A Theoretical Study of the Carbon Monofluoride Radical in Comets

INSTITUTO DE ASTRONOMIA,
GEOFÍSICA E CIÊNCIAS
ATMOSFÉRICAS

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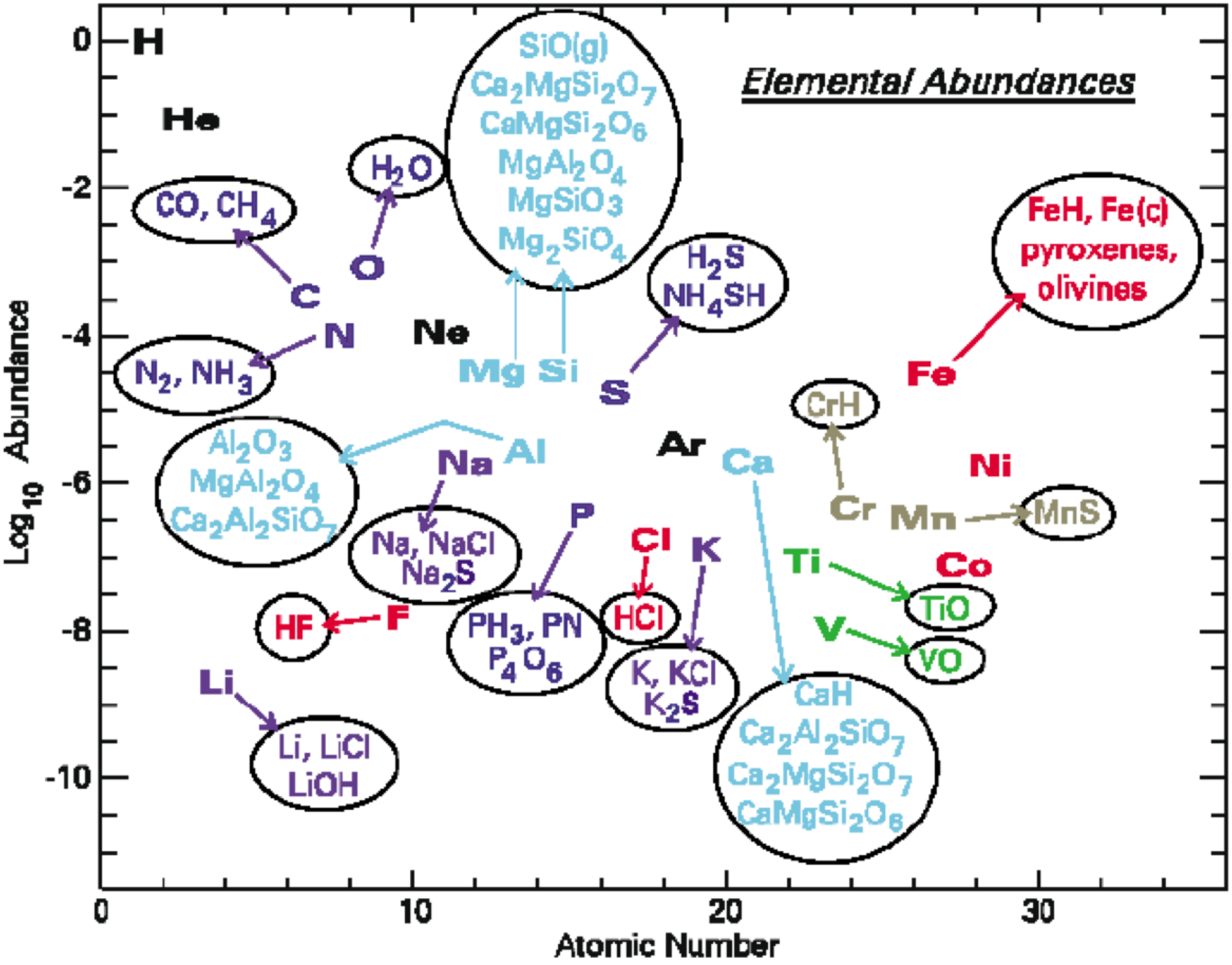
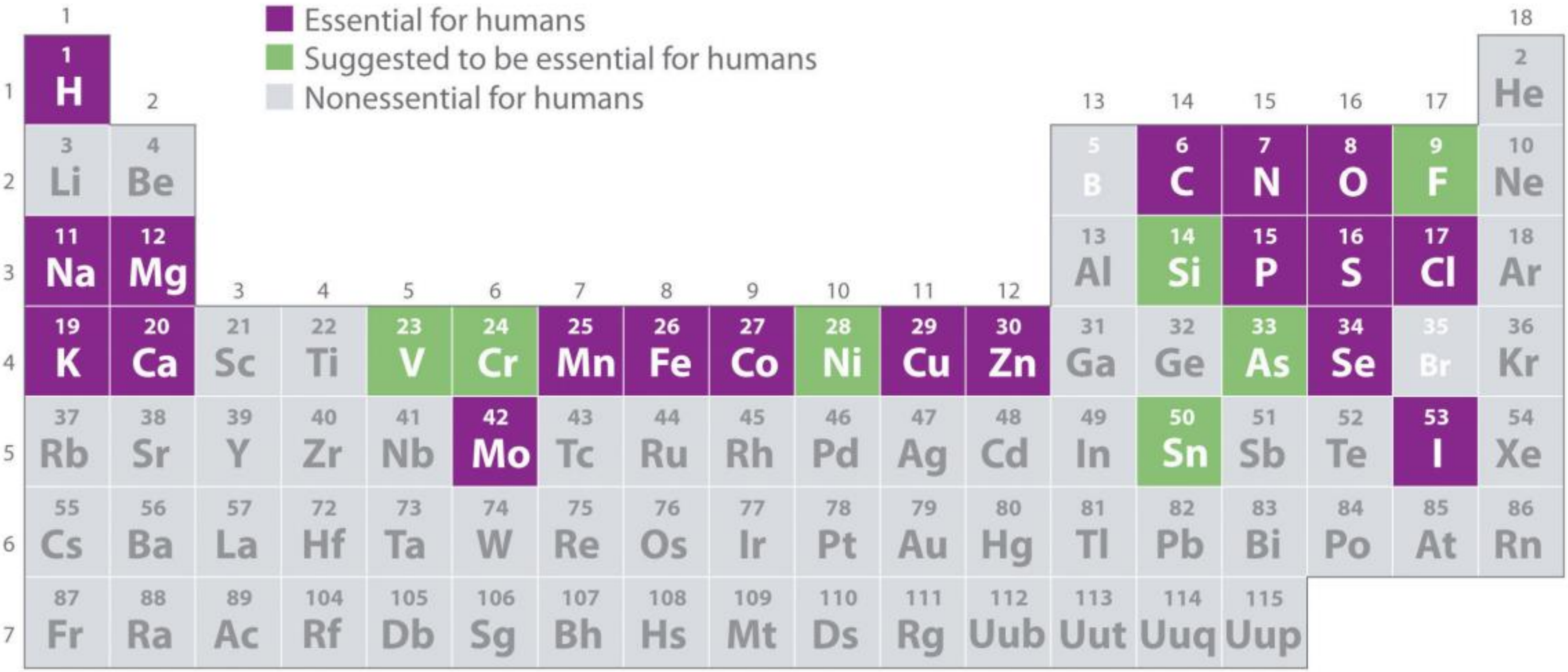
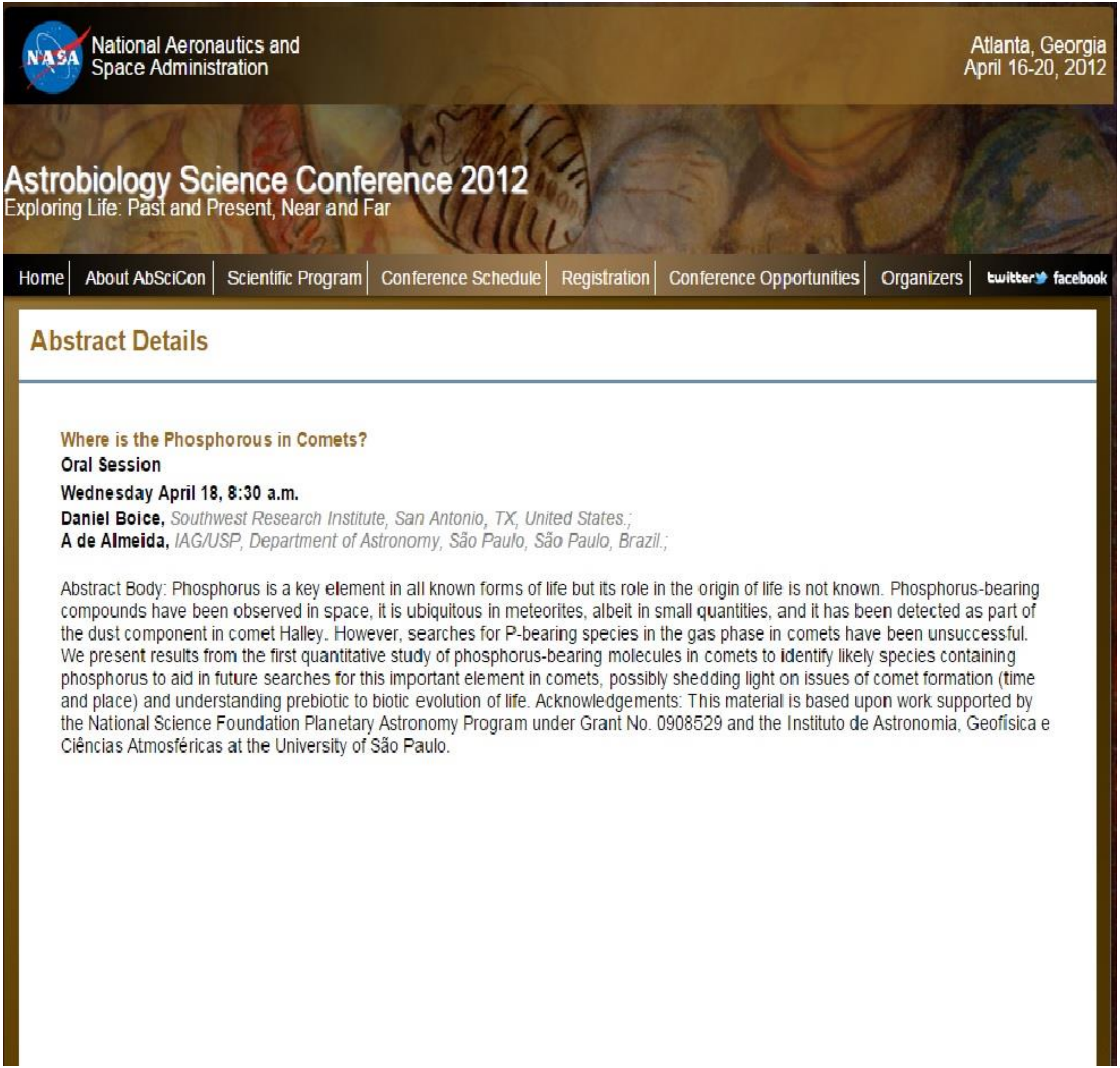

Elemental Abundances
Log$_{10}$ Abundance
Atomic Number
0
-2
-4
-6
-8
-10
0
10
20
30
H
He
Li
C
N
O
F
Ne
Na
Mg
Al
Si
P
S
Cl
Ar
K
Ca
Ti
V
Cr
Mn
Fe
Co
Ni
CO, CH_4
N_2, NH_3
H_2O
$SiO(g)$
$Ca_2MgSi_2O_7$
$CaMgSi_2O_6$
$MgAl_2O_4$
$MgSiO_3$
Mg_2SiO_4
H_2S
NH_4SH
Al_2O_3
$MgAl_2O_4$
$Ca_2Al_2SiO_7$
$Na, NaCl$
Na_2S
HF
PH_3, PN
P_4O_6
HCl
K, KCl
K_2S
$Li, LiCl$
$LiOH$
CaH
$Ca_2Al_2SiO_7$
$Ca_2MgSi_2O_7$
$CaMgSi_2O_6$
CrH
MnS
TiO
VO
$FeH, Fe(c)$
pyroxenes,
olivines



🟪 Essential for humans
🟩 Suggested to be essential for humans
⬜ Nonessential for humans

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	🟪 1 H																	⬜ 2 He
2	⬜ 3 Li	⬜ 4 Be											⬜ 5 B	🟪 6 C	🟪 7 N	🟪 8 O	🟩 9 F	⬜ 10 Ne
3	🟪 11 Na	🟪 12 Mg											⬜ 13 Al	🟩 14 Si	🟪 15 P	🟪 16 S	🟪 17 Cl	⬜ 18 Ar
4	🟪 19 K	🟪 20 Ca	⬜ 21 Sc	⬜ 22 Ti	🟩 23 V	🟩 24 Cr	🟪 25 Mn	🟪 26 Fe	🟪 27 Co	🟩 28 Ni	🟪 29 Cu	🟪 30 Zn	⬜ 31 Ga	⬜ 32 Ge	🟩 33 As	🟪 34 Se	⬜ 35 Br	⬜ 36 Kr
5	⬜ 37 Rb	⬜ 38 Sr	⬜ 39 Y	⬜ 40 Zr	⬜ 41 Nb	🟪 42 Mo	⬜ 43 Tc	⬜ 44 Ru	⬜ 45 Rh	⬜ 46 Pd	⬜ 47 Ag	⬜ 48 Cd	⬜ 49 In	🟩 50 Sn	⬜ 51 Sb	⬜ 52 Te	🟪 53 I	⬜ 54 Xe
6	⬜ 55 Cs	⬜ 56 Ba	⬜ 57 La	⬜ 72 Hf	⬜ 73 Ta	⬜ 74 W	⬜ 75 Re	⬜ 76 Os	⬜ 77 Ir	⬜ 78 Pt	⬜ 79 Au	⬜ 80 Hg	⬜ 81 Tl	⬜ 82 Pb	⬜ 83 Bi	⬜ 84 Po	⬜ 85 At	⬜ 86 Rn
7	⬜ 87 Fr	⬜ 88 Ra	⬜ 89 Ac	⬜ 104 Rf	⬜ 105 Db	⬜ 106 Sg	⬜ 107 Bh	⬜ 108 Hs	⬜ 109 Mt	⬜ 110 Ds	⬜ 111 Rg	⬜ 112 Uub	⬜ 113 Uut	⬜ 114 Uuq	⬜ 115 Uup			



Abstract Details

Where is the Phosphorous in Comets?

Oral Session

Wednesday April 18, 8:30 a.m.

Daniel Boice, *Southwest Research Institute, San Antonio, TX, United States.;*
A de Almeida, *IAG/USP, Department of Astronomy, São Paulo, São Paulo, Brazil.;*

Abstract Body: Phosphorus is a key element in all known forms of life but its role in the origin of life is not known. Phosphorus-bearing compounds have been observed in space, it is ubiquitous in meteorites, albeit in small quantities, and it has been detected as part of the dust component in comet Halley. However, searches for P-bearing species in the gas phase in comets have been unsuccessful. We present results from the first quantitative study of phosphorus-bearing molecules in comets to identify likely species containing phosphorus to aid in future searches for this important element in comets, possibly shedding light on issues of comet formation (time and place) and understanding prebiotic to biotic evolution of life. Acknowledgements: This material is based upon work supported by the National Science Foundation Planetary Astronomy Program under Grant No. 0908529 and the Instituto de Astronomia, Geofísica e Ciências Atmosféricas at the University of São Paulo.

PROSPECTS FOR PHOSPHORUS-BEARING MOLECULES IN COMETARY COMAE.

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Introduction: Phosphorus is a key element in all known forms of life and phosphorus-bearing compounds have been observed in space (e.g., [1-4]). Phosphorus is ubiquitous in meteorites, albeit in small quantities, with phosphates being found in stony meteorites and phosphides have been identified in iron meteorites. Phosphorus has been detected as part of the dust component in comet Halley [5] but searches for P-bearing species in the gas phase in comets have been unsuccessful [6]. Based of its moderate cosmic abundance (eighteenth most abundant element, [P]/[N] = 4×10^{-3}) and the positive identification of P-bearing species in the interstellar medium (such as, PN, PC, HCP and PO), we would expect simple molecules, diatomics (like PH, PO, PC, PS), triatomics (like HCP and PH_2), and possibly other polyatomics (like phosphine PH_3 and diphosphine P_2H_4), to exist in cometary ices, and hence be released into the gas phase upon ice sublimation. We present results from the first quantitative study of phosphorus-bearing molecules in comets [7] to identify likely species containing phosphorus to aid in future searches for this important element in comets, possibly shedding light on issues of comet formation (time and place) and matters of the prebiotic to biotic evolution of life.

Phosphorus and the Origins of Life: Although phosphorus is relatively rare, it is essential for life! Phosphorus is a key ingredient of metabolic molecules (ATP), cell structure (phospholipids), and replication (backbone of DNA and RNA). The phosphate paradox in the evolution of life can be summarized as extreme stability (~10^8 yrs) versus rapid manipulability (~10^{-3} sec). Since P is present in biomolecules – replication, metabolism, & cell structure, and actively scavenged from the environment by life, then perhaps P was also important in the origins of life on Earth. How is P constrained in this matter? Were there extraterrestrial sources? These are unanswered questions in our quest to understand the origins of life.

Coma Chemistry Modeling: SUISEI, our fluid dynamics model with chemistry of cometary comae [8-12], has been adapted to study this problem. SUISEI produces cometocentric abundances of the coma gas

We have used a generic volatile composition for the comet nucleus initial conditions, based primarily on the Comet Halley mixing ratios with respect to water [11]. For example, nitrogen is 10 times more depleted with respect to the solar abundance in comets so this has been considered in the coma chemistry in our study. This initial model used phosphine (PH_3) as the phosphorus-bearing parent molecule with a mixing ratio based on the cosmic abundance of phosphorus.

Phosphine Chemistry: Over 100 and gas-phase reactions appropriate for coma chemistry have been collected from databases of NIST, UMIST, and JPL, including photodissociation and photoionization of selected P-bearing molecules [13]. More than 30 P-bearing species were added to the chemical network but many electron impact processes are unknown. The chemistry of phosphine in the inner coma is illustrated in the figure. The major destruction channels are photodissociation and protonation with water-group ions. This leads recycling of PH_3 in the inner coma.

