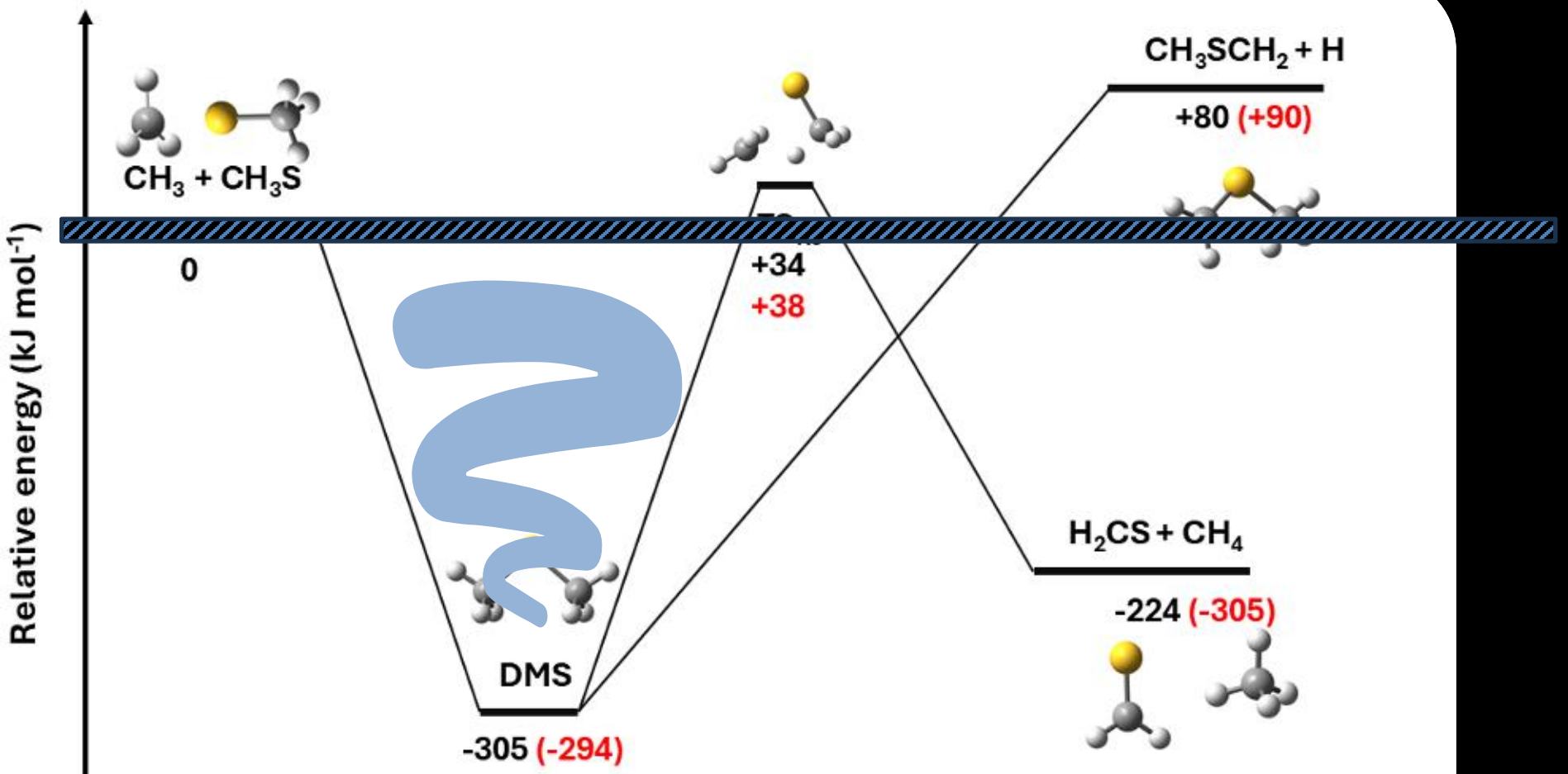


Radiative association reactions



At high pressure, collisional stabilization is common, while at low pressure the spontaneous emission of a photon is the only stabilizing process

The potential energy surface of the radiative association reaction $CH_3S + CH_3$



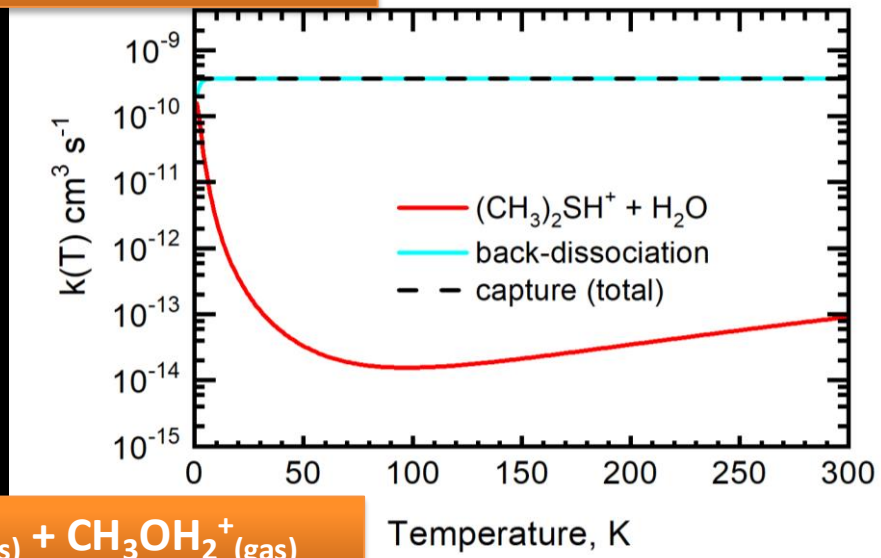
CBS (black) and CCSD(T)/aug cc-pV(Q+d)Z (red) levels of theory

The energy profile has the right shape. It remains to be seen if the spontaneous emission is faster than the backdissociation to reactants

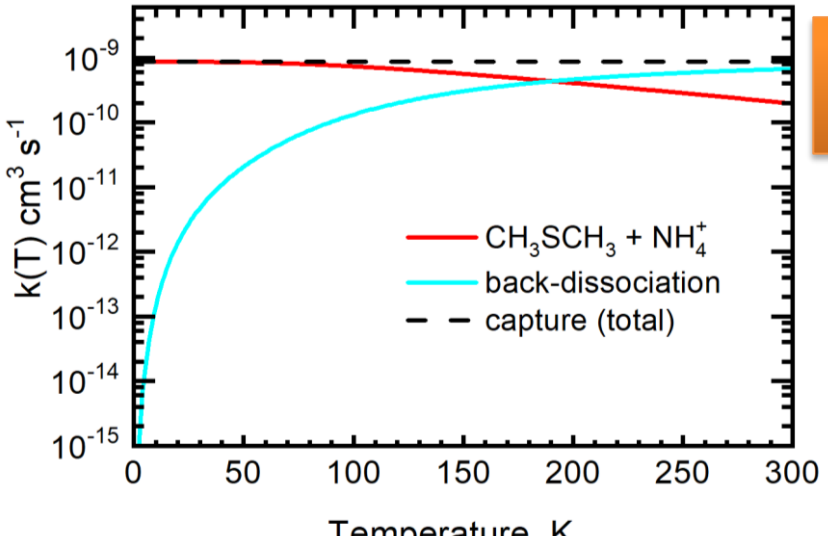
The kinetics analysis

- only the $CH_3OH_2^+ + CH_3SH$ is efficient
- radiative association is efficient only up to 20 K

