INPE MINISTÉRIO DA CIÊNCIA E TECNOLOGIA
INSTITUTO NACIONAL DE PESQUISAS ESPACIAIS

INTERNATIONAL SYMPOSIUM AND WORKSHOP ON ASTROCHEMISTRY
Understanding extraterrestrial molecular complexity through experiments and observations

Theoretical Studies of $HS+HX=H_2S+X$, with X = H, F, Cl, Br and I

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LAP/INPE – MCTIC

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Summary

- Outline of theory
- Results
- APUAMA (p.69)
- Conclusion

Transition State Theory

- For a bimolecular reaction:

$$A + BC \overset{X^{+}}{\Leftrightarrow} AB + C$$

- The thermal reaction rate is given by:

$$k_{TST} = \frac{k_B T}{h} \frac{Q_{X^{+}}}{Q_A Q_{BC}} \exp\left(-\frac{V_a^{G^{+}}}{RT} \right)$$

- and the barrier is:

$$V_a^{G^{+}} = V^{+} + \varepsilon_{ZPE}$$

Partition Function

$$Q = Q_{trans} Q_{rot} Q_{vib} Q_{elet}$$

	Degrees of freedom	Partition Function	Magnetude order
Translation	3	$Q_{trans} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2}$	10^{33} m^3
Rotation – 2D	2	$Q_{rot-2D} = \left(\frac{8\pi^2 I k_B T}{\sigma_e h^2} \right)$	10 – 10^2
Rotation – 3D	3	$Q_{rot-3D} = \left[\frac{\sqrt{\pi}}{\sigma_e} \left(\frac{8\pi^2 I_m k_B T}{h^2} \right)^{3/2} \right]$	10^2 – 10^3
Vibration	n = 3N – 5 n = 3N – 6	$Q_{vib} = \prod_{i=1}^{n} \left[1 - \exp\left(-\frac{hc\nu_i}{k_B T} \right) \right]^{-g_i}$	1 – 10^n
Electronic	–	$Q_{elet} = \sum_{i=0}^{n} g_i \exp\left(-\frac{\varepsilon_i}{k_B T} \right)$	1

- Zero point energies:

$$\varepsilon_{ZPE} = \frac{1}{2}\sum_i h d_i \omega_i$$

- Tunneling correction:

$$k_{TST}^{Z}(T) = \kappa(T) k_{TST}(T)$$

- Skew angle:

$$\beta = \arccos\left[\frac{m_A m_C}{(m_A + m_B)(m_B + m_C)}\right]^{1/2}$$

- Arrhenius Form:

$$k = AT^n \exp\left(-\frac{E_a}{RT}\right)$$

- Wigner transmission coefficient:

$$\kappa(T) = 1 + \frac{1}{24}\left|\frac{h\omega^{+}}{k_B T}\right|^2$$

- Eckart transmission coefficient:

$$\kappa(T) = \frac{\exp\left(\Delta V^{\ddagger}/RT\right)}{RT}\int_0^{\infty} \exp(-R/RT)\,\Gamma(E)\,dE$$

- Small Curvature transmission coefficient:

$$\kappa(T) = \frac{\int_0^{\infty} P(E)\exp(-E/k_B T)dE}{\int_{V_a^G}^{\infty} P(E)\exp(-E/k_B T)dE}$$