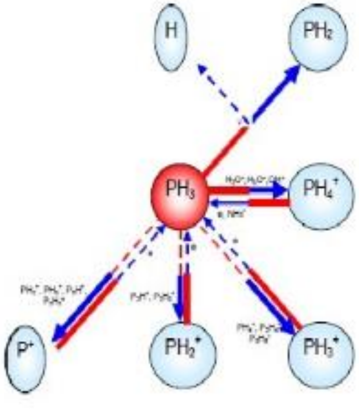

Figure. Relevant coma chemistry for PH_3 in the inner coma. The arrow thickness indicates the importance of

bearing species for optical observations and to investigate their chemical pathways in the reaction network as shown in the figure. Initial abundances are found to be on the order of 10^{-4} relative to water, about the same as isotopic species. The scale length of PH_3 in the coma is about 13,000-16,000km. Protonation reactions of PH_3 with water-group ions are important due to the high proton affinity of phosphine. Other P-bearing species likely to be found in the coma include: PH_2, PC, PN, and HCP. Electron impact reactions may also be important but little laboratory data is available. Collaborations with observers to use modern telescopic facilities (e.g., Keck 2 NIRSPEC and Subaru IRCS) are underway to search for the first phosphorus detection in cometary comae.

References: [1] Ziurys L.M. (1987) *Astrophys. J., 321*, L81-L85. [2] MacKay D.D.S. and Charnley S.B. (2001) *MNRAS, 325*, 545-549. [3] Margulès L. et al. (2002) *J. Molec. Spectr., 211*, 211-220. [4] Tenenbaum E.D. et al. (2007) *Astrophys. J., 666*, L29-L32. [5] Kissel J. and Krueger F.R. (1987) *Nature, 326*, 755-760. [6] Crovisier, J. (2004) in Astrobiology: Future Perspectives, Ehrenfreund P. et al., (eds.), Kluwer Acad. Publ., Dortdrecht, pp. 179. [7] Boice D.C. and de Almeida A.A. (2010) *38th COSPAR Scientific Assembly*, Bremen, F31-0007-10. [8] Wegmann R. et al. (1987) *Astron. Astrophys., 187*, 339-350. [9] Schmidt H.U et al. (1988) *Comp. Phys. Comm., 49*, 17-59. [10] Boice D.C. et al. (1990) *GRL, 17*, 1813-1816. [11] Huebner W.F. et al. (1991) in Comets in the Post-Halley Era, Newburn R., Jr., Neugebauer M., Rahe, J. (eds.), Springer, Berlin, pp. 907-936. [12] Boice D.C. and Wegmann R. (2007) *Adv. Space Res., 39*, 407-412. [13] Huebner W.F. et al. (1992) Solar Photo Rates for Planetary Atmospheres and Atmospheric Pollutants, Kluwer Acad. Publ., Dortdrecht, pp. 1-294.

Acknowledgements: This material is based upon work supported by the National Science Foundation Planetary Astronomy Program under Grant No. 0908529 and the Instituto de Astronomia, Geofísica e Ciências Atmosféricas at the University of São Paulo.

The Inventory of Phosphorus in Cometary Volatiles

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Phosphorus is a key element in living organisms but its role in the origins of life is not well understood. Phosphorus-bearing compounds have been observed in space, are ubiquitous in the upper atmospheres of the gas giant planets and meteorites in small quantities, and have been detected as part of the dust component in comet Halley. However, searches for P-bearing species in the gas phase in cometary comae have been unsuccessful. We present results of the first quantitative study of P-bearing molecules in comets to identify likely species containing phosphorus. We have found reaction pathways of gas-phase and photolytic chemistry for simple P-bearing molecules likely to be found in comets and important for prebiotic chemistry (see Figure for PN chemistry). We hope these results will aid future searches for this important element, possibly shedding light on issues of comet formation (time and place) and understanding prebiotic to biotic evolution of life.

Acknowledgements. We greatly appreciate support from the National Science Foundation Planetary Astronomy Program under Grant No. 0908529 and the Instituto de Astronomia, Geofísica e Ciências Atmosféricas at the University of São Paulo.

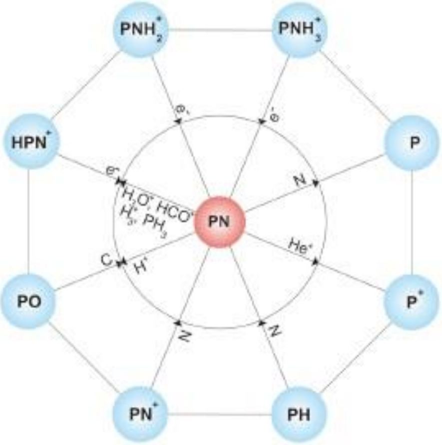

Figure. Relevant chemistry of PN in cometary comae.

INTERNATIONAL SYMPOSIUM AND WORKSHOP ON ASTROCHEMISTRY

Understanding extraterrestrial molecular complexity
through experiments and observations

Understanding phosphorous chemistry in cometary comae

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Key Words: *phosphorous chemistry; comets; reactive gas dynamics; prebiotic chemistry; origins of life.*

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The radiative association of P and O atoms

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ABSTRACT

The formation of PO from the radiative association of phosphorus and oxygen atoms has been estimated by accurate quantum chemistry calculations. The radiative association of P and O atoms along the $B^2\Sigma^+$ potential energy curve is the most efficient way of producing PO in the $X^2\Pi$ ground state. For temperatures ranging between 300 and 14 000 K, the rate coefficients are found to vary from 1.61×10^{-24} to 1.99×10^{-18} cm^{3}s^{-1}, respectively. These values indicate that only a very small amount of PO molecules can be formed by radiative association in dense and hot gas close to the photosphere of evolved oxygen-rich stars and other hostile environments.

Key words: atomic data – atomic processes – molecular data – circumstellar matter – ISM: molecules.

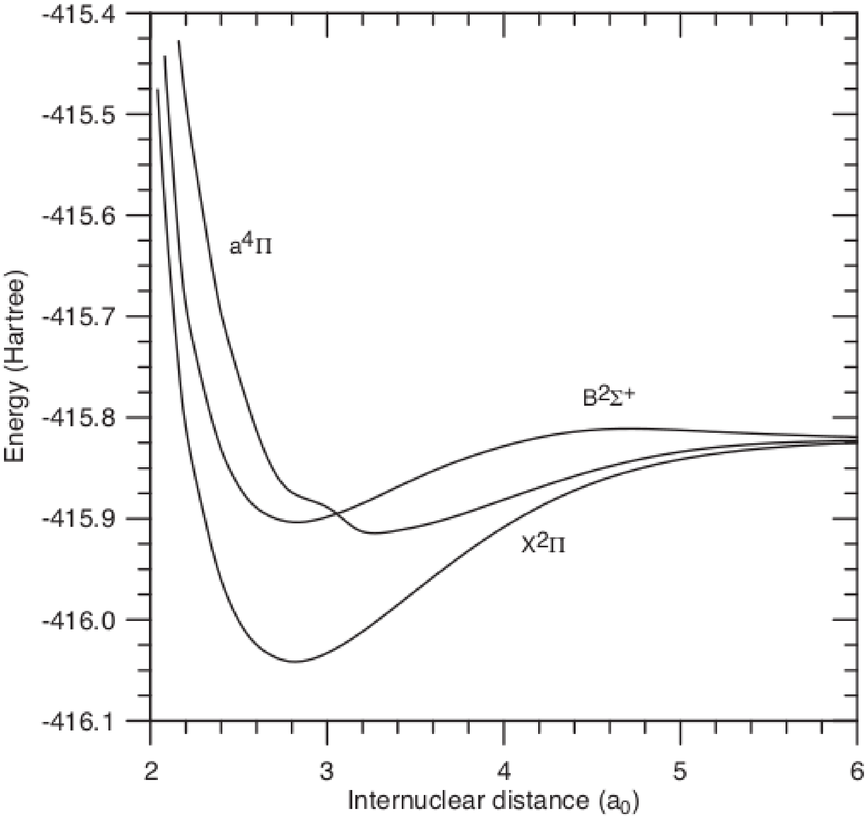


Figure 1. Potential energy curves for the doublet states of PO.

Table 1. Molecular constants for the electronic states of PO.

		$X^2\Pi$	$a^4\Pi$	$B^2\Sigma^+$
R_e (Å)	This work	1.489	1.731	1.494
	Exp.[a, b]	1.476	(1.750)[f]	1.463
	MRCI+Q[c]	1.489	1.732	1.478
	MRCI+Q[d]	1.474	1.714	1.455
	MRCI[e]	1.482	1.713	1.463
ω_e (cm^{-1})	This work	1243	1156	1042
	Exp.[a, b]	1233		1164
	MRCI+Q[c]	1218	753	1129
	MRCI+Q[d]	1234	766	1186
	MRCI[e]	1215	771	1174
T_e (eV)	This work		3.43	3.75
	Exp.[a, b]		(3.00)	3.81
	MRCI+Q[c]		3.41	3.84
	MRCI+Q[d]		3.52	3.78
	MRCI[e]		3.43	3.85

Notes. [a] Huber & Herzberg (1979). [b]Grein & Kapur (1983). [c]Spielfiedel & Handy (1999) (MRCI+Q: MRCI methods plus the Dadidson correction (+Q)). [d]Liu et al. (2013). [e]Izzaouihda et al. (2014). [f]The results in brackets are not accurate.

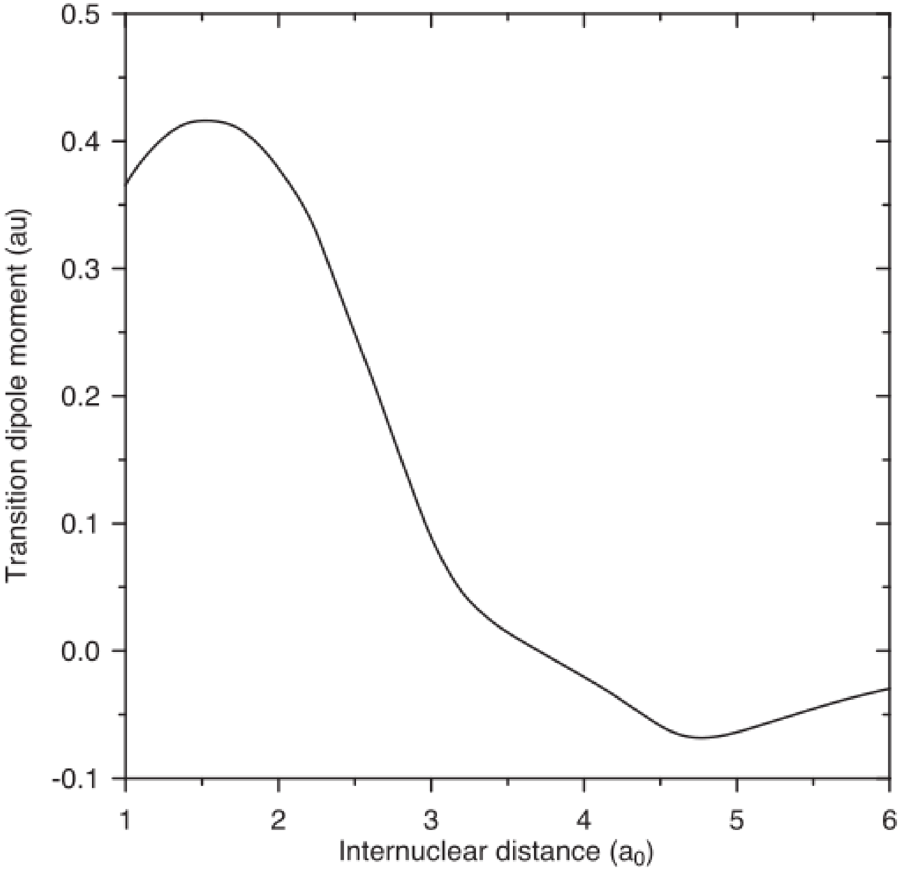


Figure 2. Electronic transition moment function between the doublet states of PO.

Table 2. Radiative association rate coefficients of PO.

T (K)	k ($\mathrm{cm^3\,s^{-1}}$)
300	1.61×10^{-24}
700	5.06×10^{-21}
1000	2.79×10^{-20}
1500	1.10×10^{-19}
2000	2.27×10^{-19}
2500	3.58×10^{-19}
3000	4.90×10^{-19}
3500	6.19×10^{-19}
4000	7.41×10^{-19}
4500	8.56×10^{-19}
5000	9.62×10^{-18}
6000	1.15×10^{-18}
7000	1.31×10^{-18}
8000	1.45×10^{-18}
10 000	1.68×10^{-18}
12 000	1.85×10^{-18}
14 000	1.99×10^{-18}

values of R_e, ω_e and T_e are also in good agreement with those cal-

Carbon, hydrogen, oxygen, and nitrogen make up the bulk of living matter, because they form

MOLECULES

"CHNOPS"

P is a major atom in DNA, RNA

S is found in two amino acids that are found in all proteins

Carbon
Hydrogen
Nitrogen
Oxygen

Phosphorus
Sulfur

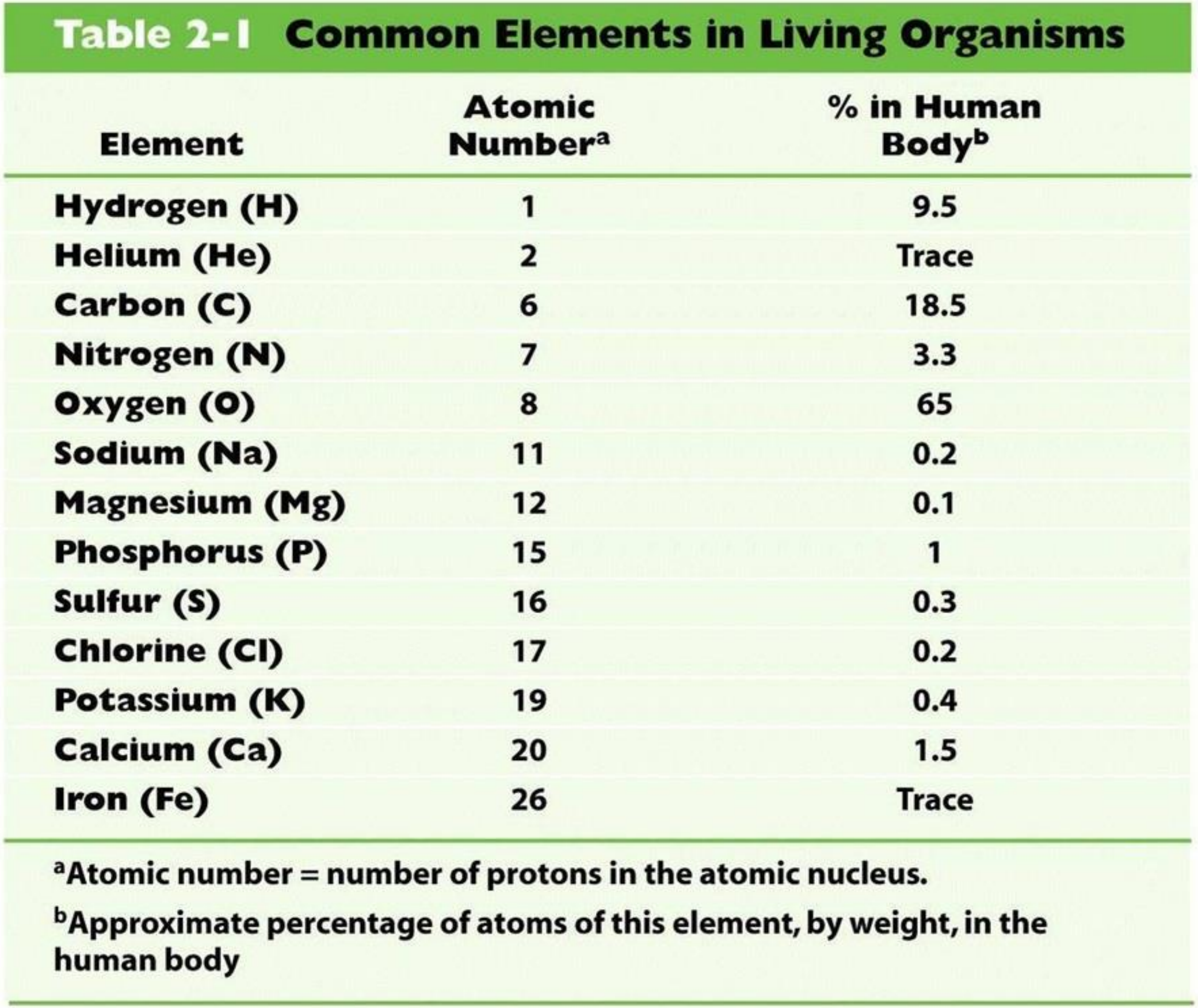


Table 2-1 Common Elements in Living Organisms

Element	Atomic Number[a]	% in Human Body[b]
Hydrogen (H)	1	9.5
Helium (He)	2	Trace
Carbon (C)	6	18.5
Nitrogen (N)	7	3.3
Oxygen (O)	8	65
Sodium (Na)	11	0.2
Magnesium (Mg)	12	0.1
Phosphorus (P)	15	1
Sulfur (S)	16	0.3
Chlorine (Cl)	17	0.2
Potassium (K)	19	0.4
Calcium (Ca)	20	1.5
Iron (Fe)	26	Trace

[a] Atomic number = number of protons in the atomic nucleus.