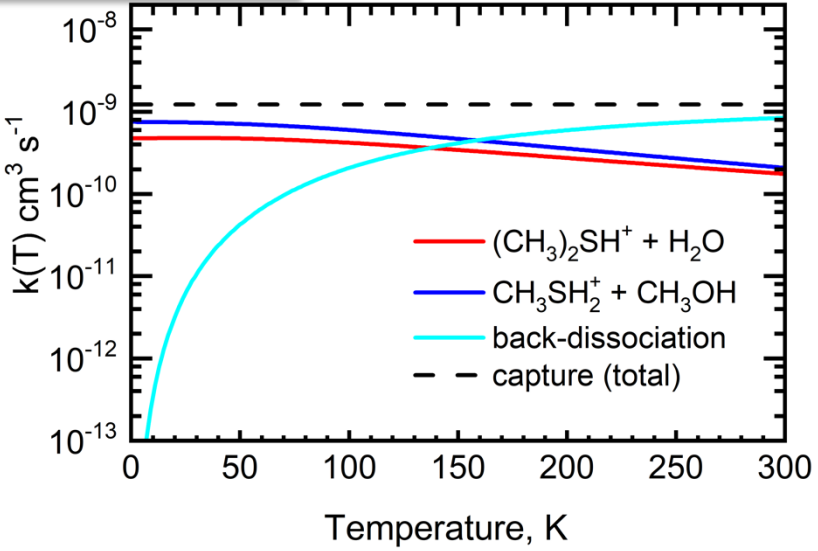
$CH_3OH_{(gas)} + CH_3SH_2^+{}_{(gas)}$



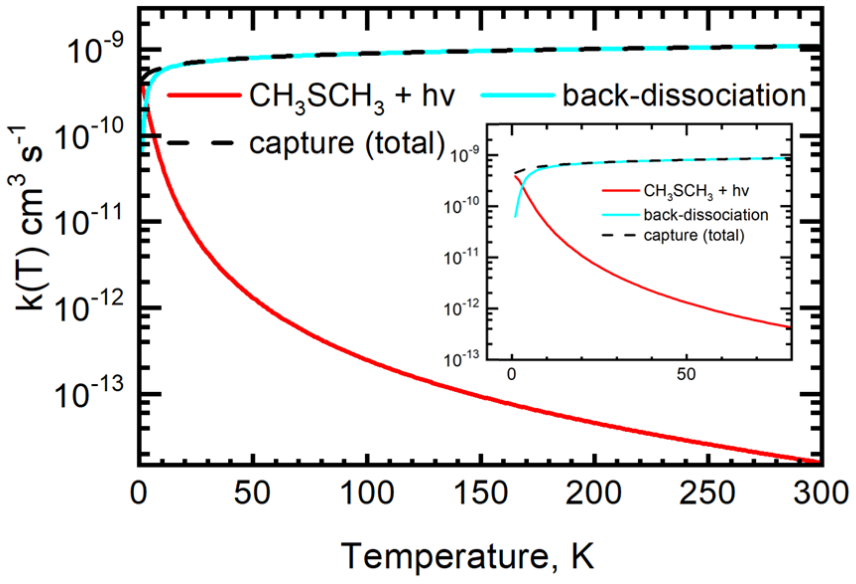
$CH_3SHCH_3^+{}_{(gas)} + NH_3$ (gas)



$CH_3SH_{(gas)} + CH_3OH_2^+{}_{(gas)}$



Radiative association



$$\frac{[DME]}{[DMS]} \propto \frac{rate_{DME_{formation}}}{rate_{DMS_{formation}}}$$

$$= \frac{k_6 \times [CH_3OH] \times [CH_3OH_2^+]}{k_{(3a)} \times [CH_3SH] \times [CH_3OH_2^+]}$$

$$= \frac{k_6 \times [CH_3OH]}{k_{(3a)} \times [CH_3SH]} \approx \frac{[CH_3OH]}{[CH_3SH]}$$

$[DME]/[DMS] = 30 \pm 4$

$[CH_3OH]/[CH_3SH] \cong 31$

The reaction between methanethiol and protonated methanol is a compelling candidate to explain the formation of DMS in the galactic center molecular cloud G+0.693-0.027.

The Astrophysical Journal Letters, 973:L38 (10pp), 2024 October 1 https://doi.org/10.3847/2041-8213/ad74da

Abiotic Production of Dimethyl Sulfide, Carbonyl Sulfide, and Other Organosulfur Gases via Photochemistry: Implications for Biosignatures and Metabolic Potential

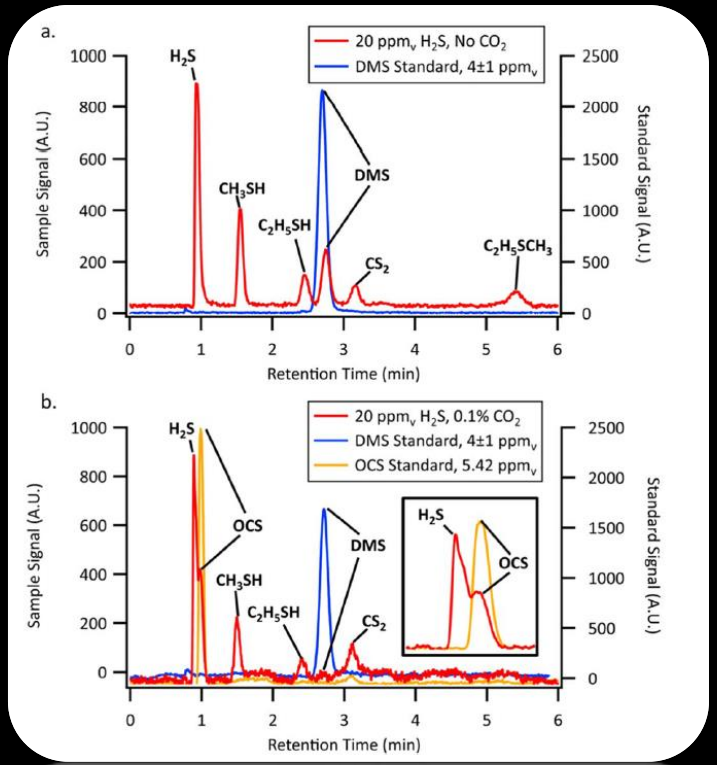
Nathan W. Reed[1,2], Randall L. Shearer[2], Shawn Erin McGlynn[3,4], Boswell A. Wing[5], Margaret A. Tolbert[1,2], and Eleanor C. Browne[1,2]

[1] Department of Chemistry, University of Colorado Boulder, Boulder, CO, USA
[2] Cooperative Institute for Research in Environmental Sciences, University of Colorado Boulder, Boulder, CO, USA
[3] Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1 I7E Ookayama, Meguro, Tokyo, 152-8550, Japan
[4] Blue Marble Space Institute of Science, Seattle, WA, USA
[5] Department of Geological Sciences, University of Colorado Boulder, Boulder, CO, USA; eleanor.browne@colorado.edu
Received 2024 July 3; revised 2024 August 23; accepted 2024 August 25; published 2024 September 23

Abstract

Among the atmospheric gases that have been proposed as possible biosignatures in exoplanetary atmospheres, organosulfur gases are currently considered one of the more robust indicators of extant life. These gases include dimethyl sulfide (DMS; CH_3SCH_3), carbonyl sulfide (OCS), and carbon disulfide (CS_2), which are predominantly secondary metabolic products of living organisms on Earth. Here we present results that challenge this interpretation and provide constraints on the robustness of organosulfur gases as biosignatures. Through laboratory photochemical experiments, we show the abiotic production of organosulfur gases, including DMS, OCS, methane thiol (CH_3SH), ethane thiol (C_2H_5SH), CS_2, and ethyl methyl sulfide ($CH_3CH_2SCH_3$) via photochemistry in analog atmospheres. Gas-phase products of $H_2S/CH_4/N_2$ haze photochemistry, with or without CO_2, were collected and analyzed using gas chromatography equipped with sulfur chemiluminescence detection. Depending on the starting conditions, we estimate that DMS, OCS, CH_3SH, CH_3CH_2SH, CS_2, and $CH_3CH_2SCH_3$ are produced in mixing ratios $>10^{-1}$ ppm_v. We further demonstrate that as the mixing ratio of CO_2 increases, so does the relative importance of OCS compared to DMS. Although our results constrain the robustness of common organosulfur gases as biosignatures, the presence of these compounds may serve as an indicator of metabolic potential on exoplanets.