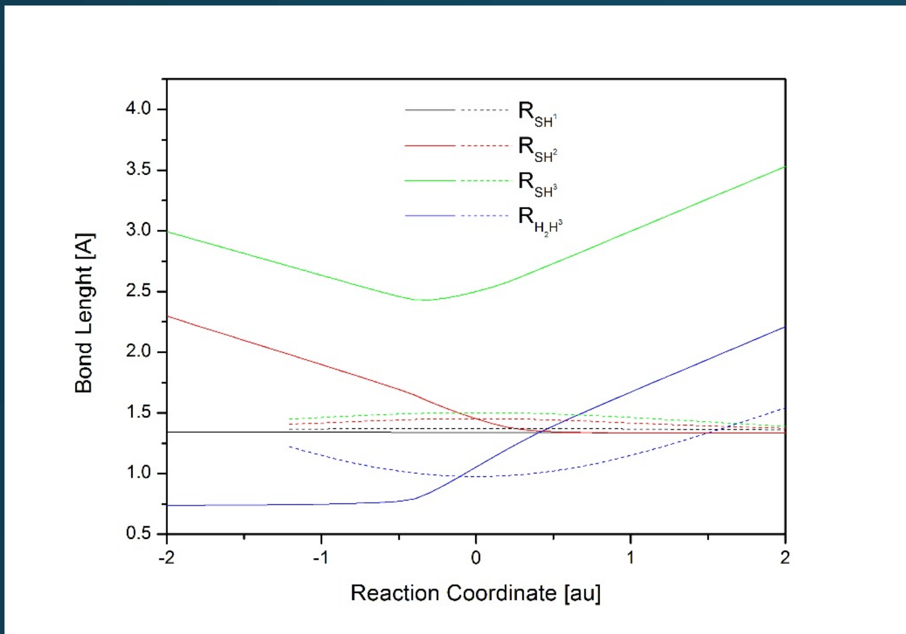
Results – HS+HS=H_2S+X

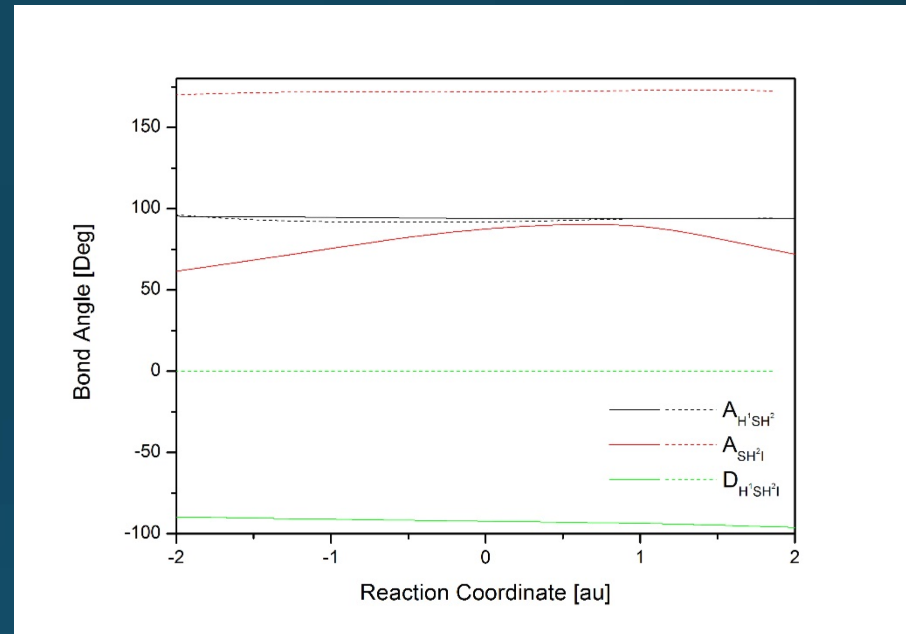
- Gaussian09
- Geometries and frequencies at MP2/aug-cc-pVTZ, iodine with DGZVP
- Energies at CCSD(T)/aug-cc-pVQZ
- IRC
- APUAMA (p. 69)
- Reactants and Products $\Rightarrow$ D_e, ΔH_f, S, C_p, H, α

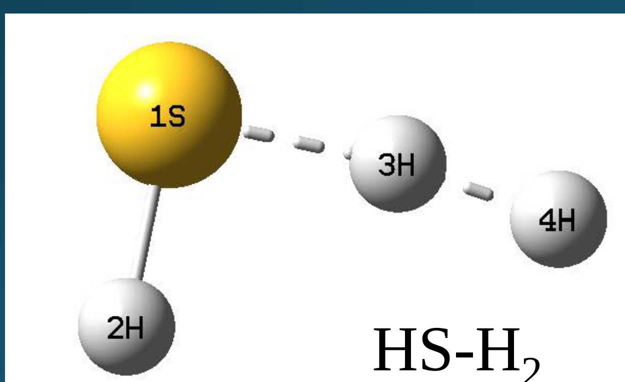
	R [Å]	A [Deg]
HS	1.3466	
HS^+	1.3670	
H_2	0.7431	
HF	0.9210	
HCl	1.2787	
HBr	1.4133	
HI	1.5969	
H_2S	1.3419	92.31
H_2S^+	1.3614	93.08
H_3S^+	1.3537	94.33

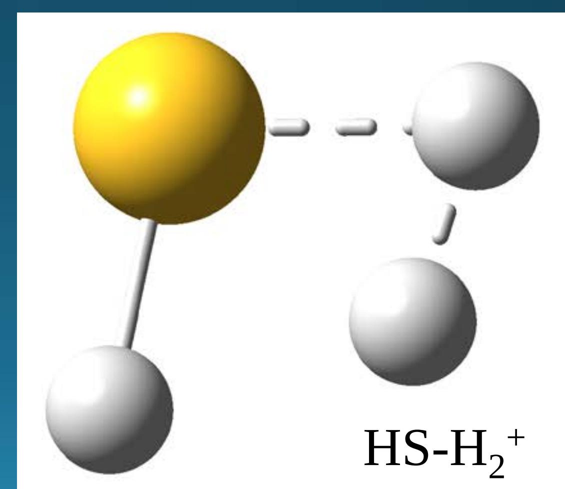
	ω_1	ω_2	ω_3	ω_4	ω_5	ω_6
H_2	4400.44					
HBr	2696.15					
HCl	2992.74					
HF	4125.47					
HI	2391.05					
HS	2685.91					
HS^+	2568.28					
H_2S	1206.28	2710.87	2727.33			
H_2S^+	1185.75	2590.71	2597.93			
H_3S^+	1058.31	1222.50	1222.83	2626.53	2634.38	2634.39
HS-H_2	-1695.19	481.74	533.72	1115.00	1401.81	2767.15
HS-HF	-1151.89	570.48	1064.48	1206.95	2414.77	2774.52
HS-HCl	-1129.49	243.98	460.96	1033.34	1667.44	2764.15
HS-HBr	-1344.79	191.56	428.55	880.58	1099.35	2757.32
HS-HI	-1321.67	158.90	257.39	413.00	751.55	2744.59
HS-H_2^+	-1323.64	829.24	1354.59	2003.99	2381.60	2569.03
HS-HF^+	-1651.22	669.41	867.75	945.73	2080.57	2665.18
HS-HCl^+	-1215.39	497.89	699.06	903.15	1929.47	2677.56
HS-HBr^+	-1106.53	407.14	617.33	863.70	1908.39	2685.26
HS-HI^+	-1190.34	336.65	585.12	810.35	1647.87	2711.26