[b] Approximate percentage of atoms of this element, by weight, in the human body

Table 2-1 Biology: Life on Earth, 8/e

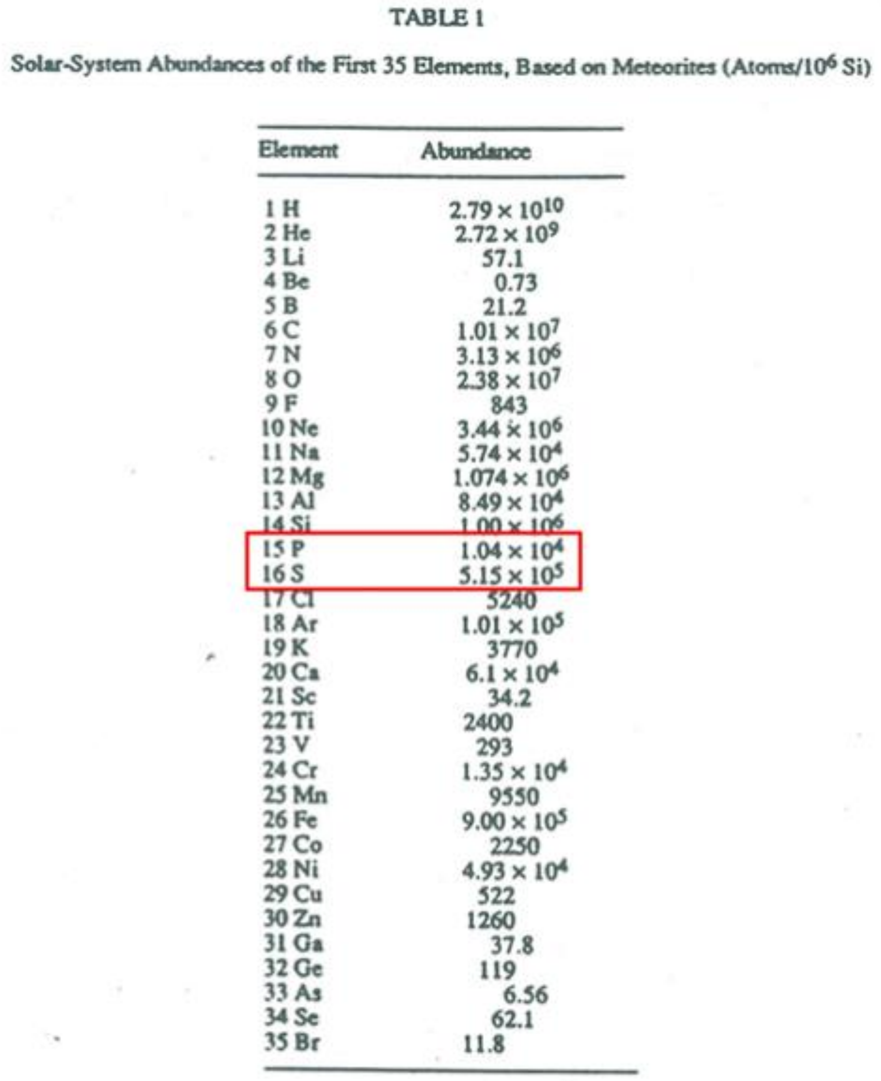
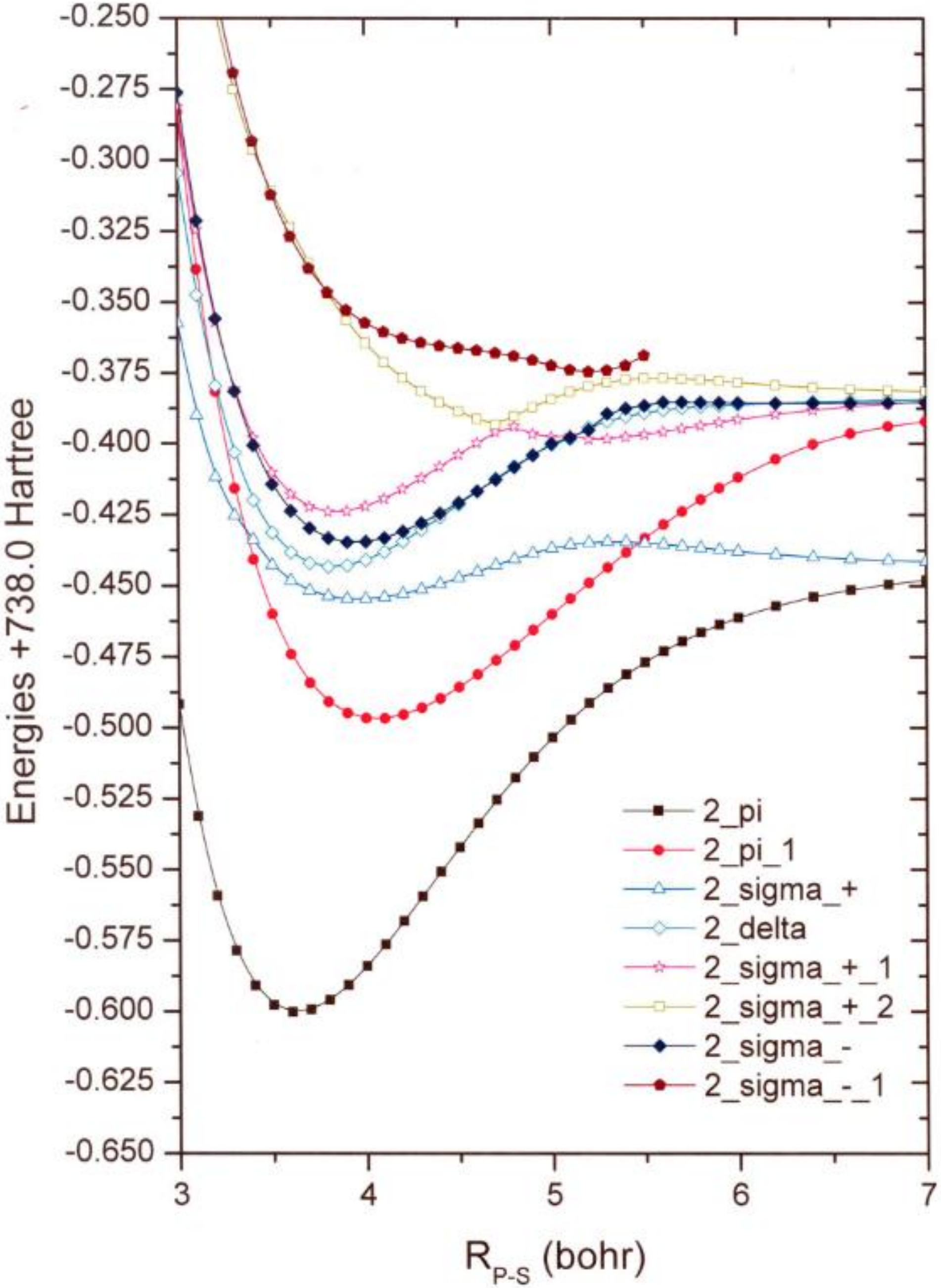


TABLE 1

Solar-System Abundances of the First 35 Elements, Based on Meteorites (Atoms/10^6 Si)

Element	Abundance
1 H	2.79×10^{10}
2 He	2.72×10^{9}
3 Li	57.1
4 Be	0.73
5 B	21.2
6 C	1.01×10^{7}
7 N	3.13×10^{6}
8 O	2.38×10^{7}
9 F	843
10 Ne	3.44×10^{6}
11 Na	5.74×10^{4}
12 Mg	1.074×10^{6}
13 Al	8.49×10^{4}
14 Si	1.00×10^{6}
15 P	1.04×10^{4}
16 S	5.15×10^{5}
17 Cl	5240
18 Ar	1.01×10^{5}
19 K	3770
20 Ca	6.1×10^{4}
21 Sc	34.2
22 Ti	2400
23 V	293
24 Cr	1.35×10^{4}
25 Mn	9550
26 Fe	9.00×10^{5}
27 Co	2250
28 Ni	4.93×10^{4}
29 Cu	522
30 Zn	1260
31 Ga	37.8
32 Ge	119
33 As	6.56
34 Se	62.1
35 Br	11.8



Energies +738.0 Hartree
-0.250
-0.275
-0.300
-0.325
-0.350
-0.375
-0.400
-0.425
-0.450
-0.475
-0.500
-0.525
-0.550
-0.575
-0.600
-0.625
-0.650
3
4
5
6
7
R_P-S (bohr)
2_pi
2_pi_1
2_sigma_+
2_delta
2_sigma_+_1
2_sigma_+_2
2_sigma_-
2_sigma_-_1

Formation of PS through radiative association

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ABSTRACT

The thermal rate coefficient for the radiative association of phosphorus and sulfur atoms to form phosphorus monosulfide (PS) is estimated. This rate constant is obtained using accurate ab initio molecular data calculated at the MRCI level of theory, with a CASSCF zero-order wavefunction. The contribution of the $1^2\Sigma^+$ state to spontaneous radiative association of the P(^{4}S) and S(^{3}P) atoms is more significant for forming PS. The computed radiative association rate constant is represented over the 300-450 K temperature range by the expression $k(T) = 2.07 \times 10^{-22}(T/300)^{6.21}\exp(-371/\mathrm{T})$ cm^{3}s^{-1} and over the 450-14000 K temperature range by $k(T) = 3.68 \times 10^{-18}(T/300)^{0.337}\exp(-3603/\mathrm{T})$ cm^{3}s^{-1}, where T is in K.

Key words: atomic data - atomic process - circumstellar matter - ISM: molecules.

Table 1. Molecular constants for the $X^2\Pi$ and $1^2\Sigma^+$ states of PS (r_e is expressed in Å, all other constants in cm^{-1})

	T_e	w_e	$w_e x_e$	B_e	α_e	r_e	Ref.
$X^2\Pi$		708				1.918	This work
		732	2.98	0.2936	0.00150	1.879	CASSCF/MRCI[a]
		735.6	3.60	0.2836		1.944	MRD-CI[b]
		739.13	2.79	0.2975	0.00158	1.897	Exp[c]
		739		0.2965		1.900	Exp[d]
		739.50	2.97	0.2974	0.00156	1.898	Exp[e]
$1^2\Sigma^+$	33777.15	373				2.164	This work
	33634.09	344.4	4.24	0.2372	0.00170	2.090	CASSCF/MRCI[a]
	32343.58	277.3	2.0	0.1949		2.345	MRD-CI[b]

Notes. [a] *Yaghlane, Francisco & Hochlaf (2012).* [b] *Karna, Bruna & Grein (1988).* [c] *Kawaguchi (1988).* [d] *Balasubramanian, Dixit & Narasimham (1979).* [e] *Jenouvrier & Pascat (1978).*

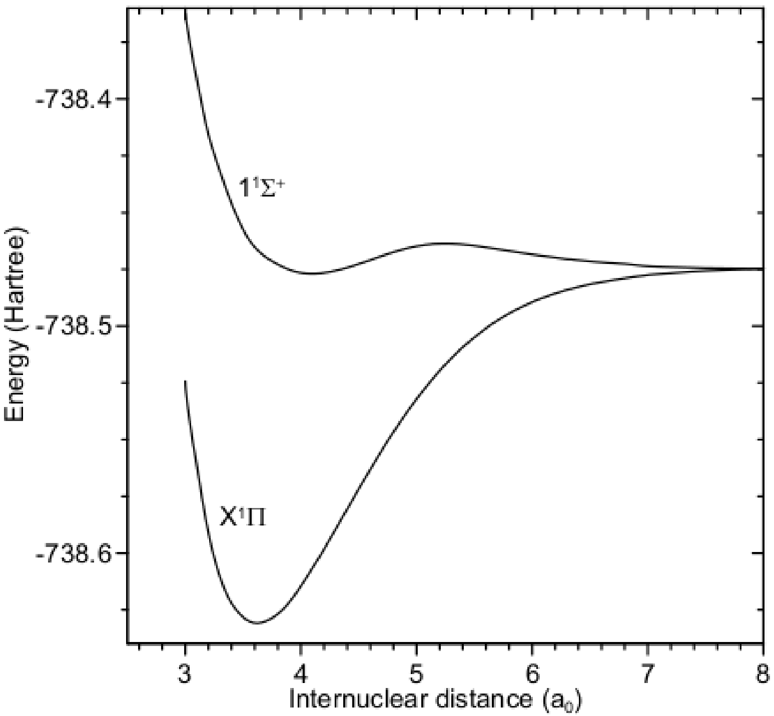


Figure 1. Calculated potential curves for the $1^2\Sigma^+$ and $X^2\Pi$ states of the PS radical

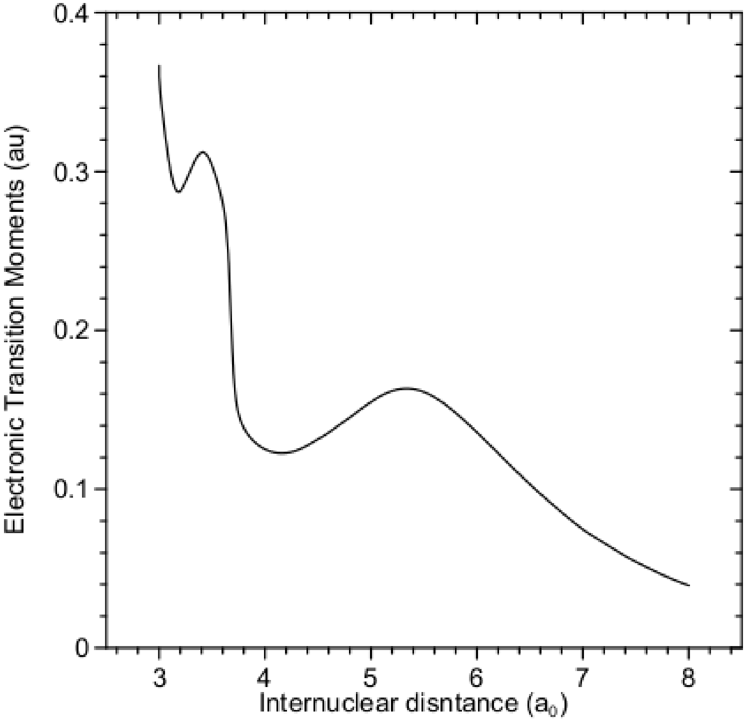


Figure 2. Ab initio transition moment function for the $1^2\Sigma^+$-$X^2\Pi$ band system of PS

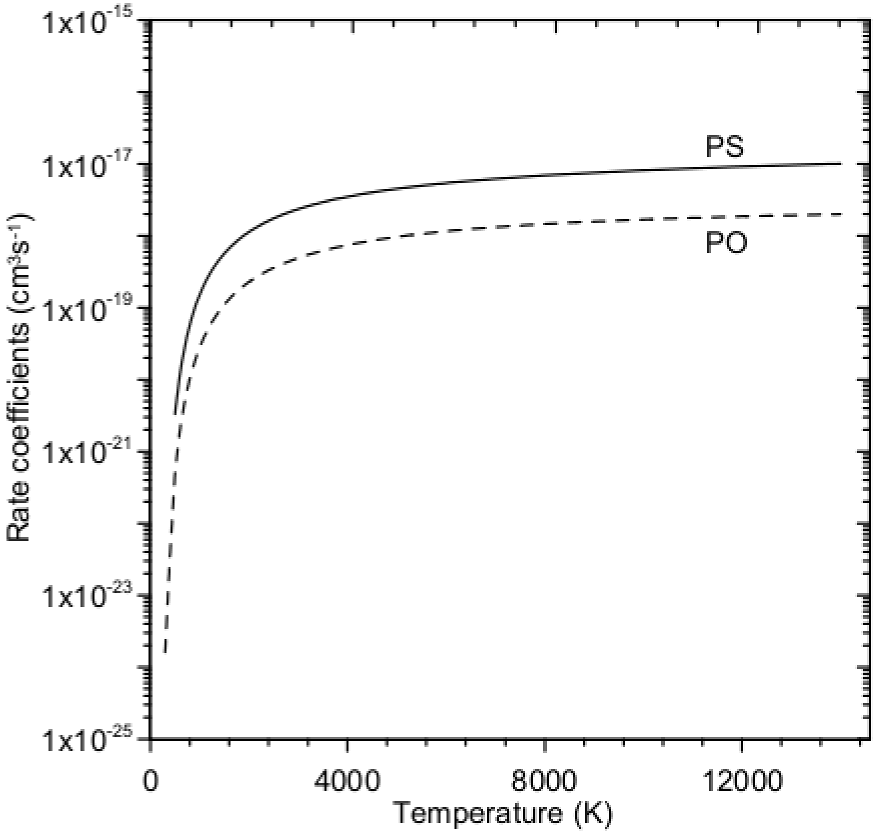
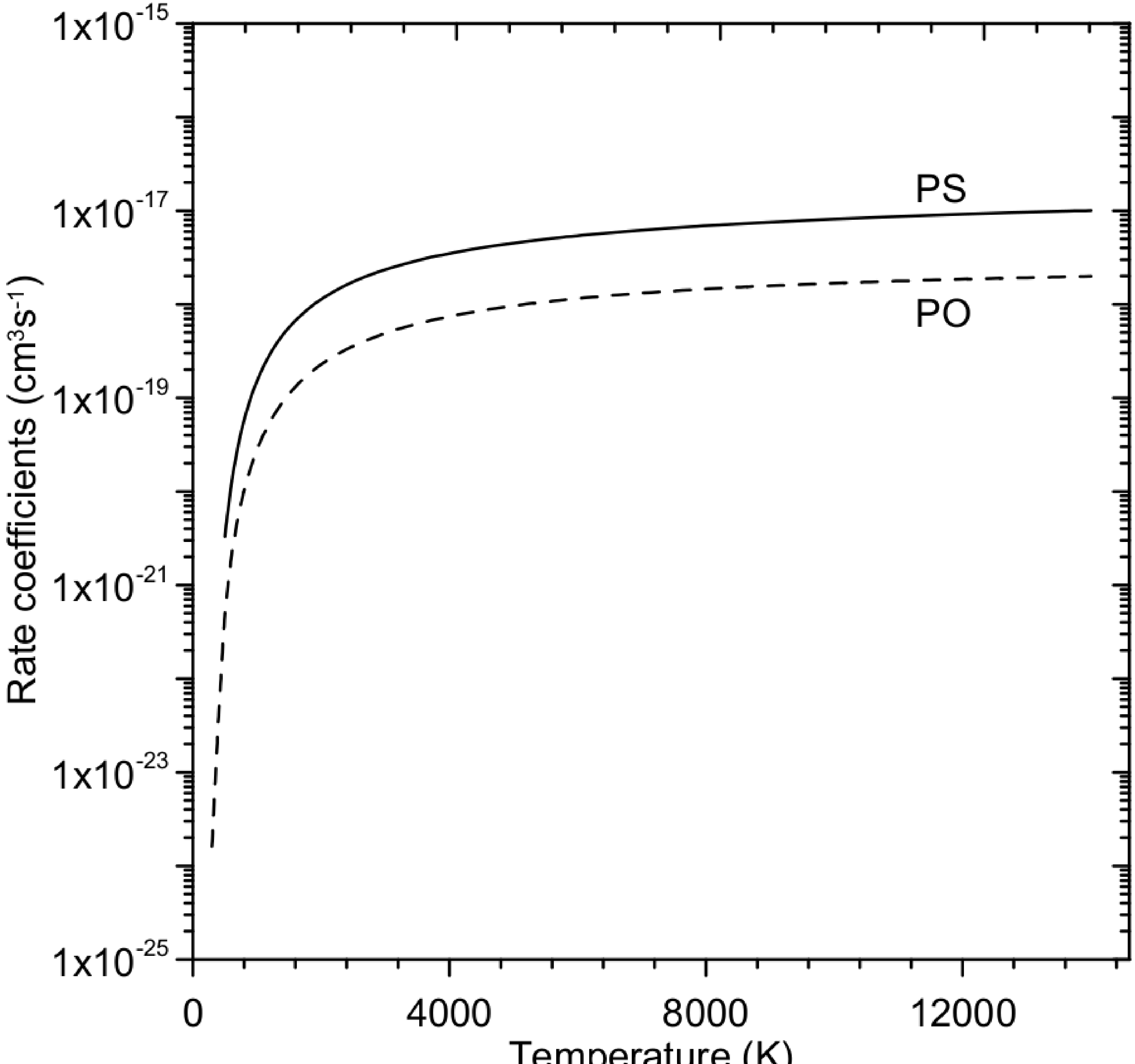
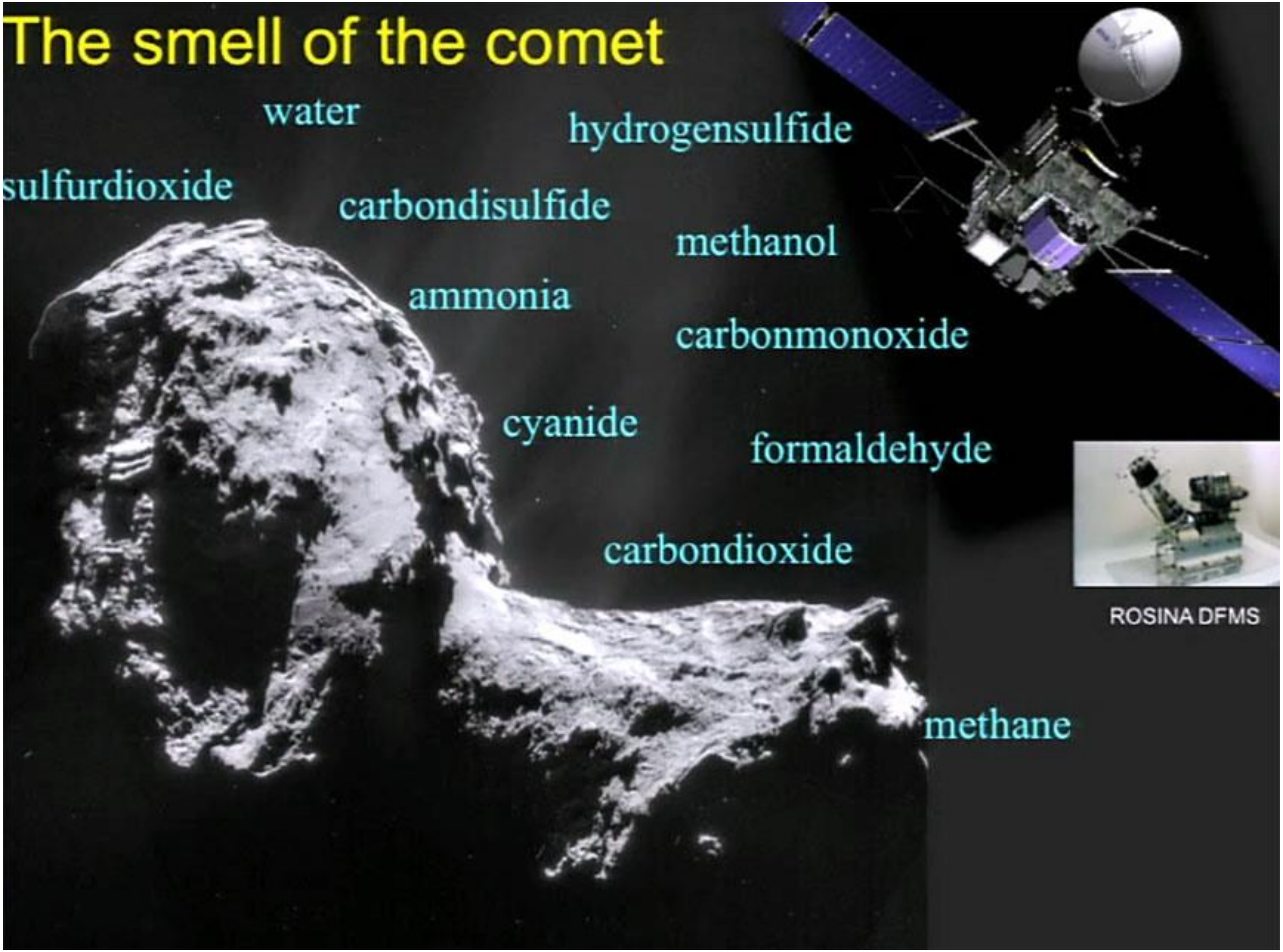