Unified Astronomy Thesaurus concepts: Pre-biotic astrochemistry (2079); Astrobiology (74); Exoplanet atmospheric composition (2021); Atmospheric composition (2120); Complex organic molecules (2256); Biosignatures (2018)



The Astrophysical Journal Letters, 973:L38 (10pp), 2024 October 1 https://doi.org/10.3847/2041-8213/ad74da

Abiotic Production of Dimethyl Sulfide, Carbonyl Sulfide, and Other Organosulfur Gases via Photochemistry: Implications for Biosignatures and Metabolic Potential

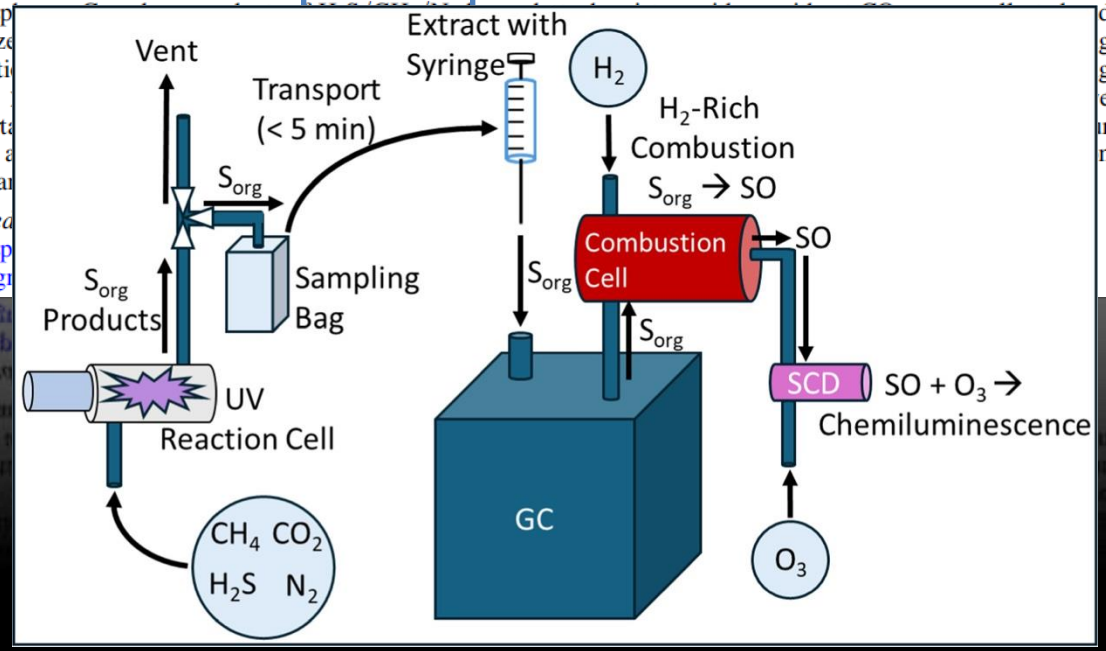
Nathan W. Reed[1,2], Randall L. Shearer[2], Shawn Erin McGlynn[3,4], Boswell A. Wing[5], Margaret A. Tolbert[1,2], and Eleanor C. Browne[1,2]

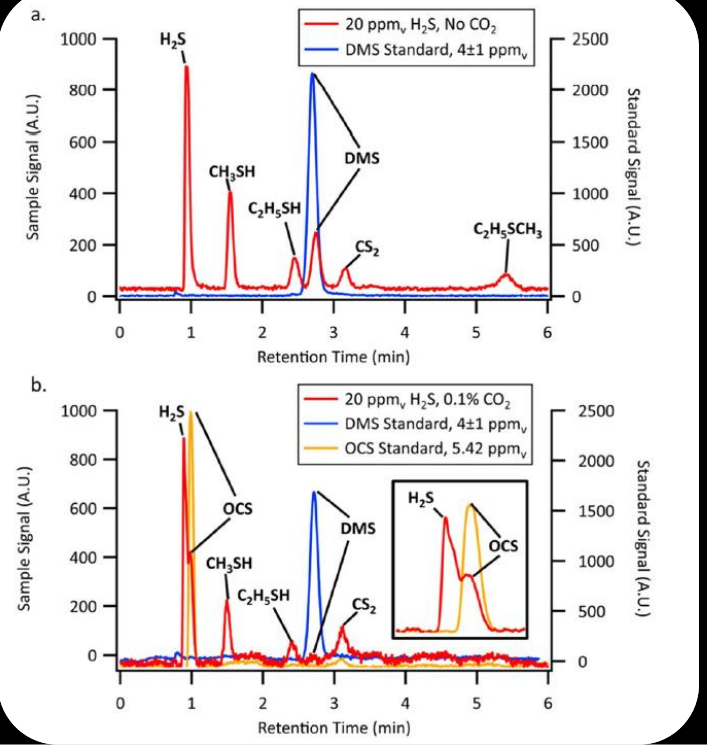
[1] Department of Chemistry, University of Colorado Boulder, Boulder, CO, USA
[2] Cooperative Institute for Research in Environmental Sciences, University of Colorado Boulder, Boulder, CO, USA
[3] Earth-Life Science Institute, Tokyo Institute of Technology, 2-12-1 I7E Ookayama, Meguro, Tokyo, 152-8550, Japan
[4] Blue Marble Space Institute of Science, Seattle, WA, USA
[5] Department of Geological Sciences, University of Colorado Boulder, Boulder, CO, USA; eleanor.browne@colorado.edu
Received 2024 July 3; revised 2024 August 23; accepted 2024 August 25; published 2024 September 23

Abstract

Among the atmospheric gases that have been proposed as possible biosignatures in exoplanetary atmospheres, organosulfur gases are currently considered one of the more robust indicators of extant life. These gases include dimethyl sulfide (DMS; CH_3SCH_3), carbonyl sulfide (OCS), and carbon disulfide (CS_2), which are predominantly secondary metabolic products of living organisms on Earth. Here we present results that challenge this interpretation and provide constraints on the robustness of organosulfur gases as biosignatures. Through laboratory photochemical experiments, we show the abiotic production of organosulfur gases, including DMS, OCS, methane thiol (CH_3SH), ethane thiol (C_2H_5SH), CS_2, and ethyl methyl sulfide ($CH_3CH_2SCH_3$) via photochemistry in analog atmosp… d analyze… g conditi… g ratios … e import… r gases a… n exopla…