$HS+H_2=H_2S+H$ or $HS^++HF=H_3S^+$

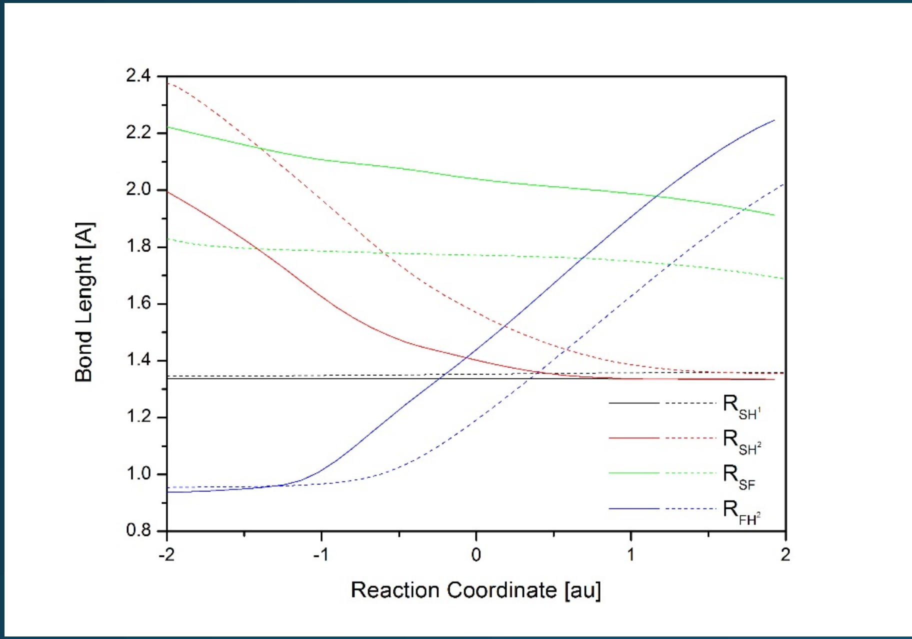


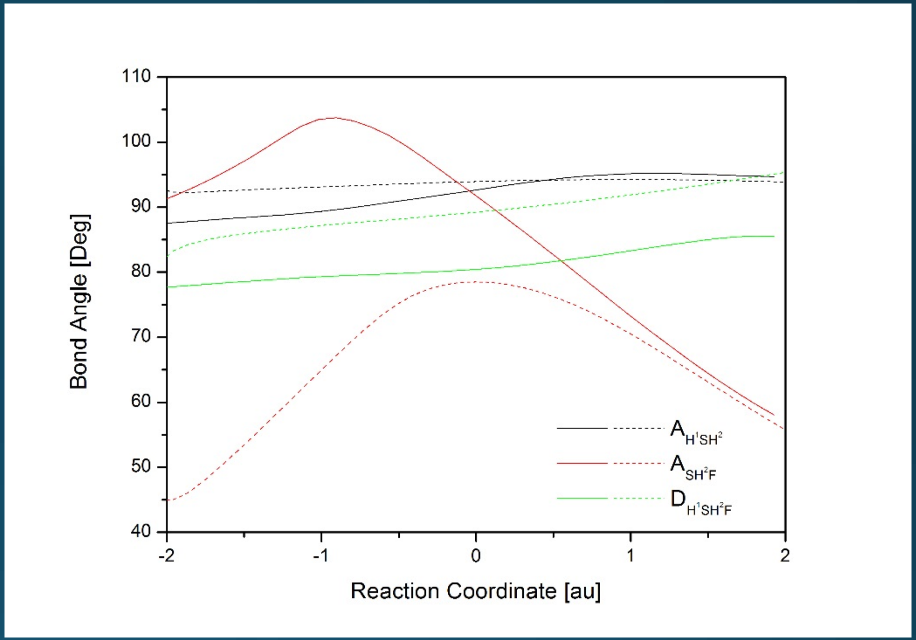


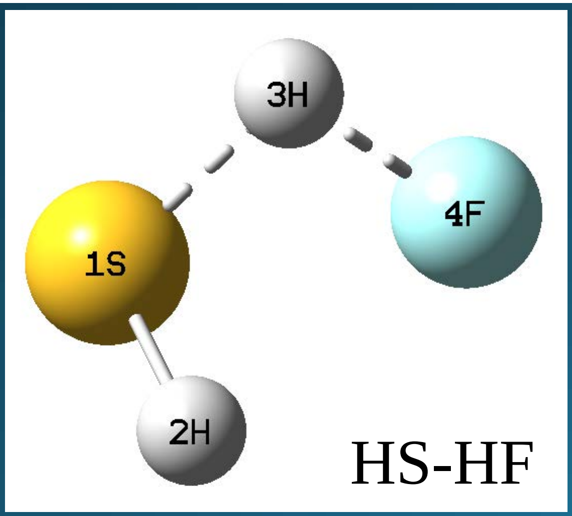