Figure 3. P^{4}S)+O(^{3}P) and P(^{4}S)+O(^{3}P) radiative association rate constants


1x10^-15
1x10^-17
1x10^-19
1x10^-21
1x10^-23
1x10^-25
Rate coefficients (cm³s⁻¹)
0
4000
8000
12000
Temperature (K)
PS
PO

The smell of the comet



water

hydrogensulfide

sulfurdioxide

carbondisulfide

methanol

ammonia

carbonmonoxide

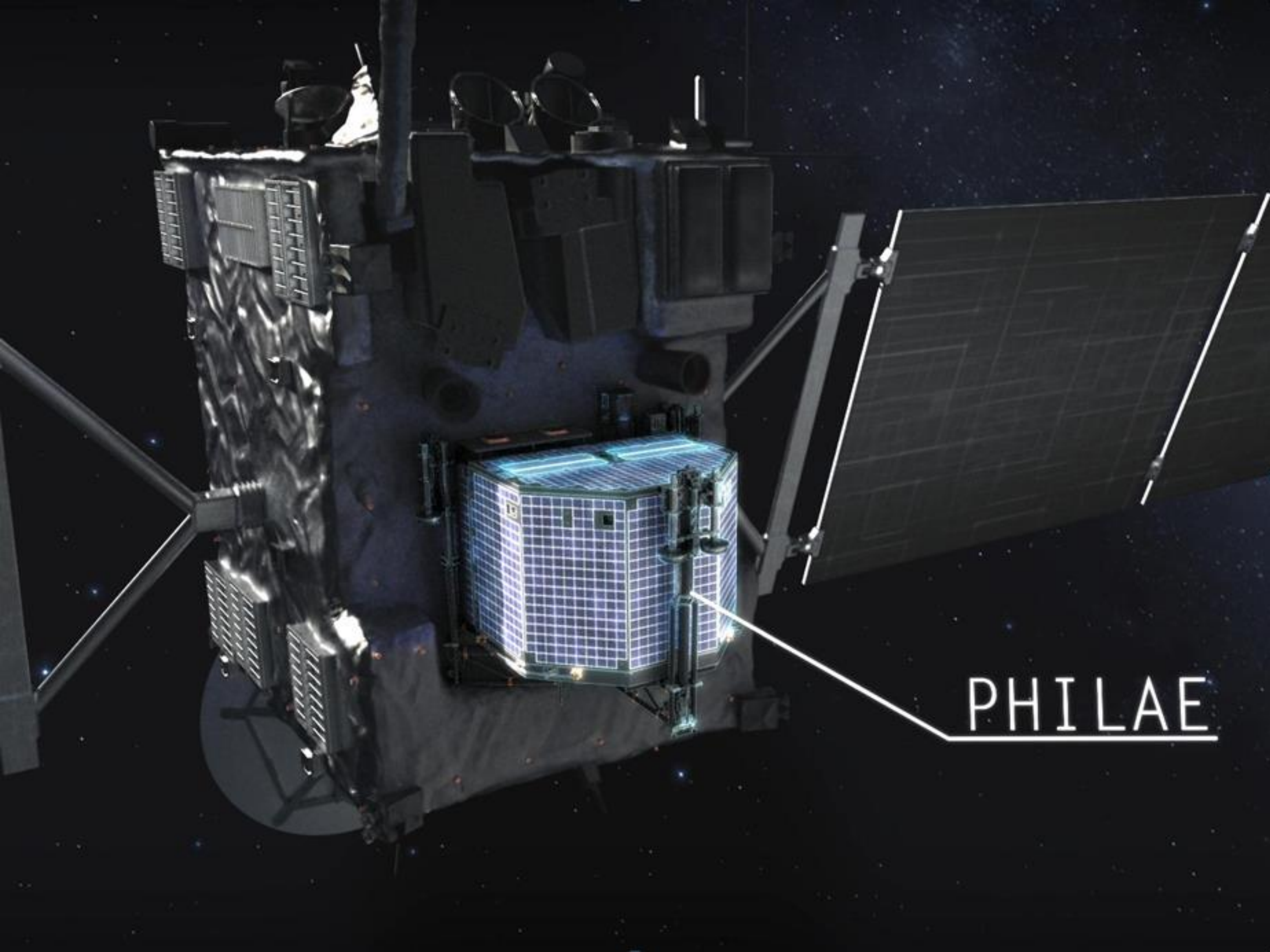
cyanide

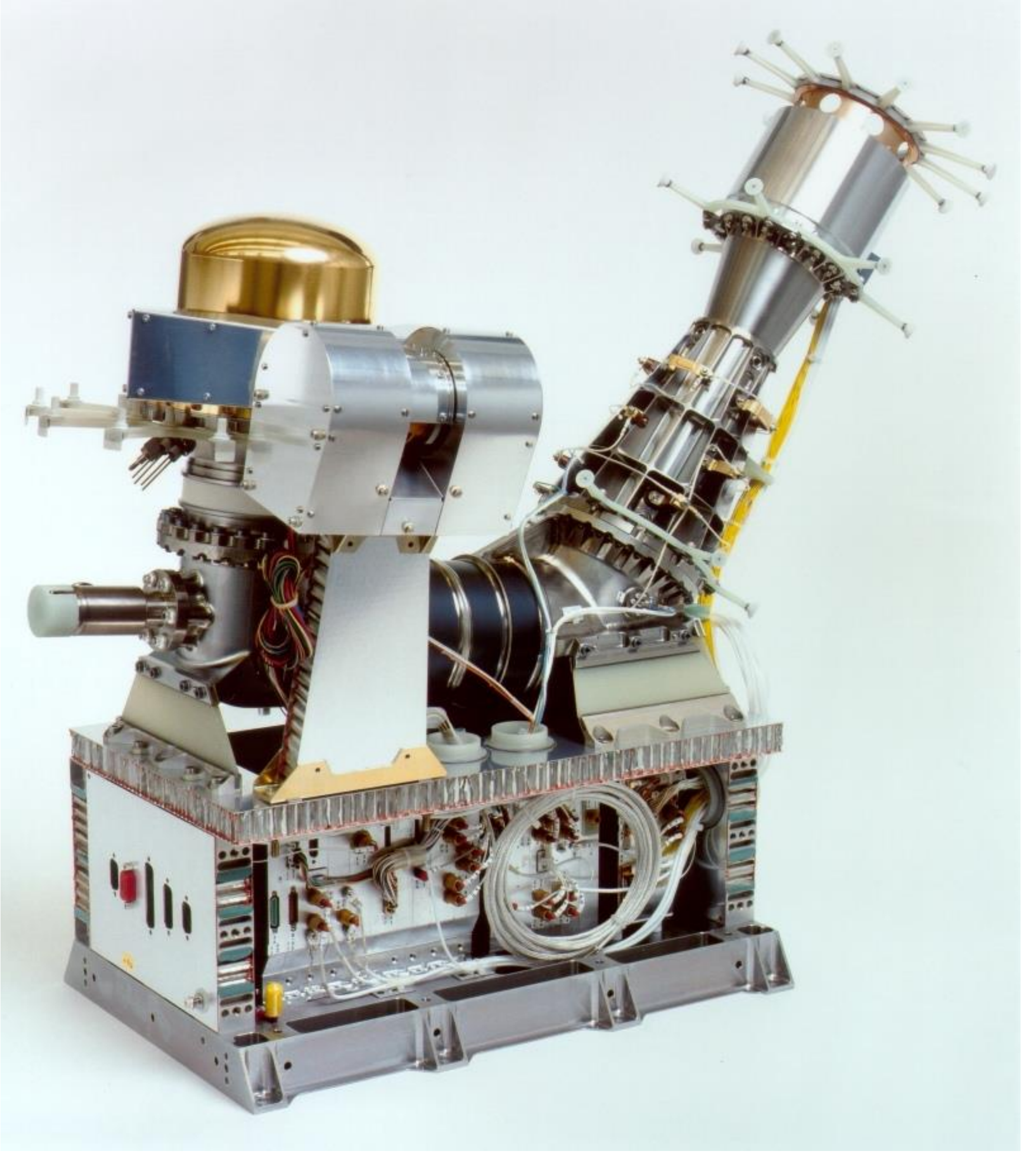
formaldehyde

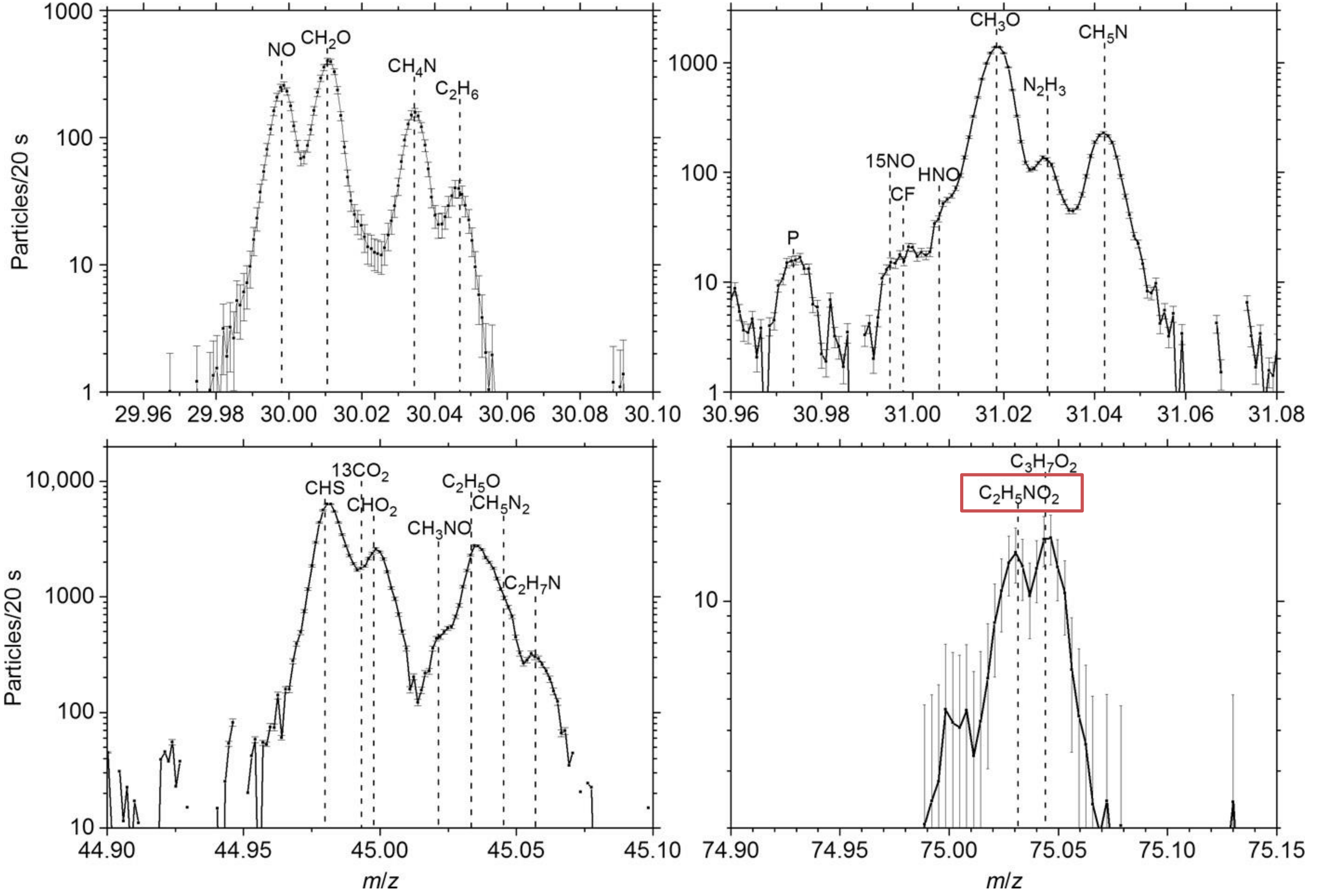
carbondioxide

methane

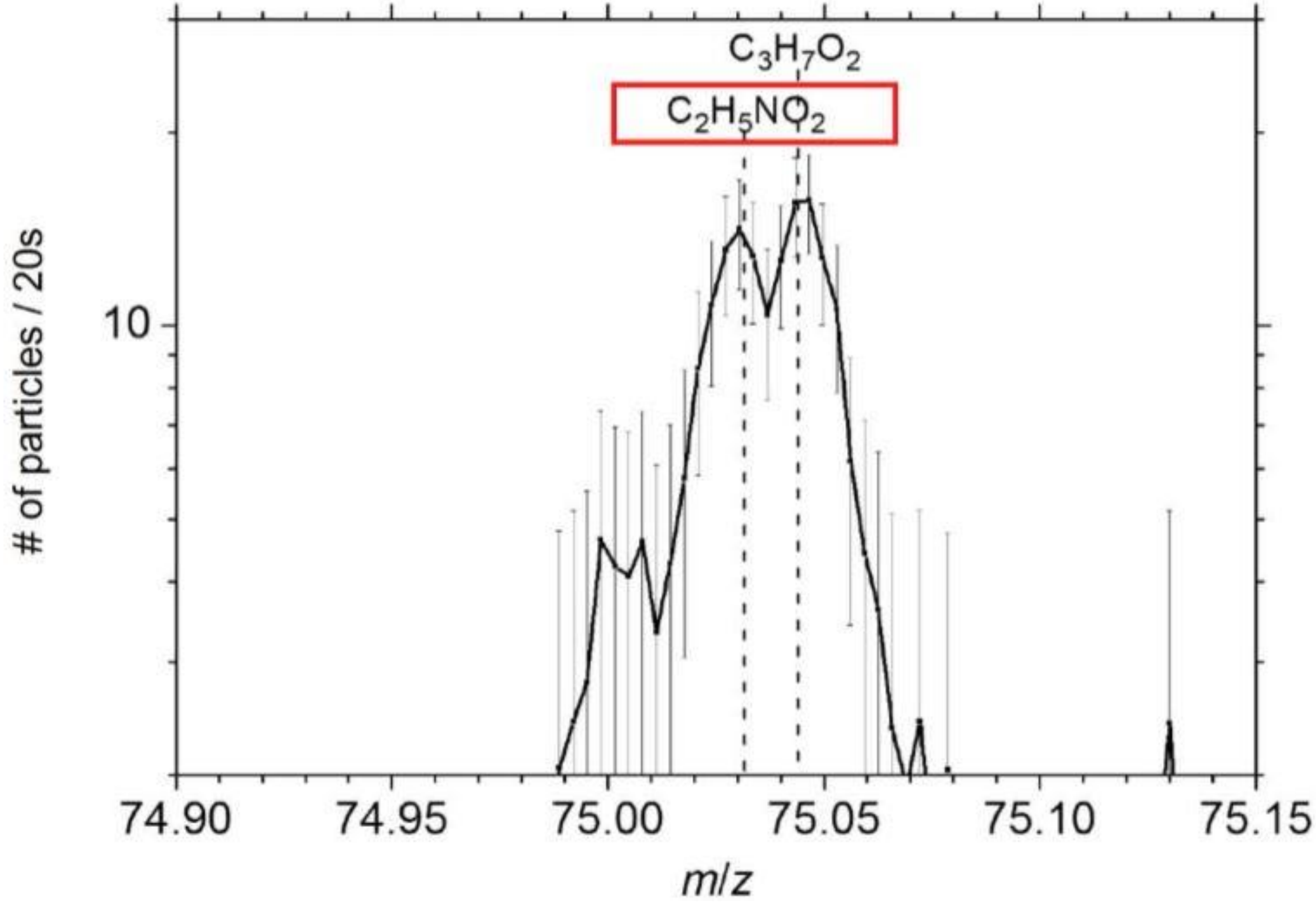
ROSINA DFMS

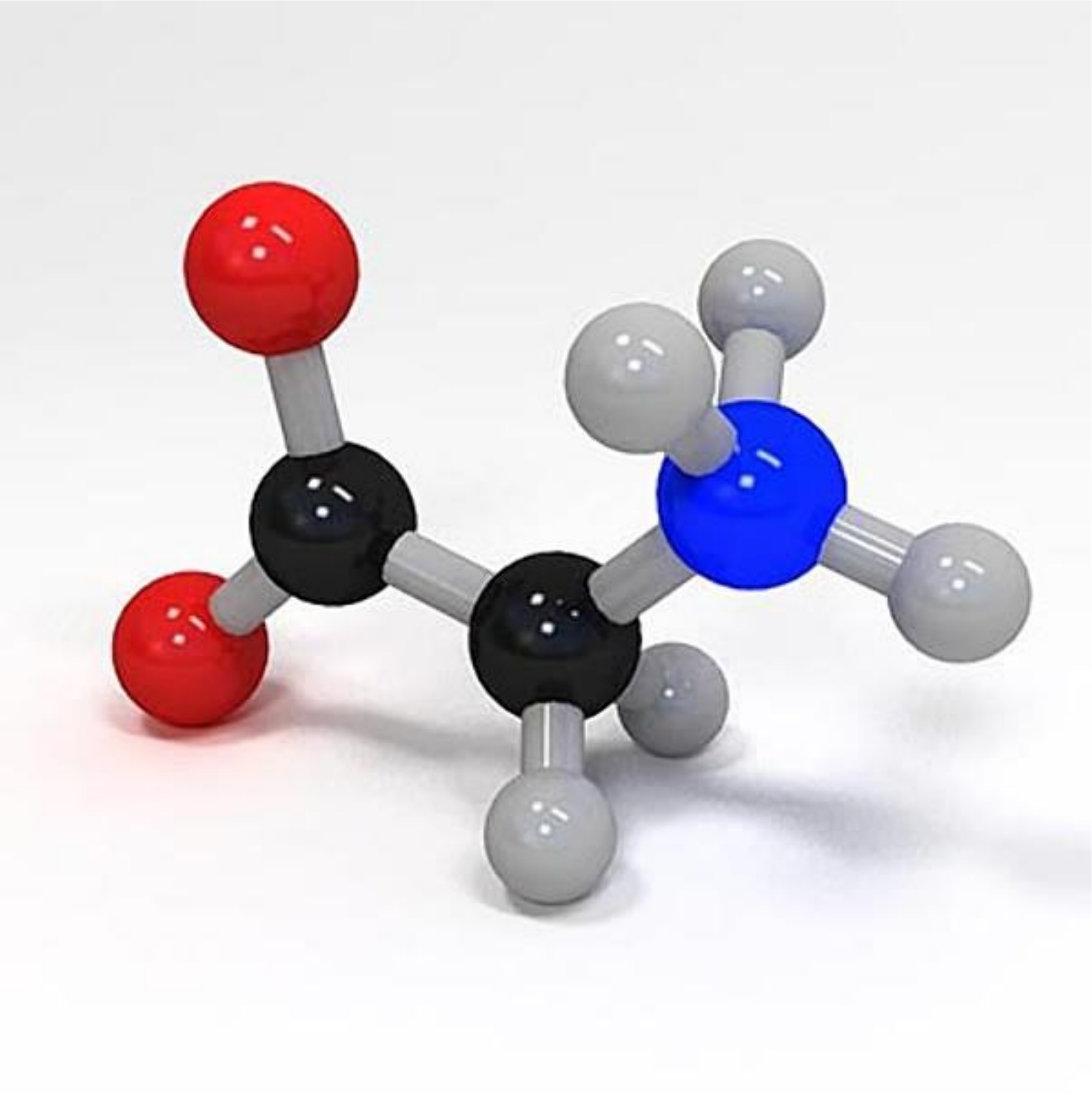