Unified atmosp… Biosig…





3.3. Potential Reaction Mechanisms for the Formation of DMS and Other Organosulfur Products

Although several organosulfur gases have garnered attention as potential biosignatures, DMS has been of particular interest due to an absence of known false positives. However, our experiments demonstrate an abiotic pathway to DMS. We propose the following set of reactions as one possible mechanism for DMS formation within our experiment:

$$H_2S + h\nu \rightarrow HS\cdot + H\cdot \quad \text{(R1)}$$

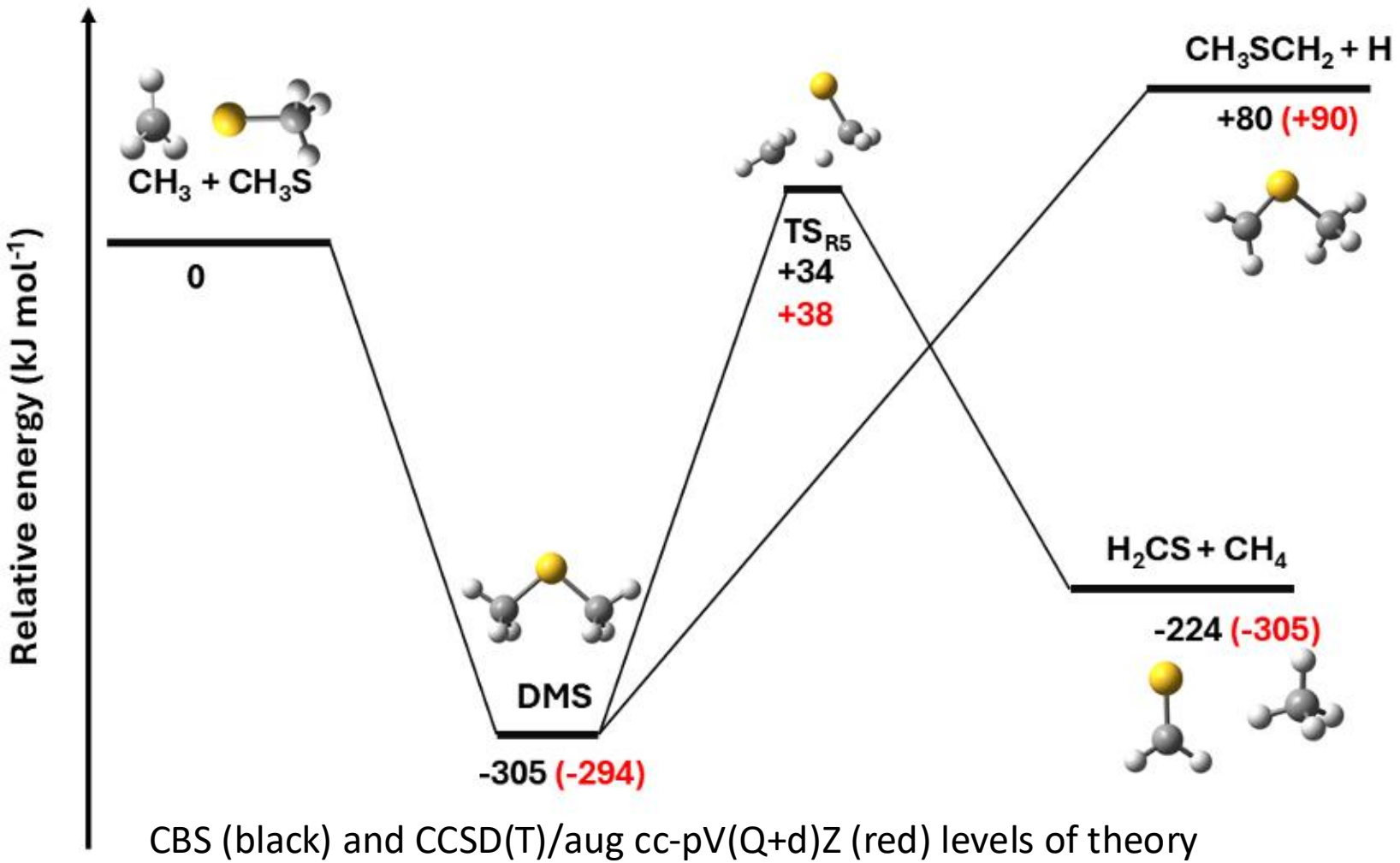
$$CH_4 + h\nu \rightarrow \cdot CH_3 + H\cdot \quad \text{(R2)}$$

$$\cdot CH_3 + HS\cdot \rightarrow CH_3SH \quad \text{(R3)}$$

$$CH_3SH + h\nu \rightarrow CH_3S\cdot + H\cdot \quad \text{(R4)}$$

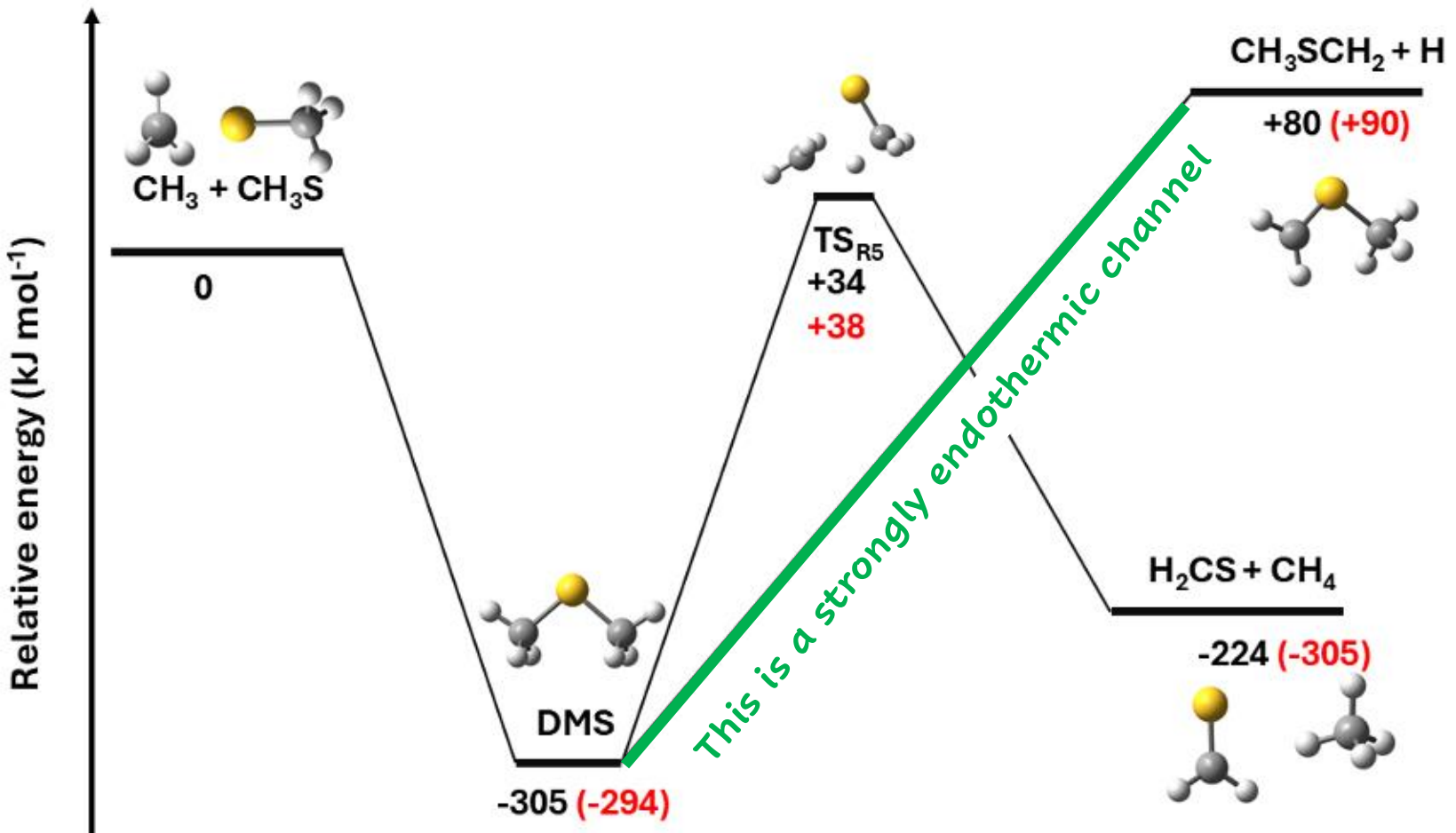
$$CH_3S\cdot + \cdot CH_3 \rightarrow CH_3SCH_3 \quad \text{(R5)}$$