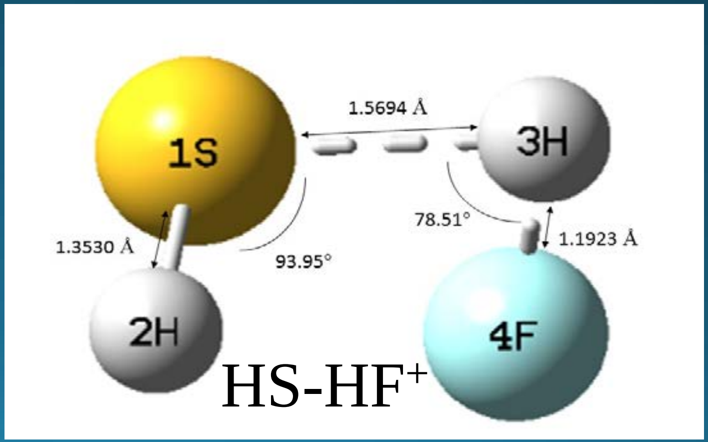


$HS+HF=H_2S+F$ or $HS^+ + H2 = H_2S^+ + F$

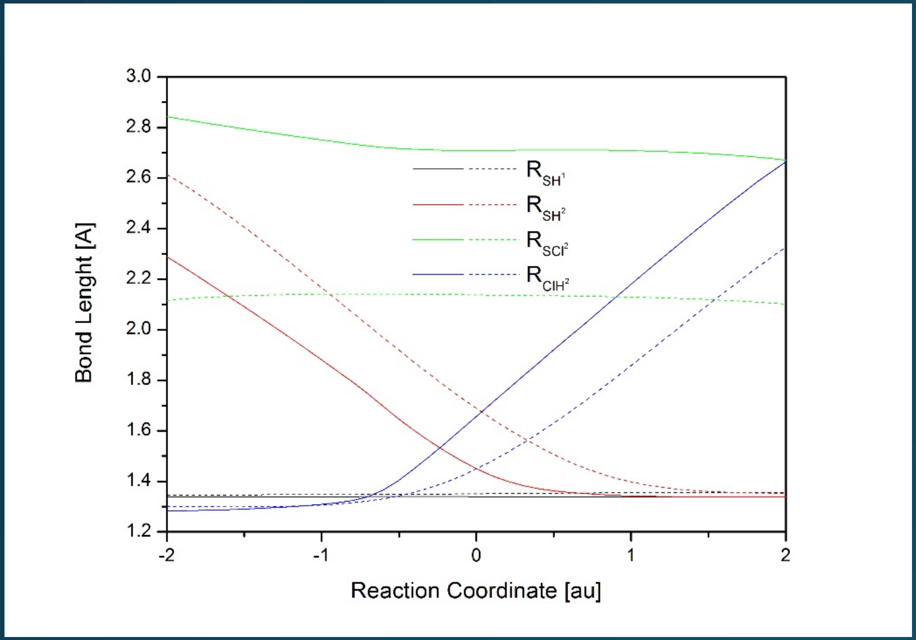


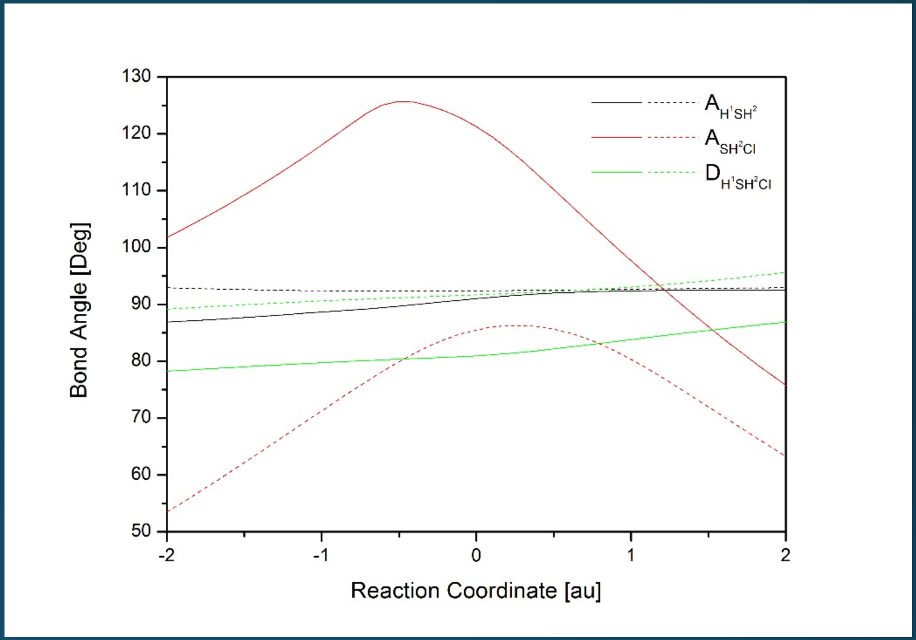