PHILAE



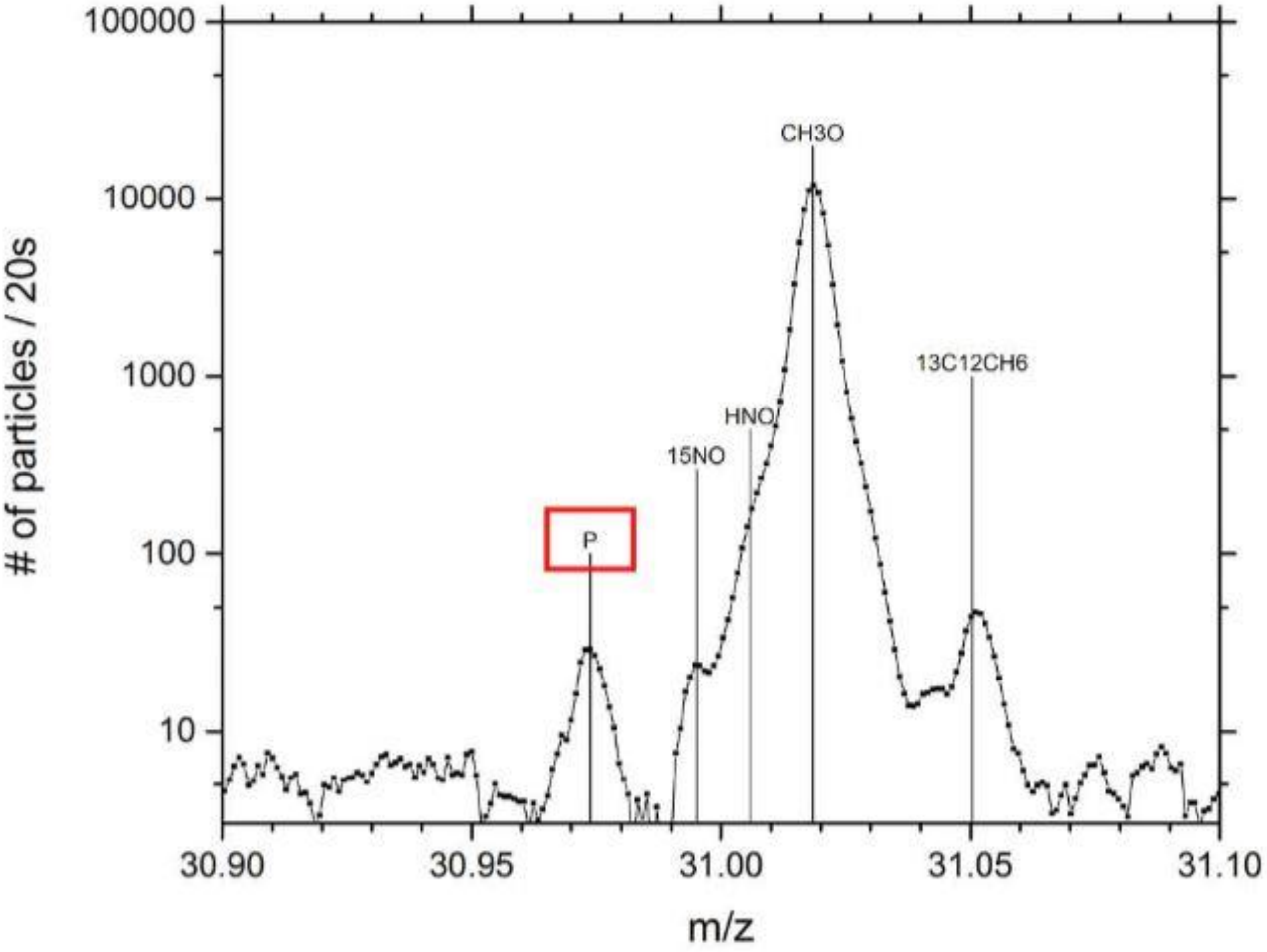

Particles/20 s
1000
100
10
1
NO
CH2O
CH4N
C2H6
29.96
29.98
30.00
30.02
30.04
30.06
30.08
30.10
1000
100
10
1
CH3O
CH5N
N2H3
15NO
HNO
CF
P
30.96
30.98
31.00
31.02
31.04
31.06
31.08
Particles/20 s
10,000
1000
100
10
13CO2
CHS
CHO2
C2H5O
CH5N2
CH3NO
C2H7N
44.90
44.95
45.00
45.05
45.10
m/z
C3H7O2
C2H5NO2
10
74.90
74.95
75.00
75.05
75.10
75.15
m/z

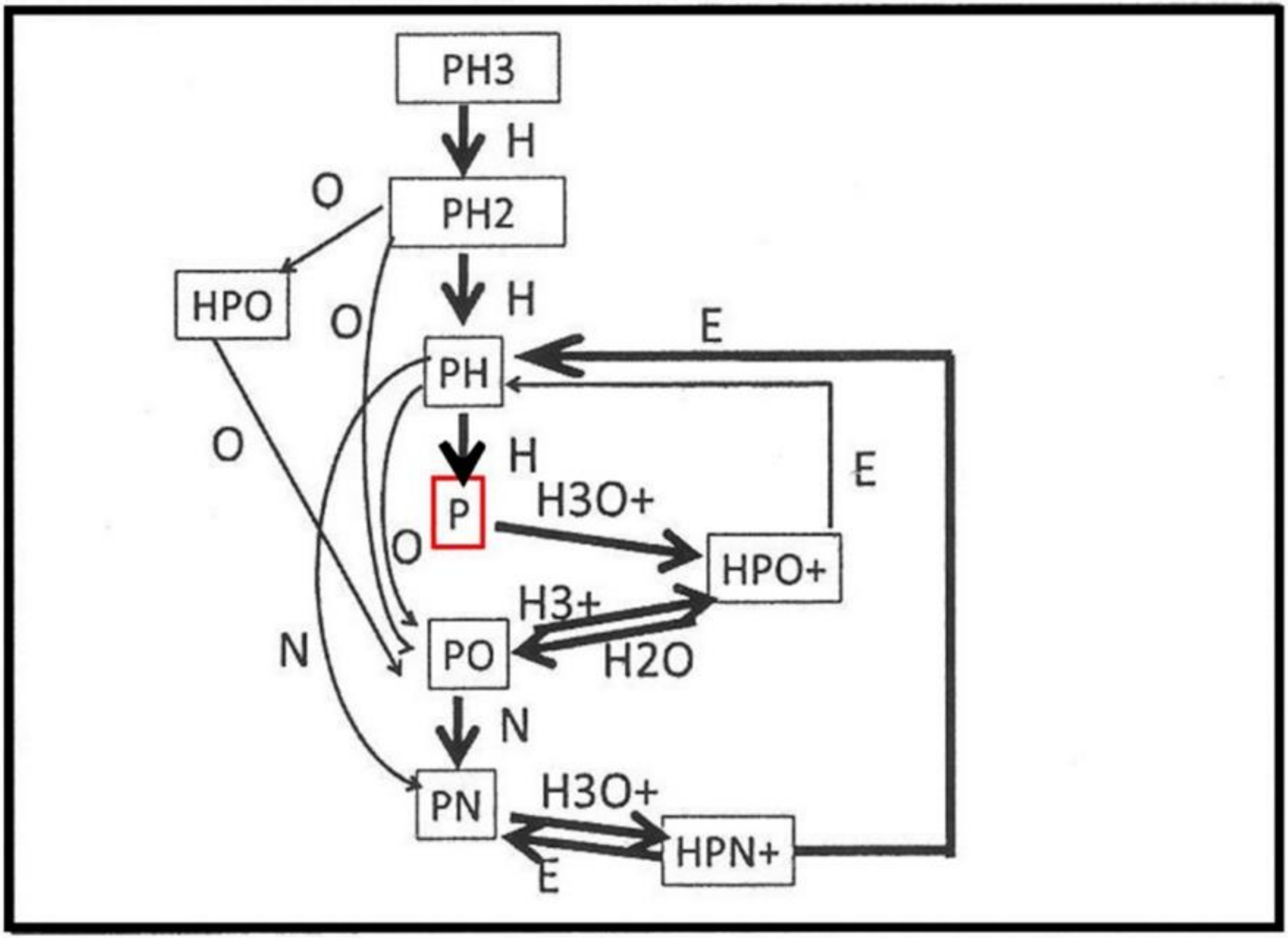
Glycine detection





Phosphorus detection





Reaction network of P-bearing species in the shocked gas.

Aota & Aikawa, ApJ 761 (2012) 74.