The potential energy surface of the radiative association reaction $CH_3S + CH_3$



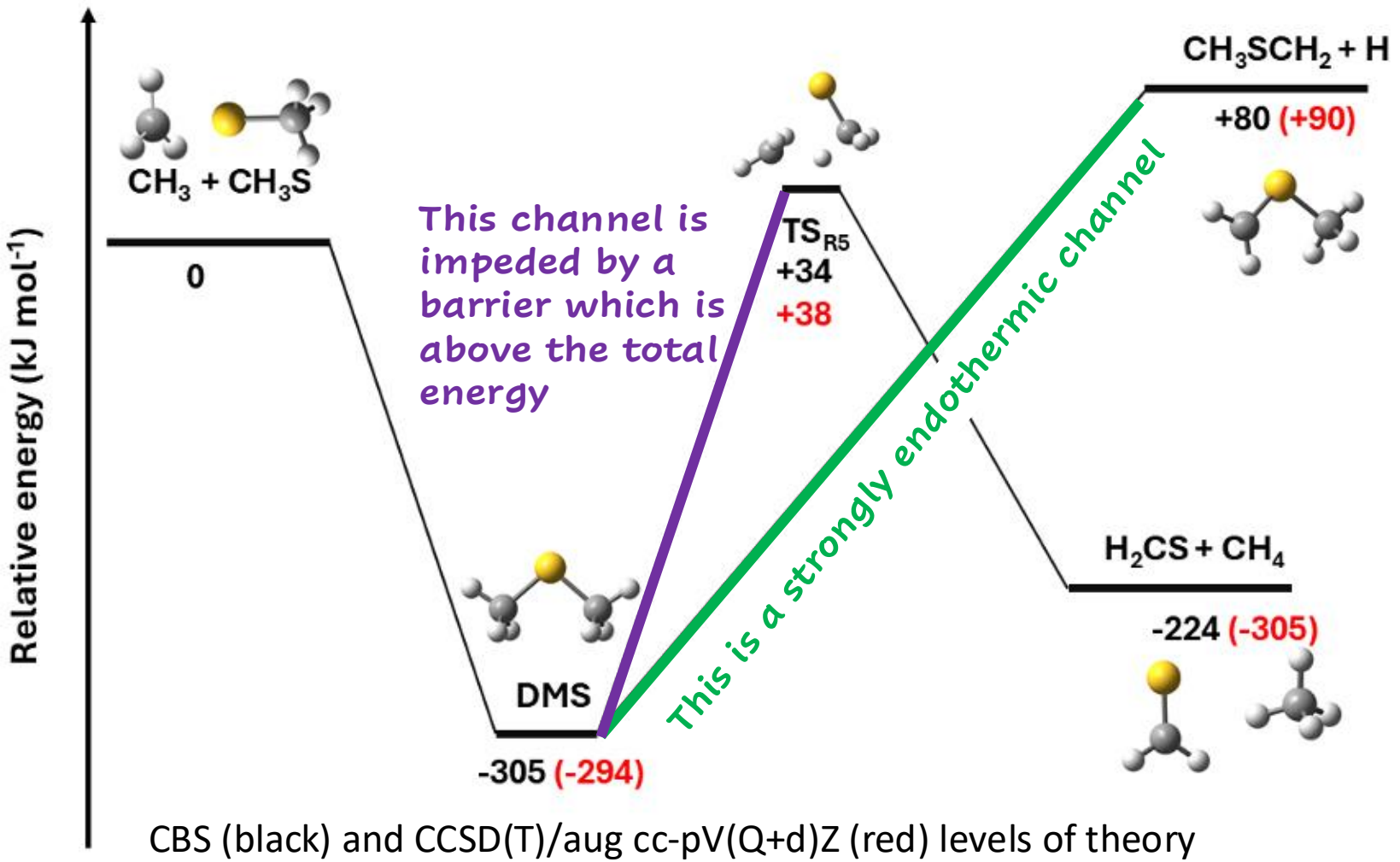
CBS (black) and CCSD(T)/aug cc-pV(Q+d)Z (red) levels of theory

The potential energy surface of the radiative association reaction $CH_3S + CH_3$



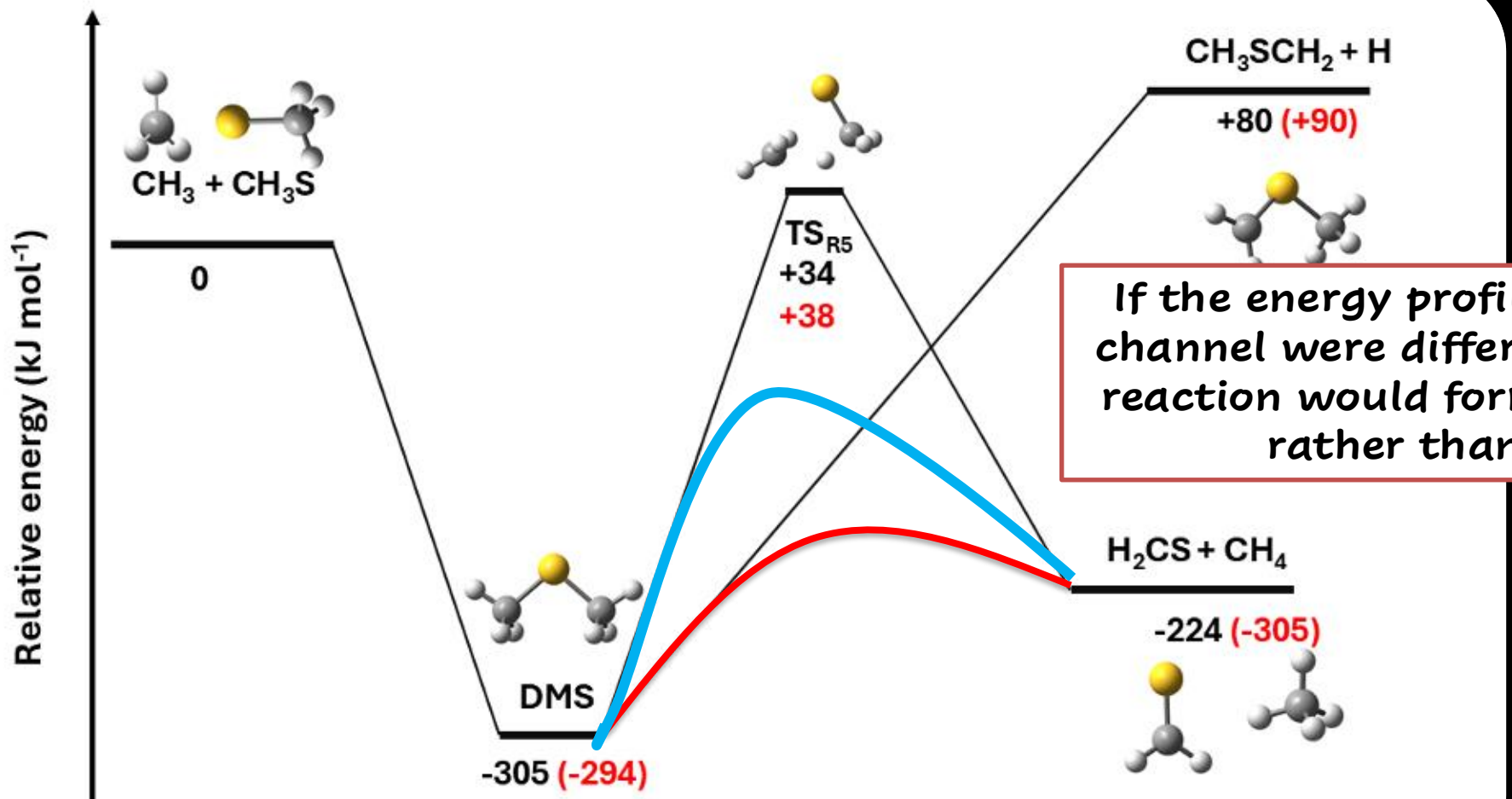
CBS (black) and CCSD(T)/aug cc-pV(Q+d)Z (red) levels of theory