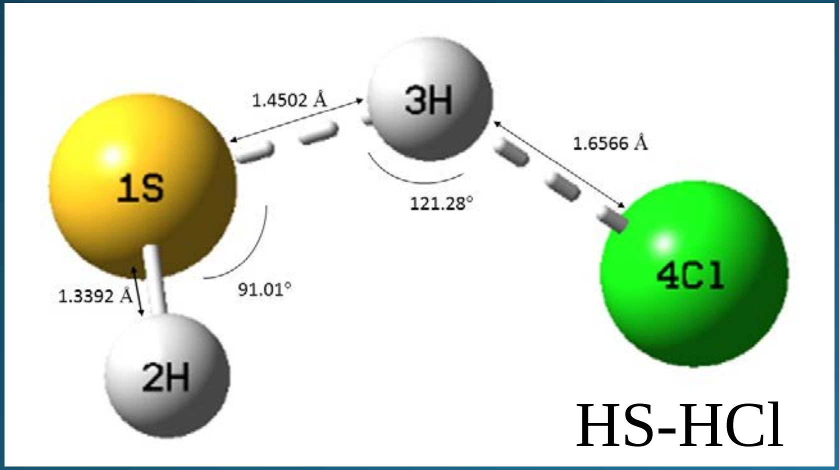


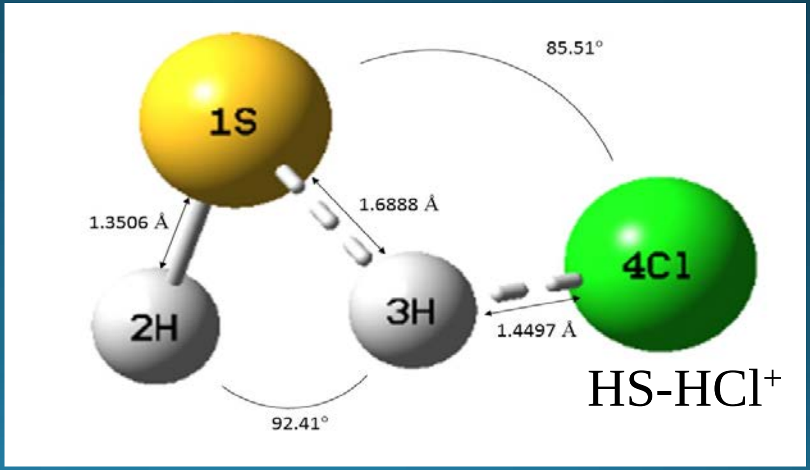


$HS+HCl=H_2S+Cl$ or $HS^+ + HCl=H_2S^+ + Cl$

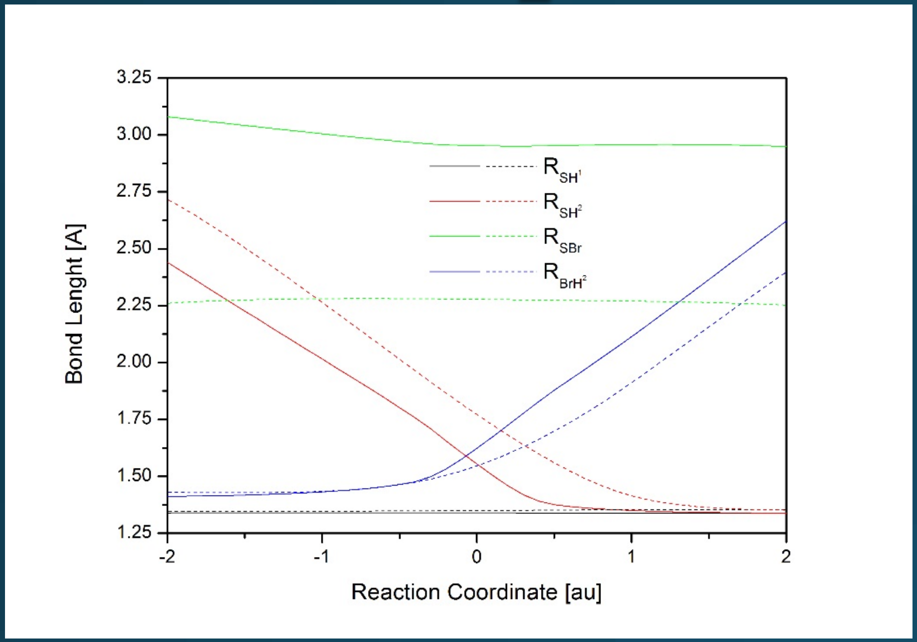