Figure 1: Phosphorus Nitride

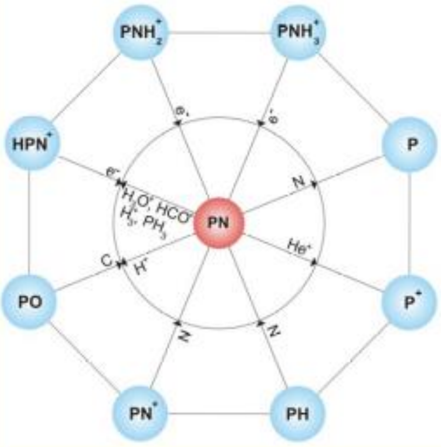


Figure 2: Phosphorus Monoxide

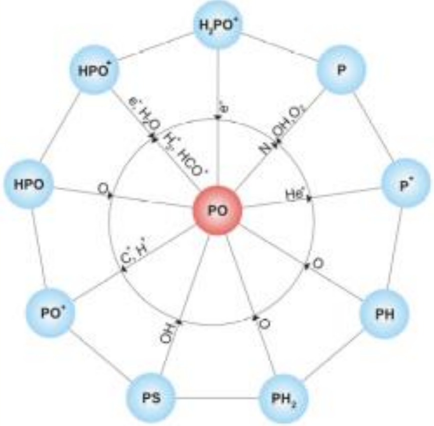


Figure 3: Carbon Phosphide

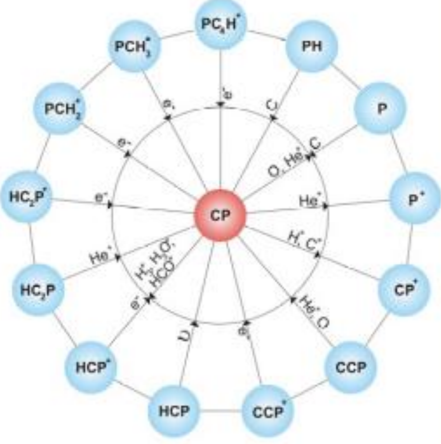


Figure 4: Phosphorus Monohydride

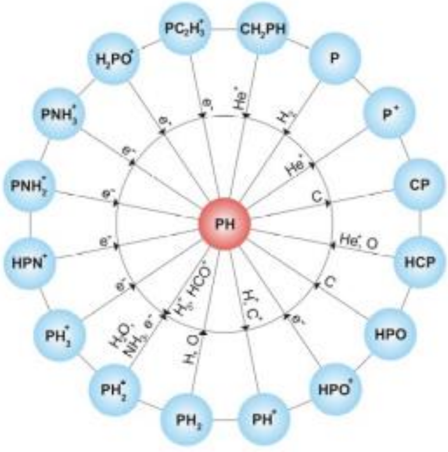


Figure 5: HCP species

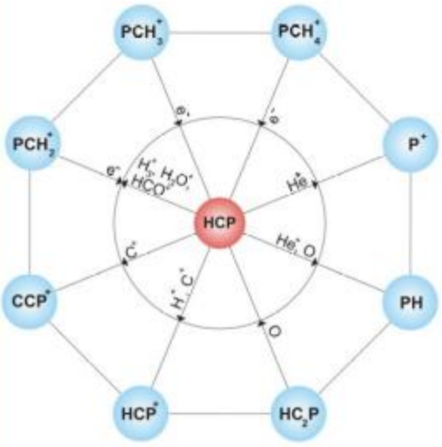


Figure 6: HPO species

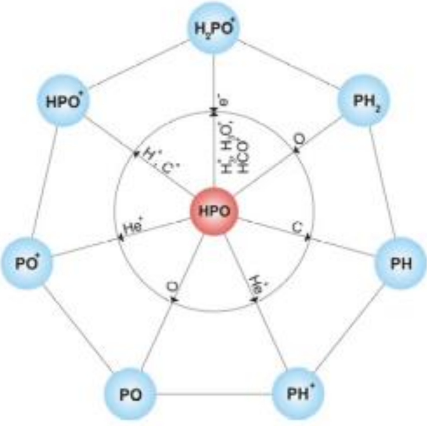


Figure 7: PH_2 species

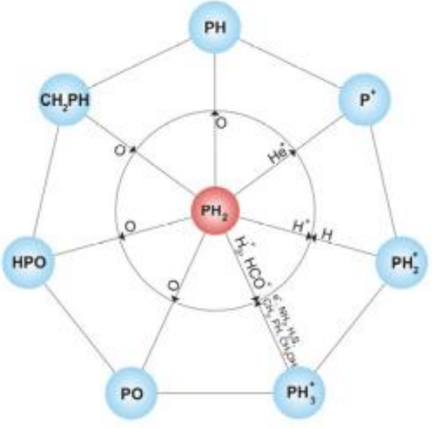


Figure 8: CCP species

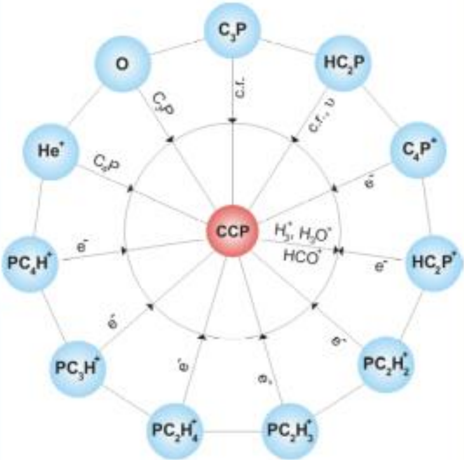
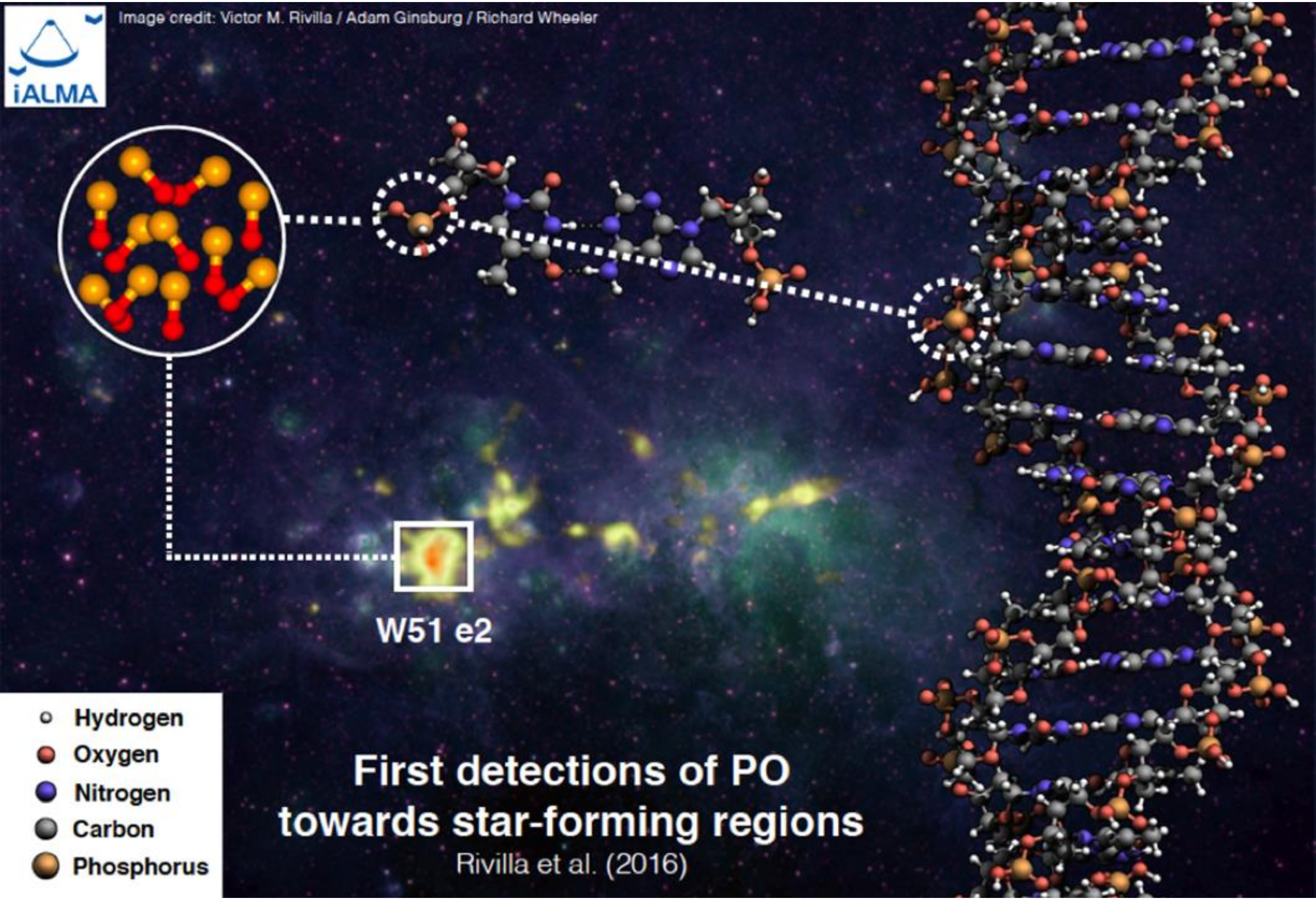


Image credit: Victor M. Rivilla / Adam Ginsburg / Richard Wheeler



- ● Hydrogen
- ● Oxygen
- ● Nitrogen
- ● Carbon
- ● Phosphorus

First detections of PO towards star-forming regions

Rivilla et al. (2016)

Elemental and molecular abundances in comet 67P/Churyumov-Gerasimenko

Martin Rubin[1,*], Kathrin Altwegg[1], Hans Balsiger[1], Jean-Jacques Berthelier[2], Michael R. Combi[3], Johan De Keyser[4], Maria Drozdovskaya[5], Björn Fiethe[6], Stephen A. Fuselier[7,8], Sébastien Gasc[1], Tamas I. Gombosi[3], Nora Hänni[1], Kenneth C. Hansen[3], Urs Mall[9], Henri Rème[10], Isaac R. H. G. Schroeder[1], Markus Schuhmann[1], Thierry Sémon[1], Jack H. Waite[7], Susanne F. Wampfler[5], and Peter Wurz[1,5]

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[7]Space Science Directorate, Southwest Research Institute, 6220 Culebra Rd., San Antonio, TX 78228, USA.
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Table 2 cont.

Molecule	**Deduced bulk abundance**	**Northern vs southern hemispheres at 3.1 au** a)	**Name (of some isomers)**	**Reference & notes**
H_2O	100	100 / 100	Water	definition
H_2S	1.10 ± 0.46	0.67 / 1.75	Hydrogen sulfide	i)
OCS	$0.041^{+0.082}_{-0.020}$	0.017 / 0.098	Carbonyl sulfide	i)
SO	$0.071^{+0.142}_{-0.037}$	0.004 / 0.0014	Sulfur monoxide	i)
SO_2	$0.127^{+0.254}_{-0.064}$	0.011 / 0.041	Sulfur dioxide	i)
CS_2	$0.0057^{+0.0114}_{-0.0028}$	0.003 / 0.024	Carbonyl sulfide	i)
S_2	$0.0020^{+0.0040}_{-0.0010}$	0.0004 / 0.0013	Sulfur dimer	i)
H_2CS	$0.0027^{+0.0058}_{-0.0024}$		Thioformaldehyde	i)
S	0.46 ± 0.36		Atomic sulfur	i)
CH_3SH	$0.038^{+0.079}_{-0.028}$		Methanethiol	i)
CH_3CH_2SH CH_3SCH_3	$0.00058^{+0.00123}_{-0.00049}$		Ethanethiol Dimethyl sulfide	i)
Ar	0.00058 ± 0.00022	0.00012 to 0.0027 d)	Argon	h)
Kr	0.000049 ± 0.000022		Krypton	h)
Xe	0.000024 ± 0.000011		Xenon	h)
Ne	< 0.000005		Neon	h), upper limit
HF	$0.011^{+0.037}_{-0.008}$		Hydrogen fluoride	i), range given
HCl	$0.014^{+0.045}_{-0.012}$		Hydrogen chloride	i), range given
HBr	$0.00030^{+0.00053}_{-0.00018}$		Hydrogen bromide	i), range given
PO	$0.011^{+0.022}_{-0.006}$		Phosphorous oxide	k)

NITROGEN SULFIDE IN COMETS HYAKUTAKE (C/1996 B2) AND HALE–BOPP (C/1995 O1)

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(Received 4 March 2002; Accepted 20 June 2002)

Abstract. The chemistry of both nitrogen and sulfur presents interesting problems in comets. In this paper, we use a model of cometary comae with gas-phase chemical kinetics and gas dynamics to predict molecular abundances in the inner coma region for two of the brightest comets in the past 20 years, Hyakutake (C/1996 B2) and Hale–Bopp (C/1995 O1). In this progress report we concentrate on the gas-phase chemistry of the nitrogen sulfide (NS) radical at a heliocentric distance of 1 AU to study the abundance of NS using a detailed photo and chemical reaction network with over 100 species and about 1000 reactions. The results are compared with recent observations of Comet Hale–Bopp and reveal that conventional gas-phase reactions schemes do not produce NS in sufficient quantities to explain the observations. We plan to continue the refinement of the model to improve agreement with observational constraints.

Keywords: Abundance, comet C/1995 O1 Hale–Bopp, comet C/1996 B2 Hyakutake, cometary comae, nitrogen sulfide

1. Introduction

Nitrogen sulfide (NS) was first identified in the giant molecular cloud, Sgr B2 (Gottlieb et al., 1975) at 115 GHz (transition $J = 5 \rightarrow 3$), and is now known to be common in dense interstellar clouds in regions of massive star formation (McGonagle et al., 1992). It has been detected also in cold dark clouds (McGonagle et al., 1994). Recently, Irvine et al. (2000) reported the first detection of the NS radical in the coma of a comet using the James Clerk Maxwell Telescope (JCMT) on March 22, 1997, to observe Hale–Bopp (C/1995 O1) at a heliocentric distance of

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‡ E-mail: gsanzovo@uel.br

Earth, Moon and Planets **90:** 335–347, 2002.

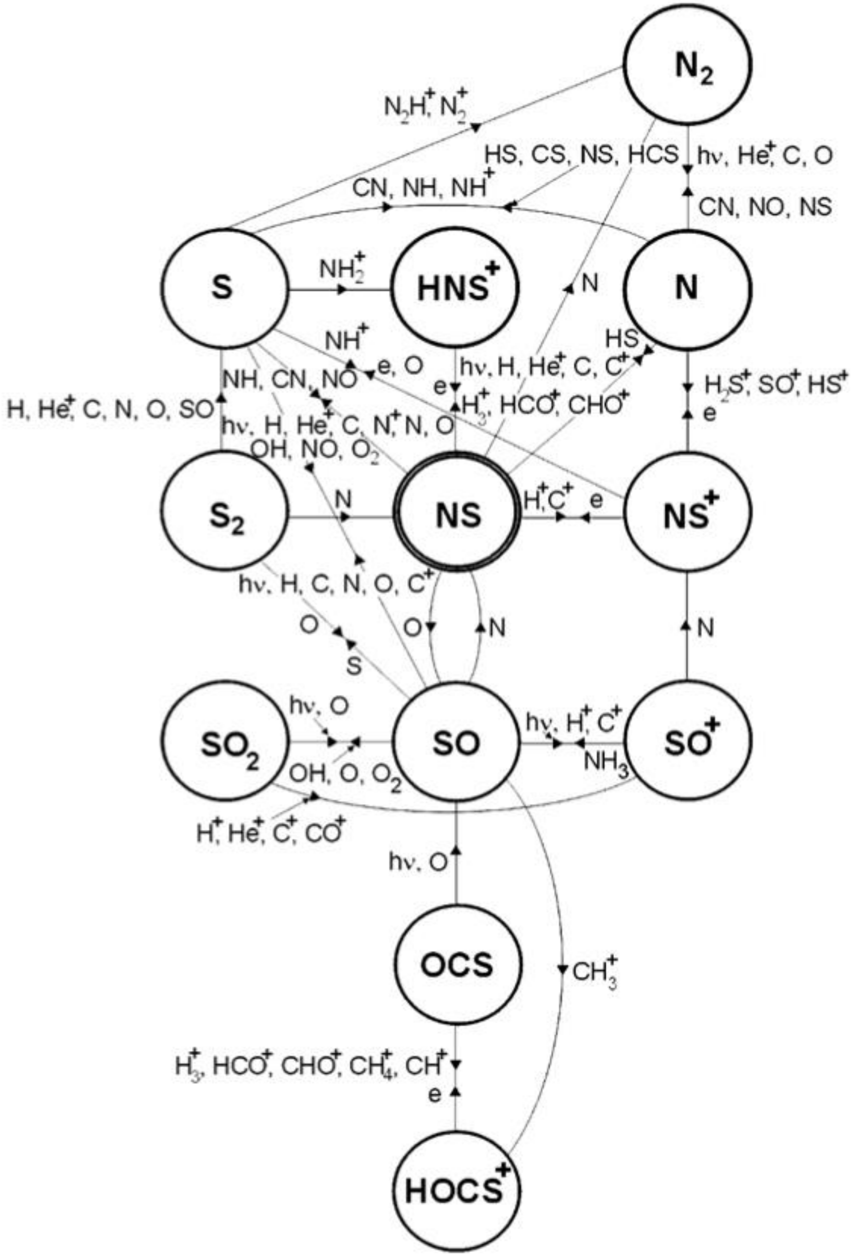

Figure 1. Schematic diagram showing the major sulfur reactions relevant to the inner coma for the NS radical. Symbols next to the arrows are the reactants; $h\nu$ indicates photodissociation.

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Advances in Space Research 39 (2007) 451–457

ADVANCES IN SPACE RESEARCH
(a COSPAR publication)

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On the chemistry of CS and NS in cometary comae

M.V. Canaves [a], A.A. de Almeida [a,*], D.C. Boice [b], G.C. Sanzovo [c]

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[b] *Southwest Research Institute, Department of Space Science, Instrumentation and Space Research Division, P.O. Drawer 28510, San Antonio, TX 78228-0510, USA*
[c] *Laboratory of Molecular Astrophysics, Department of Physics, State University of Londrina, Perobal, CEP 86051-970, Londrina, PR, Brazil*

Received 28 November 2002; received in revised form 23 June 2003; accepted 11 November 2006

Abstract

We have developed a multifluid chemical model of cometary comae which is an improvement to a recent work by Canaves et al. [Canaves, M.V., de Almeida, A.A., Boice, D.C., Sanzovo, G.C., Nitrogen sulfide in comets Hyakutake (C/1996 B2) and Hale-Bopp (C/1995 O1), Earth Moon Planets, 90, 1–13, 2002.] with the purpose to predict the abundances of carbon monosulfide (CS) and nitrogen sulfide (NS). The model is applied to the recent bright comets Hyakutake and Hale-Bopp at a heliocentric distance of 1 AU using a detailed photo and chemical reaction network including more than 100 species and over 1000 reactions. The collisional reactions have up-to-date rate coefficients from Le Teuff et al. [Le Teuff, Y.H., Millar, T.J., Markwick, A.J., The UMIST database for astrochemistry 1999, A&AS, 146, 157–168, 2000.], while the photolytic rate coefficients were taken for minimum and maximum solar fluxes in order to estimate an lower and a upper limit for the abundances of NS and CS. The comparison of results for NS molecule in comet Hale-Bopp is in good agreement with Irvine et al. [Irvine, W.M., Senay, M., Lovell, A.J., Matthews, H.E., McGonagle, D., Meier, R., Note: detection of nitrogen sulfide in comet Hale-Bopp, Icarus, 143, 412–414, 2000.], while for CS species we show that the abundances do not seem to vary much with the cometocentric distance.

Keywords: Cometary comae; Carbon monosulfide; Nitrogen sulfide; Comets Hyakutake and Hale-Bopp

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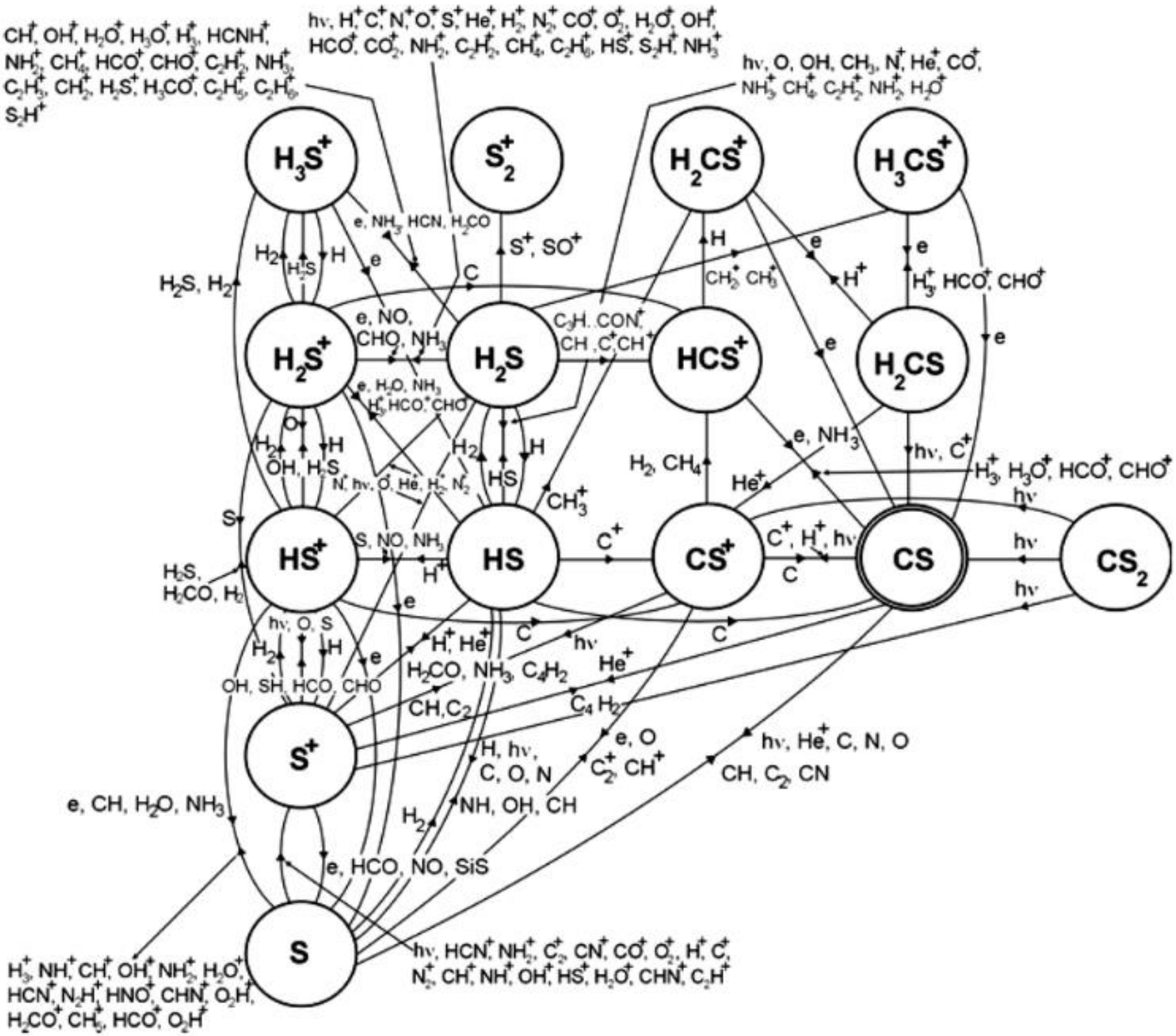

Fig. 1. Chemical reactions network for the formation and destruction of the CS species in cometary comae.