The potential energy surface of the radiative association reaction $CH_3S + CH_3$



CBS (black) and CCSD(T)/aug cc-pV(Q+d)Z (red) levels of theory

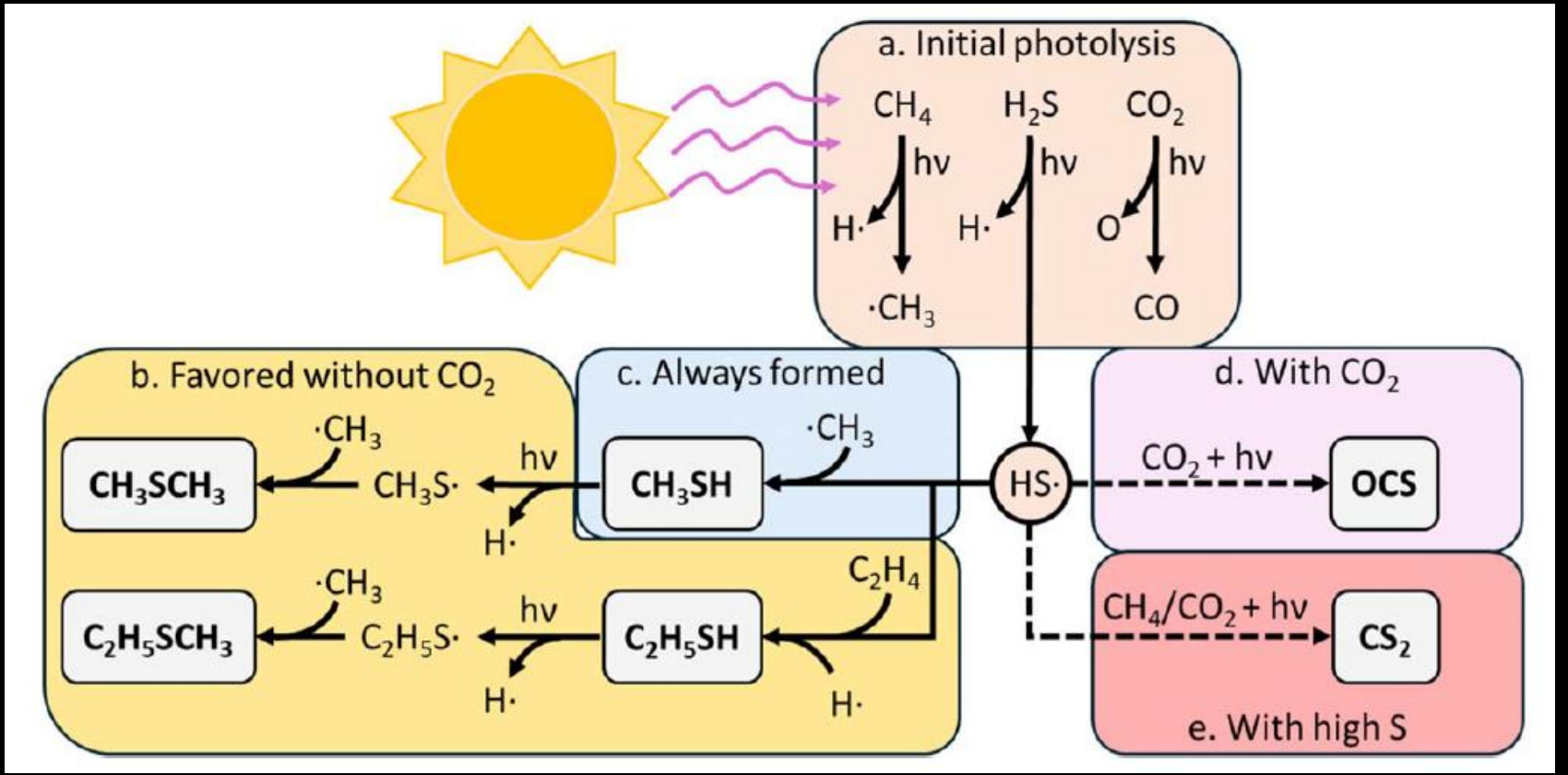
The potential energy surface of the radiative association reaction $CH_3S + CH_3$



CBS (black) and CCSD(T)/aug cc-pV(Q+d)Z (red) levels of theory

If the energy profile of the exit channel were different, then the reaction would form $H_2CS + CH_4$ rather than DMS

In high pressure conditions, three-body collisions or collisional stabilization will favor DMS formation – no radiative association needed