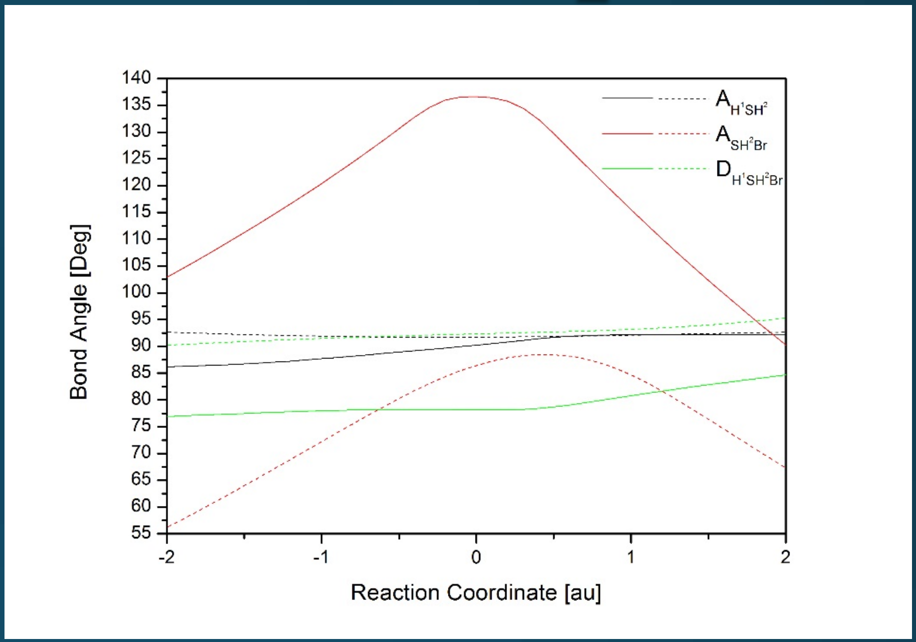


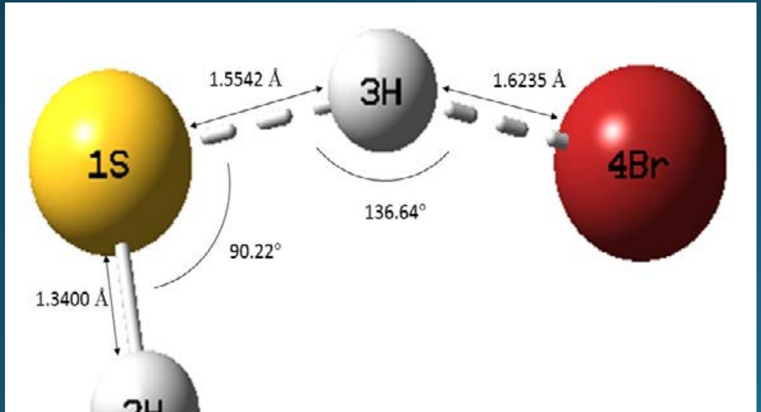




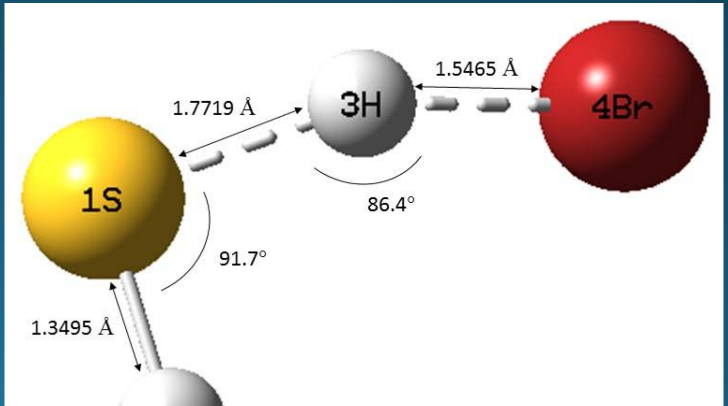
$HS+HBr=H_2S+Br$ or $HS^+ + HBr=H_2S^+ + Br$