Chemistry

Chemical Reaction Processes with Examples

Photodissocation [$h\nu + H_2O \rightarrow H + OH$]

Photoionization [$h\nu + CO \rightarrow CO^+ + e$]

Photodissociative ionization [$h\nu + CO_2 \rightarrow O + CO^+ + e$]

Electron impact dissociation [$e + N_2 \rightarrow N + N$]

Electron impact ionization [$e + CO \rightarrow CO^+ + 2e$]

Electron impact dissociative ionization [$e + CO_2 \rightarrow O + CO^+ + 2e$]

Positive ion-atom interchange [$CO^+ - H_2O \rightarrow HCO^+ + OH$]

Positive ion charge transfer [$CO^+ + H_2O \rightarrow H_2O^+ + CO$]

Electron dissociative recombination [$C_2H^+ + e \rightarrow C_2 + H$]

3-Body positive ion-neutral association [$C_2H_2^+ + H_2 + M \rightarrow C_2H_4^+ + M$]

Neutral rearrangement [$N + CH \rightarrow CN + H$]

3-Body neutral recombination [$C_2H_2 + H + M \rightarrow C_2H_3 + M$]

Radiative electronic state deexcitation [$O(^1D) \rightarrow O(^3P) + h\nu$]

Electron impact electronic state quenching [$e + O(^1D) \rightarrow e + O(^3P)$]

Radiative recombination [$e + H^+ \rightarrow H + h\nu$]

Radiation stabilized positive ion-neutral association [$C^+ + H \rightarrow CH^+ + h\nu$]

Radiation stabilized neutral recombination [$C + C \rightarrow C_2 + h\nu$]

Neutral-neutral associative ionization [$CH + O \rightarrow HCO^+ + e$]

About 700 reactions
About 130 species

Stiff differential equations

Rate coefficients (Arrhenius)

$$k = A \left(\frac{T}{300}\right)^B e^{-C/T}$$

C...activation energy

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SUISEI—A Versatile Global Model of Comets with Applications to Small Solar System Bodies

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How to cite this paper: Boice, D.C. (2017) SUISEI—A Versatile Global Model of Comets with Applications to Small Solar System Bodies. *Journal of Applied Mathematics and Physics*, **5**, 311-320.
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Abstract

SUISEI is a suite of computational tools that has been developed over the past three decades and successfully applied to comets; including ComChem, a global, multi-fluid gas dynamics simulation with detailed chemical kinetics of the cometary coma; ComDust, a model of comet dust evolution and interaction with gas; and ComNuc, a 3-D simulation of gas and heat flow within the comet nucleus porous subsurface layers. The combination of these tools have resulted in an improved knowledge of chemical species in the comet's coma and their relationship to native molecules in the nucleus ices by analyzing space- and ground-based observations and *in situ* measurements from spacecraft missions. A review of SUISEI is presented and applications are made to two cases: chemical recycling of HCN in comets and the physical conditions of the near-Sun object, 3200 Phaethon.

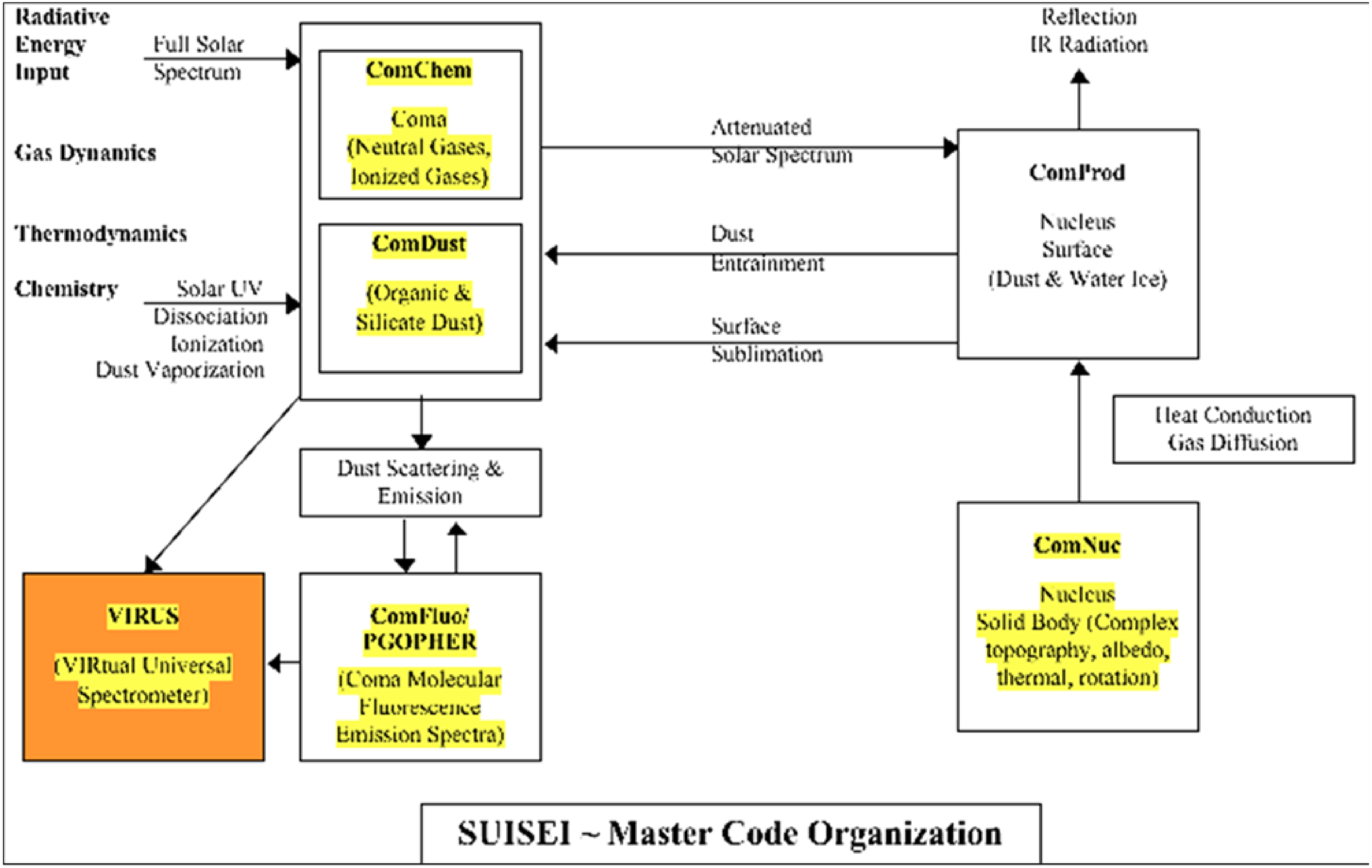
Keywords

Comets, Coma Chemistry Models, Reactive Dusty Gas Dynamics, 3200 Phaethon

1. Introduction

Comets are believed to be the remnants of the swarm of planetesimals from which the planets formed some 4.6 Gy ago. By investigating in detail the physical and chemical properties of comets, we can characterize the conditions and processes of the Solar System's earliest epoch. Comets are also thought to hold clues to the origins of life since they contain large inventories of water and organics, including prebiotic molecules, on Earth-crossing orbits.

Modeling is central to understand the important properties of the cometary environment. We have developed a comet model, SUISEI (Chinese 彗星; pro-



Radiative Energy Input

Full Solar Spectrum

Gas Dynamics

Thermodynamics

Chemistry

Solar UV
Dissociation
Ionization
Dust Vaporization

ComChem

Coma
(Neutral Gases,
Ionized Gases)

ComDust

(Organic &
Silicate Dust)

Attenuated Solar Spectrum

Dust Entrainment

Surface Sublimation

Reflection
IR Radiation

ComProd

Nucleus
Surface
(Dust & Water Ice)

Heat Conduction
Gas Diffusion

ComNuc

Nucleus
Solid Body (Complex
topography, albedo,
thermal, rotation)

Dust Scattering &
Emission

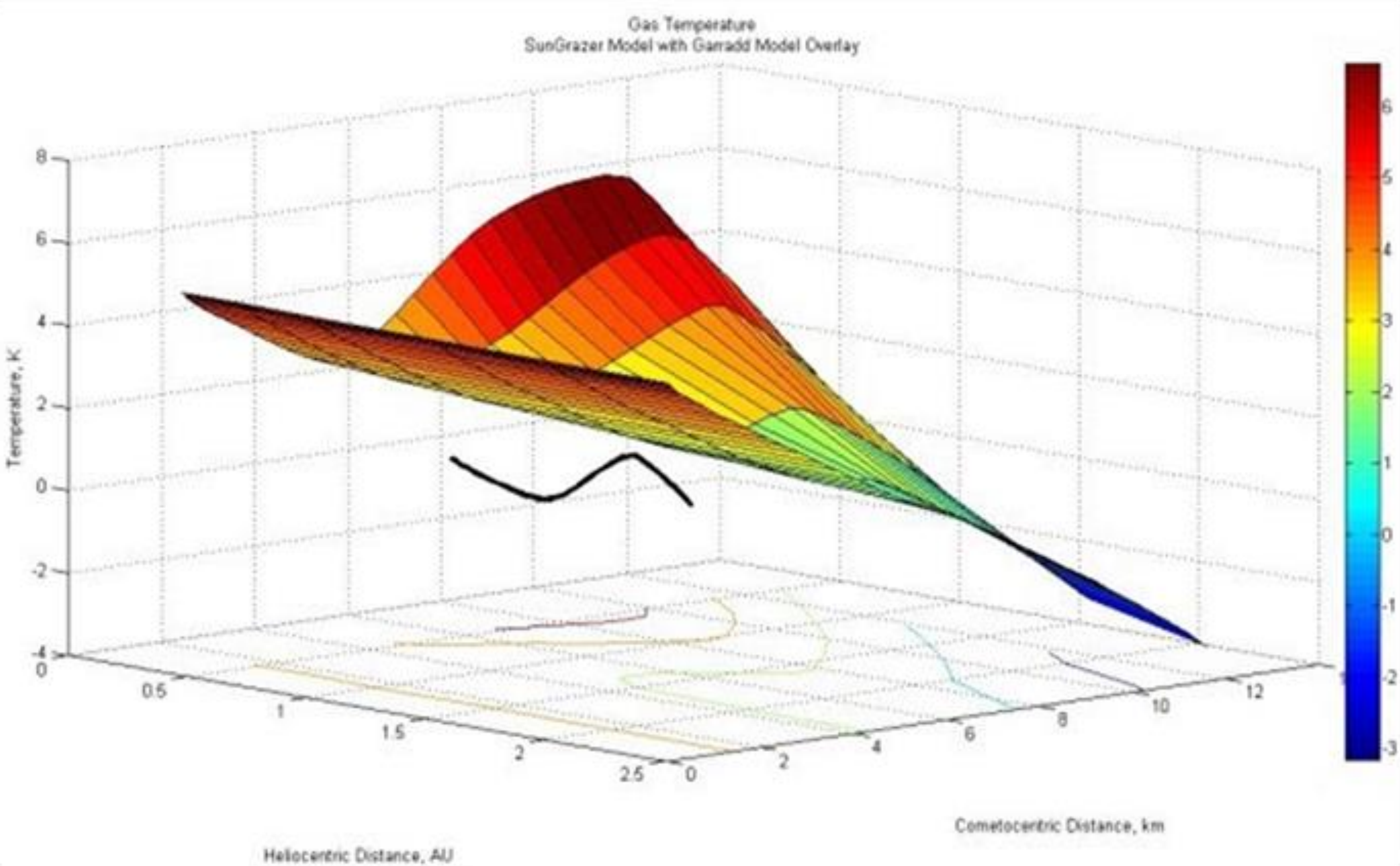
**ComFluo/
PGOPHER**

(Coma Molecular
Fluorescence
Emission Spectra)

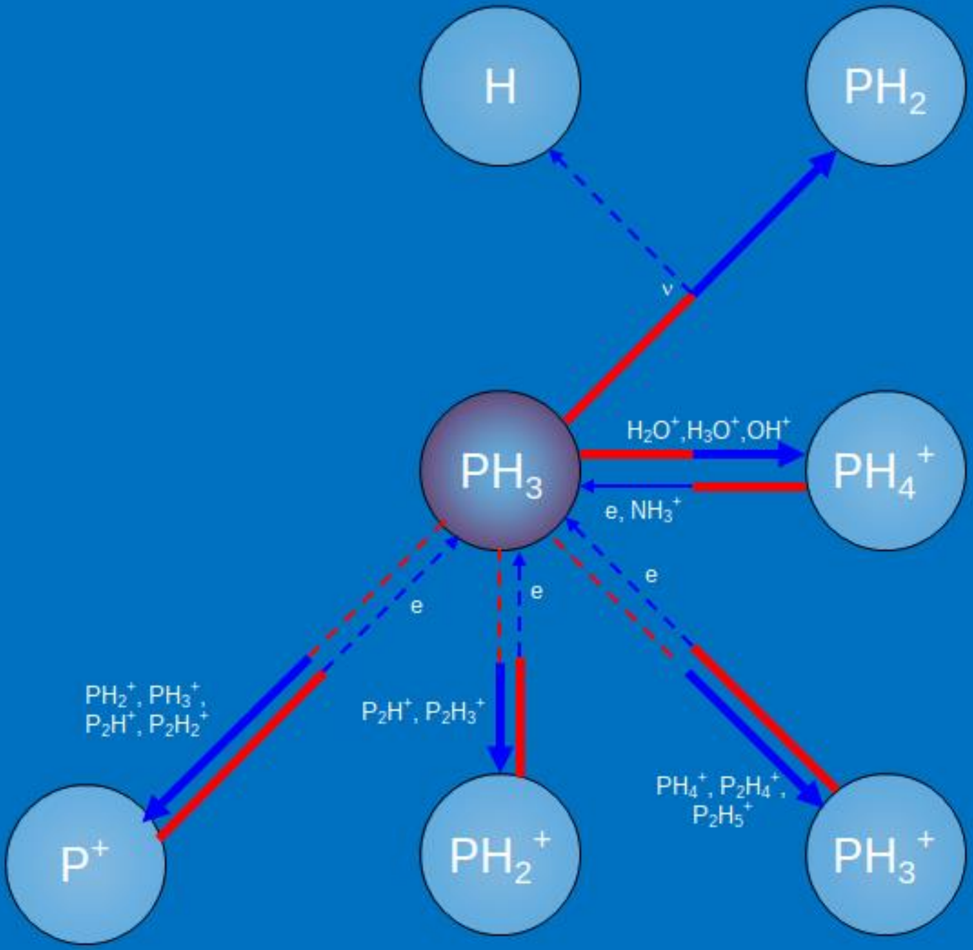
VIRUS

(VIRtual Universal
Spectrometer)

SUISEI ~ Master Code Organization


Gas Temperature
SunGrazer Model with Garradd Model Overlay
Temperature, K
8
6
4
2
0
-2
-4
Heliocentric Distance, AU
0
0.5
1
1.5
2
2.5
Cometocentric Distance, km
0
2
4
6
8
10
12
6
5
4
3
2
1
0
-1
-2
-3

PH3 Chemistry in the Inner Coma



H

PH_2

ν

PH_3

H_2O^+, H_3O^+, OH^+

PH_4^+

e, NH_3^+

e

e

e

$PH_2^+, PH_3^+,$
$P_2H^+, P_2H_2^+$

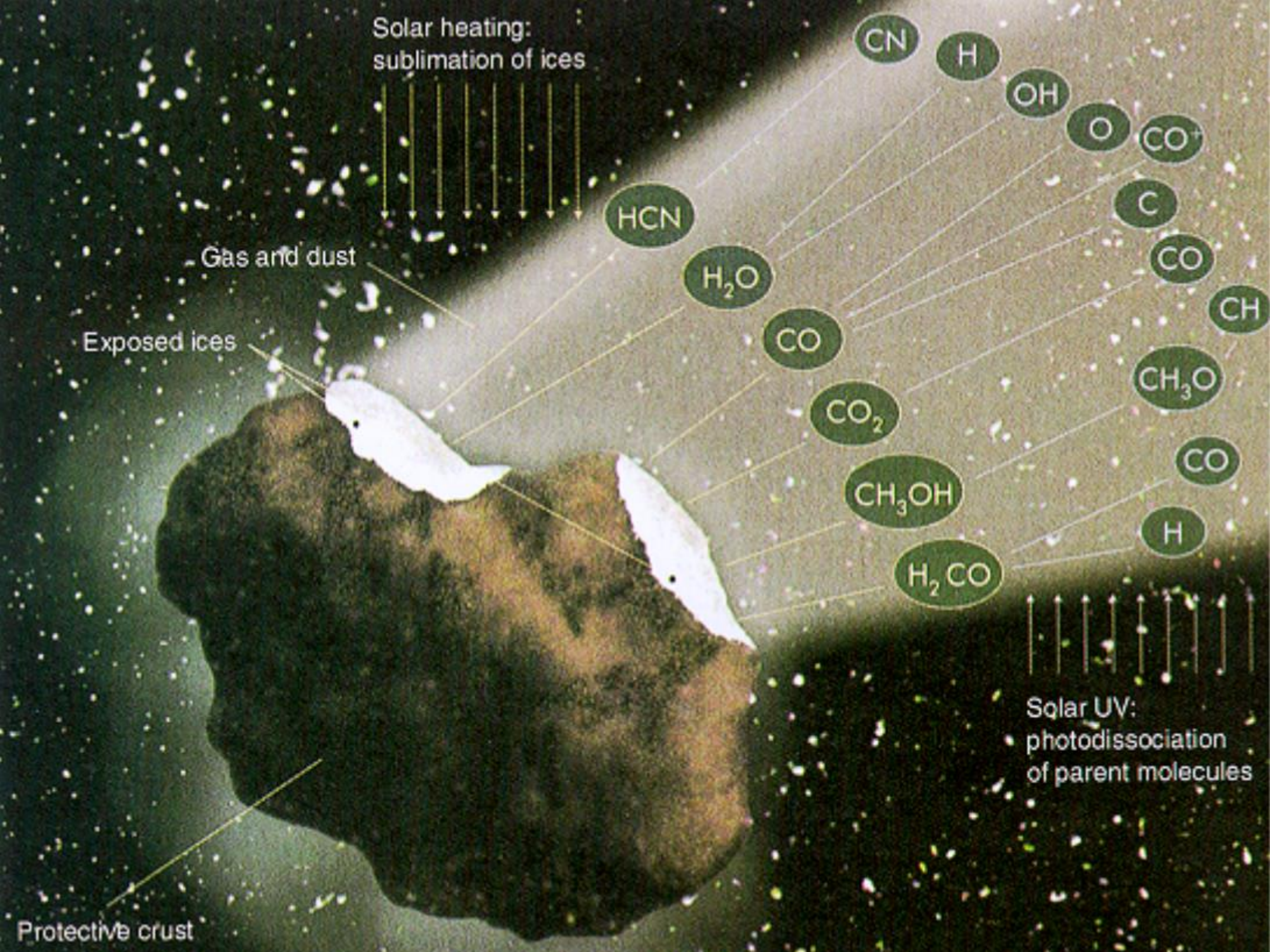
$P_2H^+, P_2H_3^+$

$PH_4^+, P_2H_4^+,$
$P_2H_5^+$

P^+

PH_2^+

PH_3^+


Solar heating:
sublimation of ices
CN
H
OH
O
CO+
HCN
C
Gas and dust
H2O
CO
CH
Exposed ices
CO
CH3O
CO2
CO
CH3OH
H
H2 CO
Solar UV:
photodissociation
of parent molecules
Protective crust