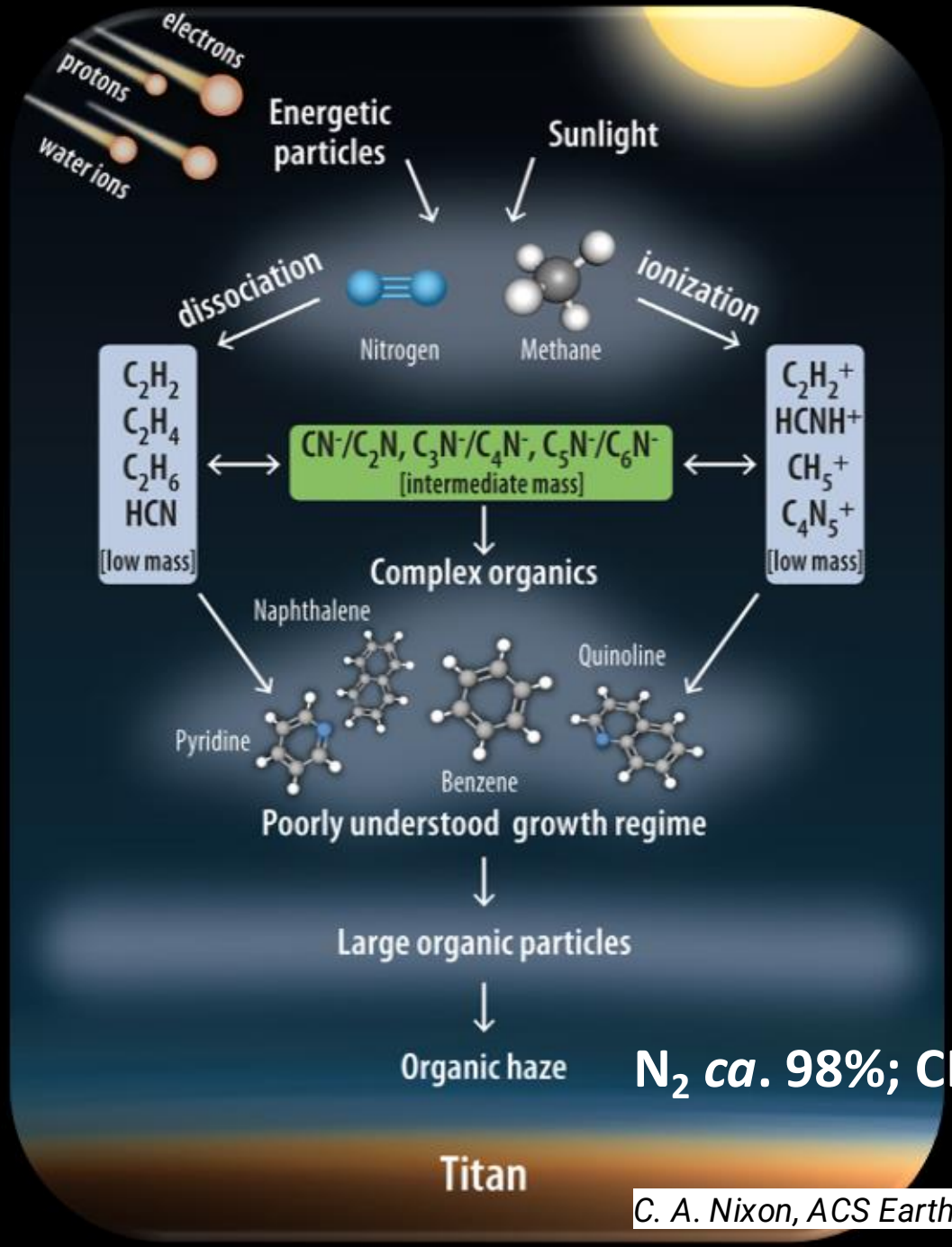


The energy profile for the CH_3 + CH_3S reaction nicely aligns with this speculation, confirming that DMS can be formed in the presence of methane and hydrogen sulfide in an exoplanetary atmosphere.

A couple of examples:

1) Dimethyl sulfide in the atmosphere of K2-18b

2) Pyridine in the atmosphere of Titan



EUV and energetic particles induce the formation of active forms of nitrogen ($N(^4S)$, $N(^2D)$, N_2^*, N^+, N_2^+)

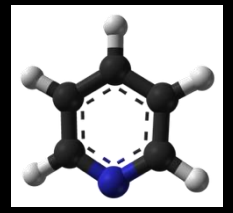
UV photons induce dissociation and ionization of methane

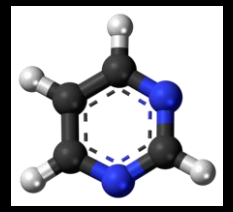
A very active chemistry begins, leading to organic macromolecules

The formation of complex organic molecules starts in the upper part of the atmosphere in the gas phase

N_2 *ca.* 98%; CH_4 *ca.* 2%

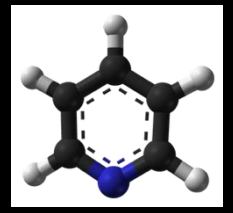
C. A. Nixon, ACS Earth Space Chem. 2024, 8, 3, 406−456

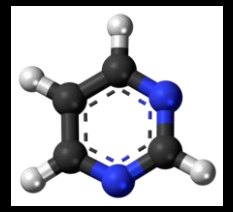




is it possible to synthesize pyridine and pyrimidine under the conditions of the upper atmosphere of Titan?

possible detection of pyridine (m/z=80) by the Ion Neutral Mass Spectometer onboard Cassini

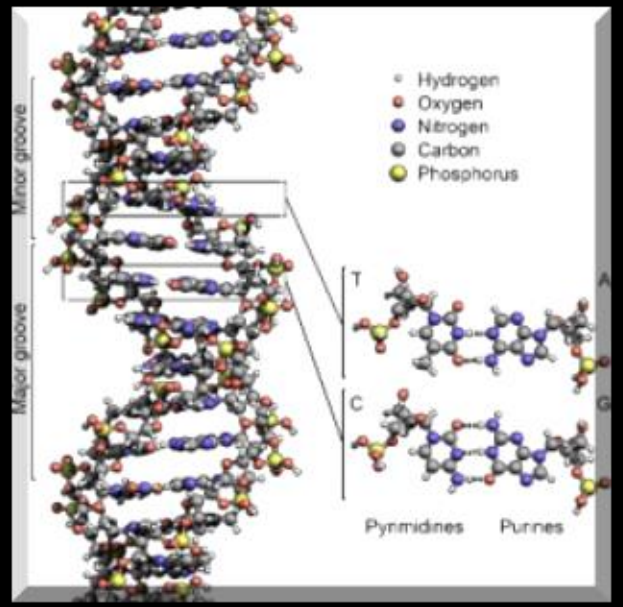


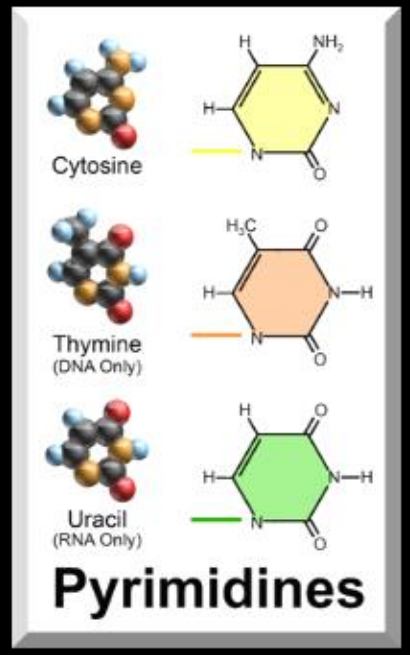


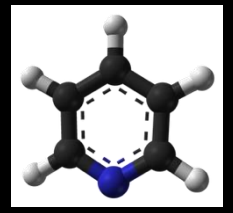
is it possible to synthesize pyridine and pyrimidine under the conditions of the upper atmosphere of Titan?

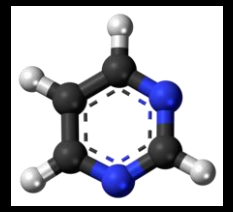
possible detection of pyridine (m/z=80) by the Ion Neutral Mass Spectometer onboard Cassini

Implications for prebiotic chemistry





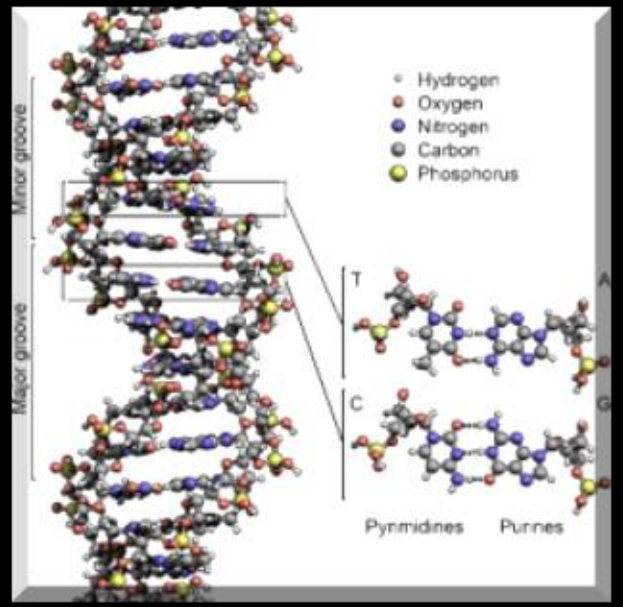


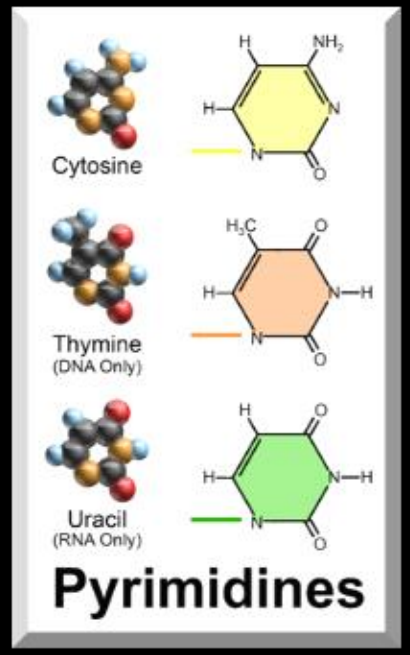


is it possible to synthesize pyridine and pyrimidine under the conditions of the upper atmosphere of Titan?