Formation of the CF radical in comets

To appear in Journal of Physics: Conference Series, August 2019

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Abstract. In March 2015 the European Space Agency´s Rosetta spacecraft performed a close flyby over the surface of comet 67P/Churyumov-Gerasimenko of just 15 km from the comet center. This comet belongs to the Jupiter family with an aphelion at 5.5 au and a perihelion at 1.25 au. Its orbital period is 6.5 years. The ROSINA (Rosetta Orbiter Sensor for Ion and Neutral Analysis)/DFMS (Double Focusing Mass Spectrometer) instrument on board Rosetta reported the first detection among others of glycine ($C_2H_5NO_2$) an amino acid, other prebiotic molecules, phosphorus atom (P), and fluoromethylidyne (CF), which is not a stable chemical species but a metastable radical [1]. In the case of phosphorus, the search for the parent (PH_3, PH, PO, PN, CP, HCP, HPO, CCP) was unsuccessful although these species have been detected mostly in the interstellar medium [2]. This work reports a study of model-dependent chemical networks, based on several databases such as UMIST and NIST among others, to explain the formation of CF radical in comets from gaseous tetrafluoromethane (CF_4).

2. Observations and qualitative results

A sample mass spectrum measured by the ROSINA/DFMS onboard Rosetta spacecraft at 75, 45, 31 and 30 dalton in the coma of comet 67P/Churyumov-Gerasimenko is shown in Figure 1. There is a clear peak at mass 31.009 dalton, which is the exact mass of CF (carbon monofluoride) [1].

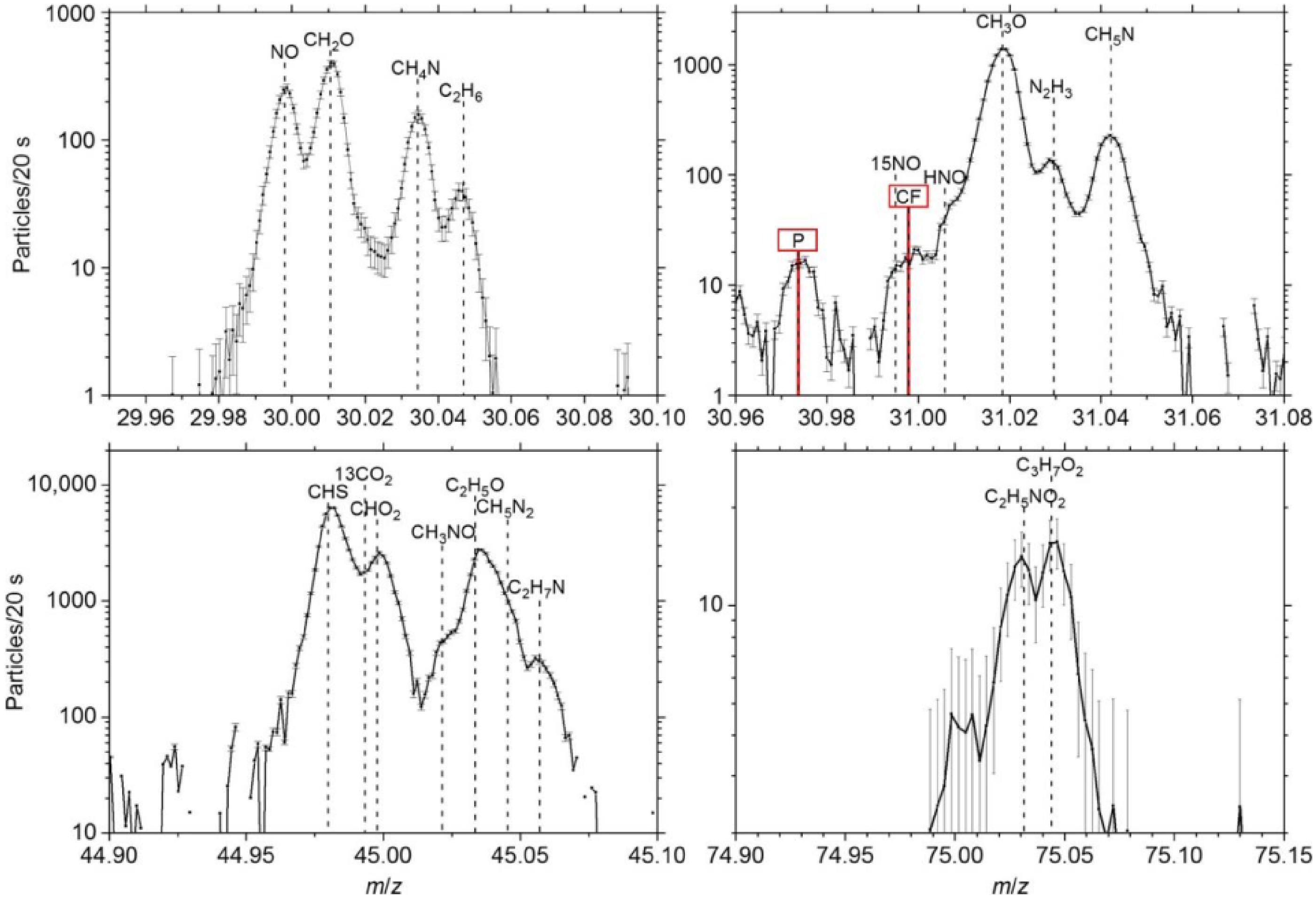

Figure 1. ROSINA DFMS mass spectra (9 July 2015) for masses 30, 31, 45, and 75 dalton. Integration time is 20s per spectrum. Error bars represent 1-σ counting statistics [1].

In this work, the possible gas-phase formation route of the CF radical in comets is studied. The Figure 2 shows the reaction network developed, starting from CF_4 (carbon tetrafluoride) and ultimately leading to CF (carbon monofluoride) in the outer coma gas, as illustrated in Figure 3.

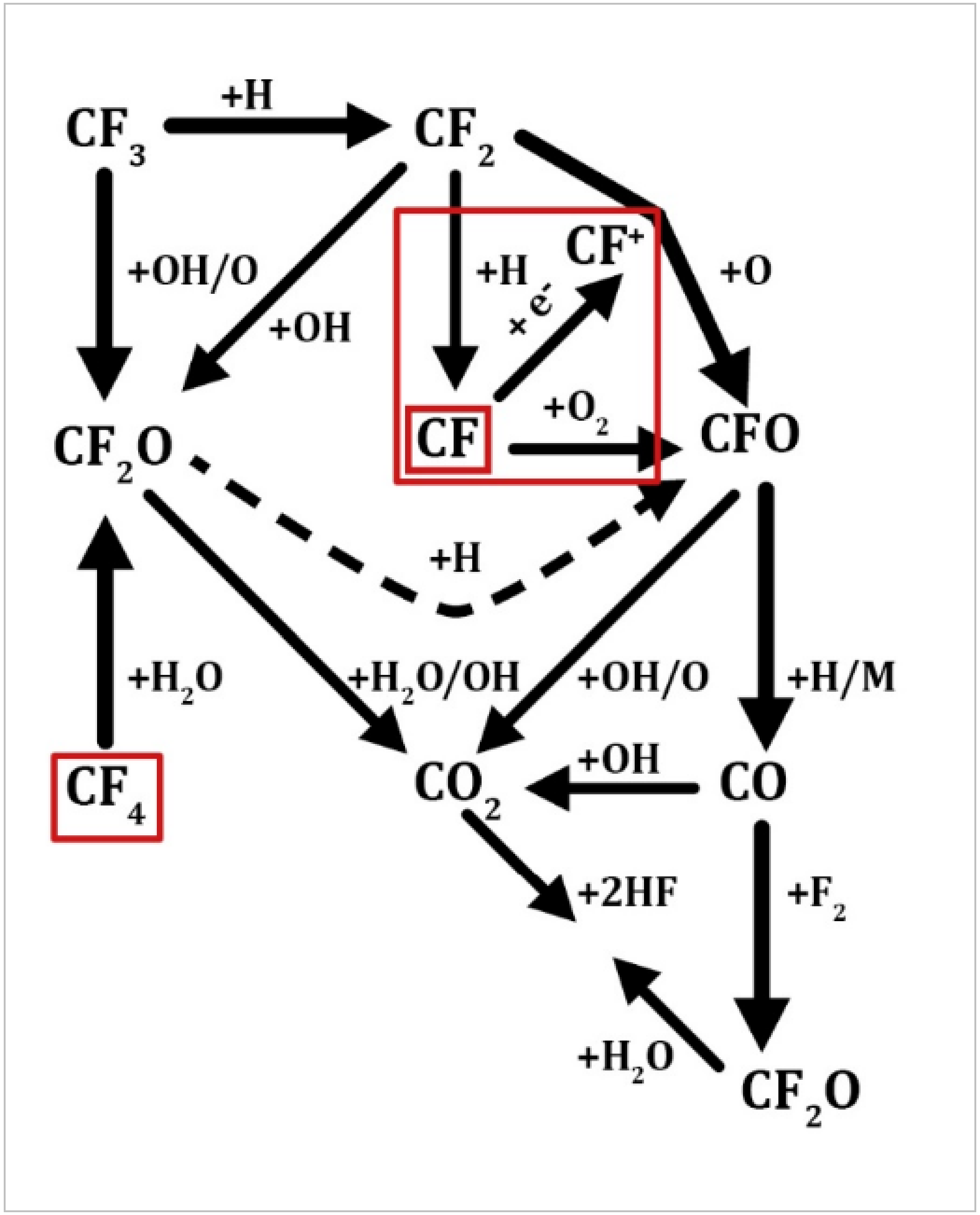

Figure 2. Possible gas-phase formation route of the CF radical in comets.

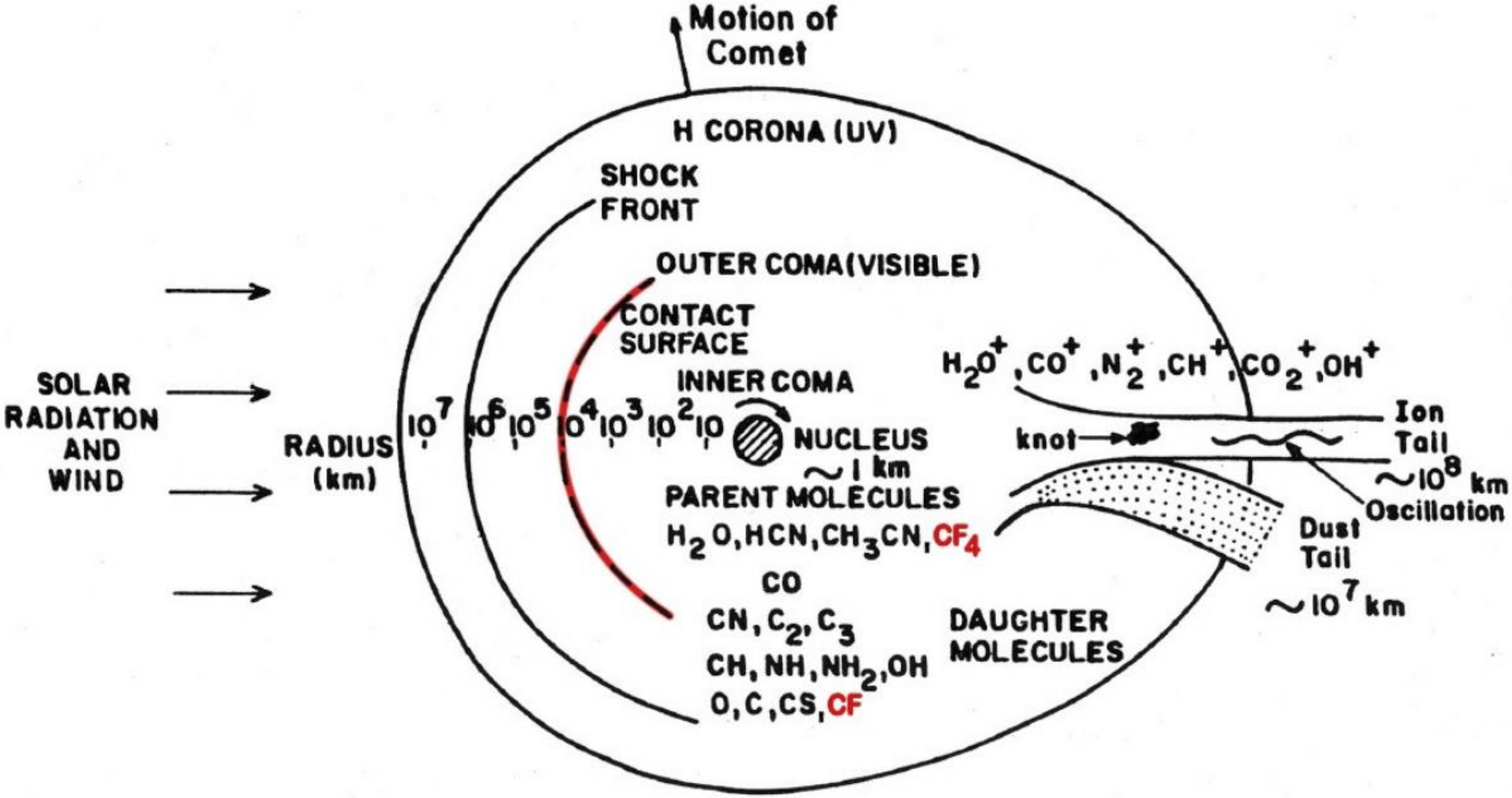

Figure 3. Descriptive sketch of a comet.

3. Summary and conclusions

In this work, a fundamental and comprehensive chemical network was developed to explain the possible origin of the CF radical in the inner coma of comet 67P/Churyumov-Gerasimenko, detected by ROSINA/DFMS. It is shown that the neutral gaseous CF radical can be formed from CF_4. Chemical reaction processes with relevant photo (dissociation, ionization), photodissociative ionization, electron impact (dissociation, ionization, dissociative ionization), protonation, positive ion (-atom interchange, charge transfer), electron dissociative recombination, 3-body (positive ion-neutral association, neutral recombination), neutral rearrangement, radiative recombination, radiation stabilized (positive ion-neutral association, neutral recombination) and neutral-neutral associative ionization reactions will be used and included as needed, in Figure 2, in the future.

Table 1. Fragmentation pattern and sensitivity used to calculate the relative abundance [16].

Species	Fragmentation pattern	Sensitivity
H_2O	M	M
CO	NIST	C
CO_2	M	M
CH_4	M	M
C_2H_2	NIST	C
C_2H_6	M	M
CH_3OH	NIST	C
H_2CO	NIST	C
HCOOH	NIST	C
CH_2OHCH_2OH	NIST	C
$HCOOCH_3$	NIST	C
CH_3CHO	NIST	C
NH_3	M	M
HCN	NIST	C
HNCO	[17]	C
CH_3CN	NIST	C
H_2S	M	M
OCS	NIST	C
SO	estimated	C
SO_2	NIST	C
CS_2	NIST	C
S_2	estimated	C
CF	this work	–

Notes. M refers to fragmentation pattern and sensitivity determined in the calibration facility. C refers to the sensitivities that were calculated from the function determined thanks to the calibration measurements.

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H_2CO	NIST	C
HCOOH	NIST	C
CH_2OHCH_2OH	NIST	C
$HCOOCH_3$	NIST	C
CH_3CHO	NIST	C
NH_3	M	M
HCN	NIST	C
HNCO	[17]	C
CH_3CN	NIST	C
H_2S	M	M
OCS	NIST	C
SO	estimated	C
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CS_2	NIST	C
S_2	estimated	C
CF	**this work**	–

Notes. M refers to fragmentation pattern and sensitivity determined in the calibration facility. C refers to the sensitivities that were calculated from the function determined thanks to the calibration measurements.

Our next step is to use the 3-D code Suisei [18], departing from a reasonable assumed initial chemical abundance for the volatile species – due to various uncertainties and errors involved in different quantities, the species listed in Table 1 [16], should be taken as an indicator of the trend of the results rather than the actual values – in order to obtain the following:

- variation of the columnar density for the CF radical as a function of the cometocentric distance along the inner and outer comae;
- variation of the average expansion speed of the neutral gaseous CF as a function of the cometocentric distance in the inner coma;
- variation of the gaseous CF temperature as a function of the cometocentric distance in the inner coma;
- profile of the columnar density for the CF radical in the case of maximum solar flux as a function of the cometocentric distance in the inner coma;
- profile of the columnar density for the CF radical in the case of minimum solar flux as a function of the cometocentric distance in the inner coma.