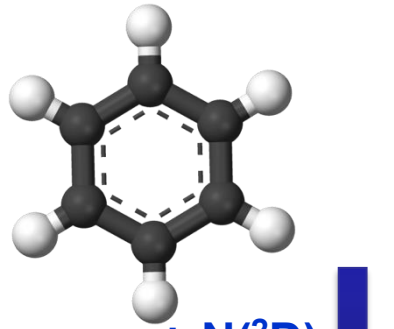
possible detection of pyridine (m/z=80) by the Ion Neutral Mass Spectometer onboard Cassini

Implications for prebiotic chemistry



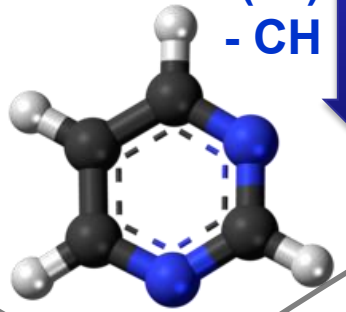


A suggested mechanism:

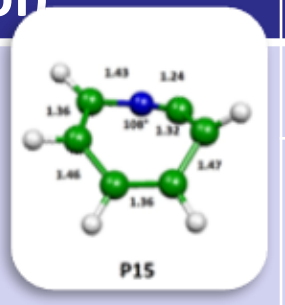


+ $N(^2D)$
- CH

+ $N(^2D)$
- CH

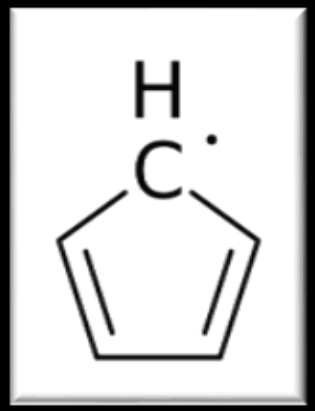


These reactions are feasible, but there are competing channels

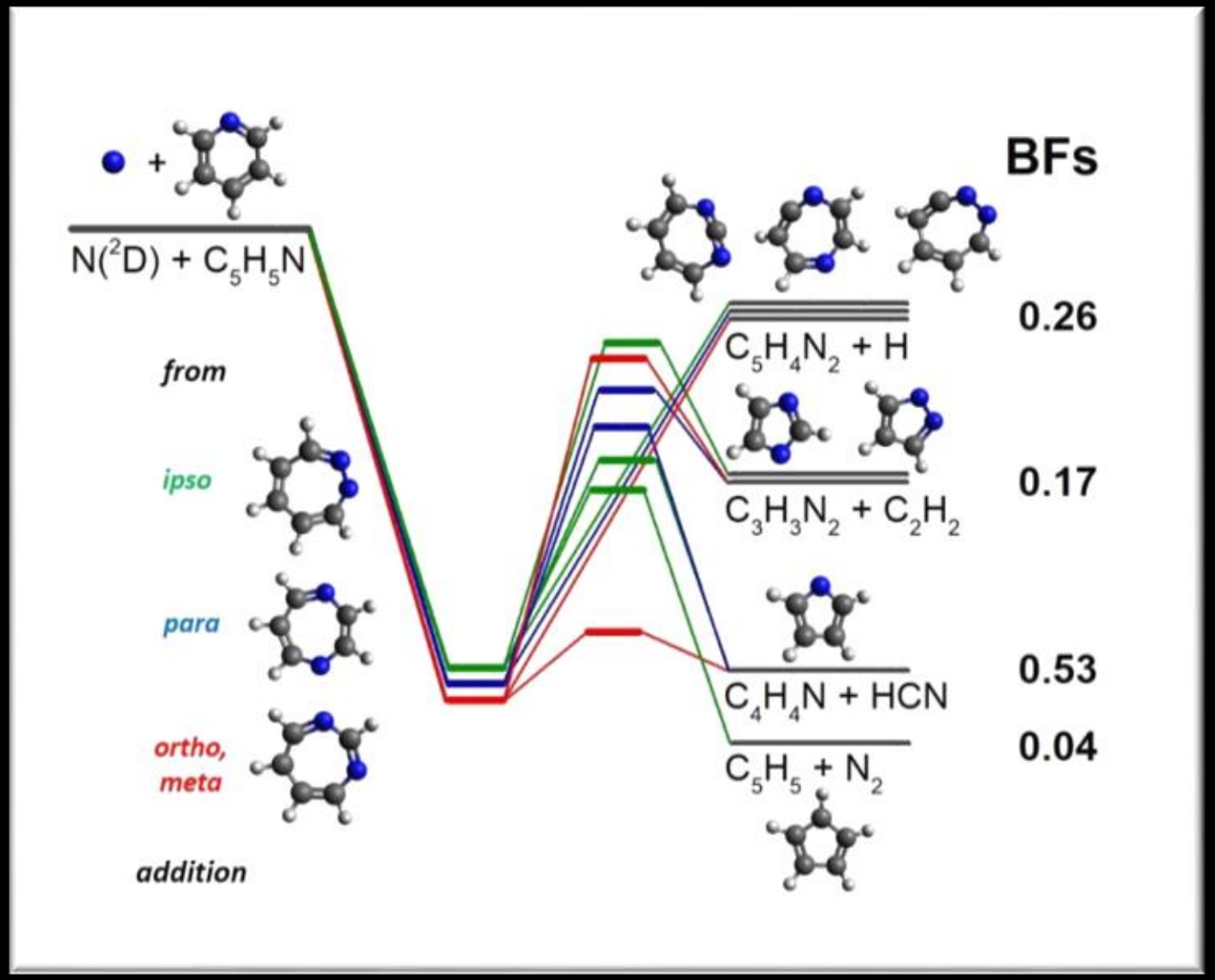
Primary products	Experimental branching fraction (E_c=31.8 kJ/mol)	RRKM branching fraction
$C_6H_5N + H$	0.05 ± 0.03 	7-atom ring: 0.12
		H-displacement with contraction of the ring: 0.02
$C_5H_5 + HCN$ or $C_4H_4N + C_2H_2$	0.95 ± 0.15	$C_5H_5 + HCN$: 0.79
		$C_4H_4N + C_2H_2$: 0.04

RRKM: Small dependence of BF on the available energy

the dominant channel is a ring-contraction reaction

$N(^2D)$ +  →  **+ HCN**

$N(^2D) + C_5H_5N$, the second step from pyridine to pyrimidine



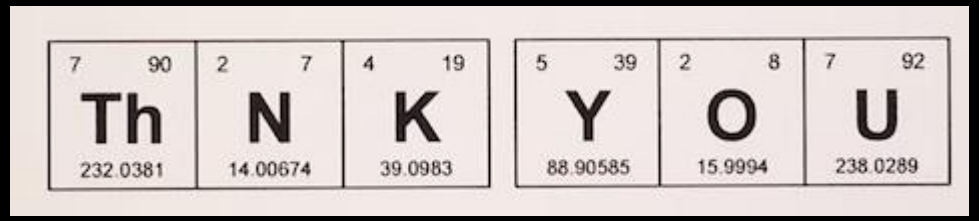
P. Recio et al., 2021
L. Mancini et al., 2024

It does not work either: also in this case, the dominant channel is a ring contraction reaction

Conclusion:

CHEMISTRY MATTERS

Don't oversimplify, don't approximate, don't neglect correct chemical patterns: if your chemistry is wrong, your physical insights will be wrong too.



for your attention