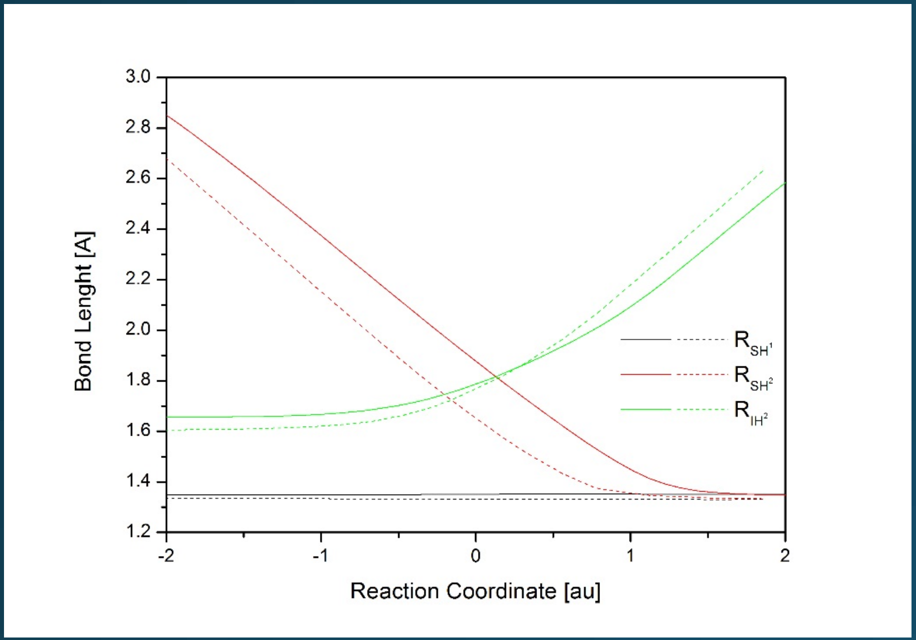


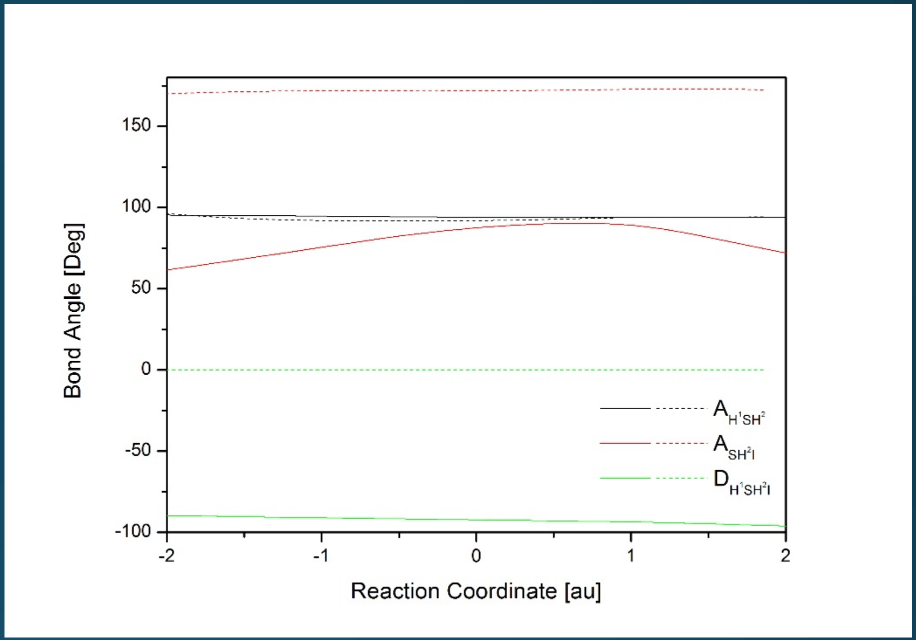
HS-HBr

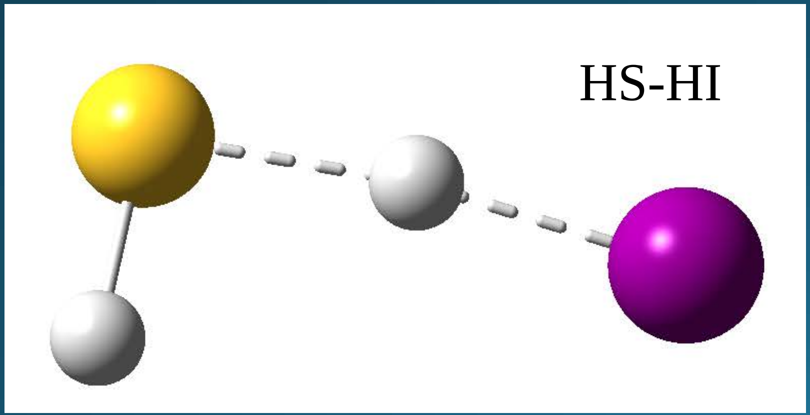


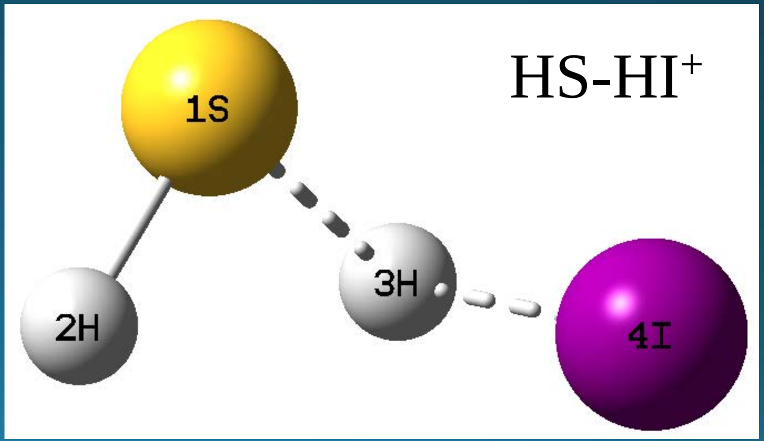
$HS-HBr^+$

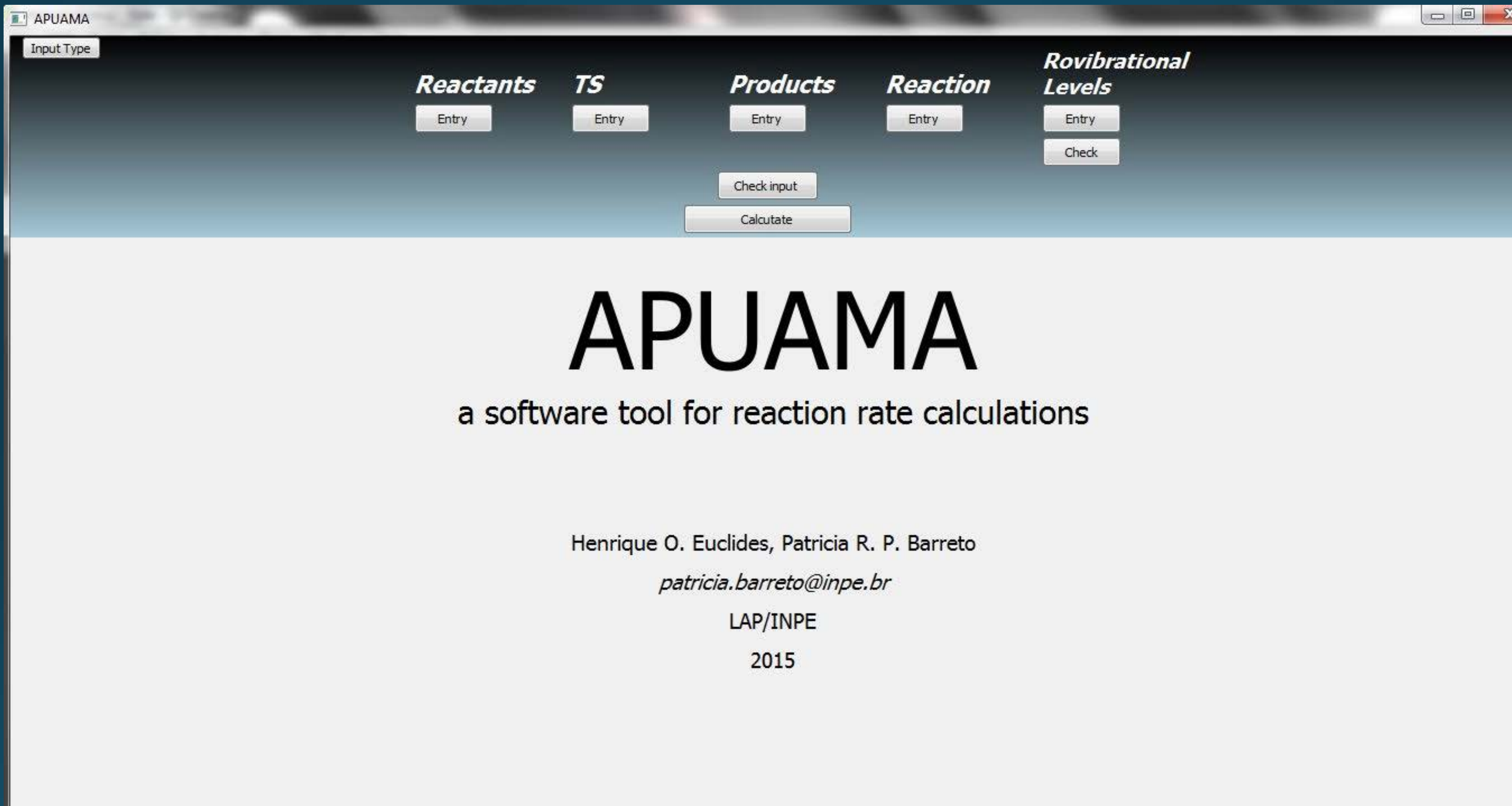
$HS + HI = H_2S + I$ or $HS^+ + HI = H_2S^+ + I$










APUAMA
Input Type
Reactants
Entry
TS
Entry
Products
Entry
Reaction
Entry
Rovibrational Levels
Entry
Check
Check input
Calcutate
APUAMA
a software tool for reaction rate calculations
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2015

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A simple program to determine the reaction rate and thermodynamic properties of reacting system

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Abstract

We developed a simple program to determine the reaction rate by using conventional transition state theory with the Wigner transmission coefficient and also the thermodynamic properties of the species. The hydrogen abstraction in the reaction $NH_3 + H \rightarrow NH_2 + H_2$ is used as a model to demonstrate the program usage. The rate constants have been computed for the gas-phase chemical reaction over the temperature range of 200–4000 K. Our data are in a good agreement with the published data for this reaction.

PACS: 82.20.Pm; 82.20.Db; 82.20.Wt; 82.30.Hk; 82.30.Lp; 51.30. + i; 82.60. − s

Keywords: Kinetics; Thermal rate constants; Conventional transition state theory; Direct dynamics; Bimolecular abstraction; GAUSSIAN 98; Thermodynamic properties

Theoretical Study of the Reactions $BF_3 + BX$, Where X = H or N

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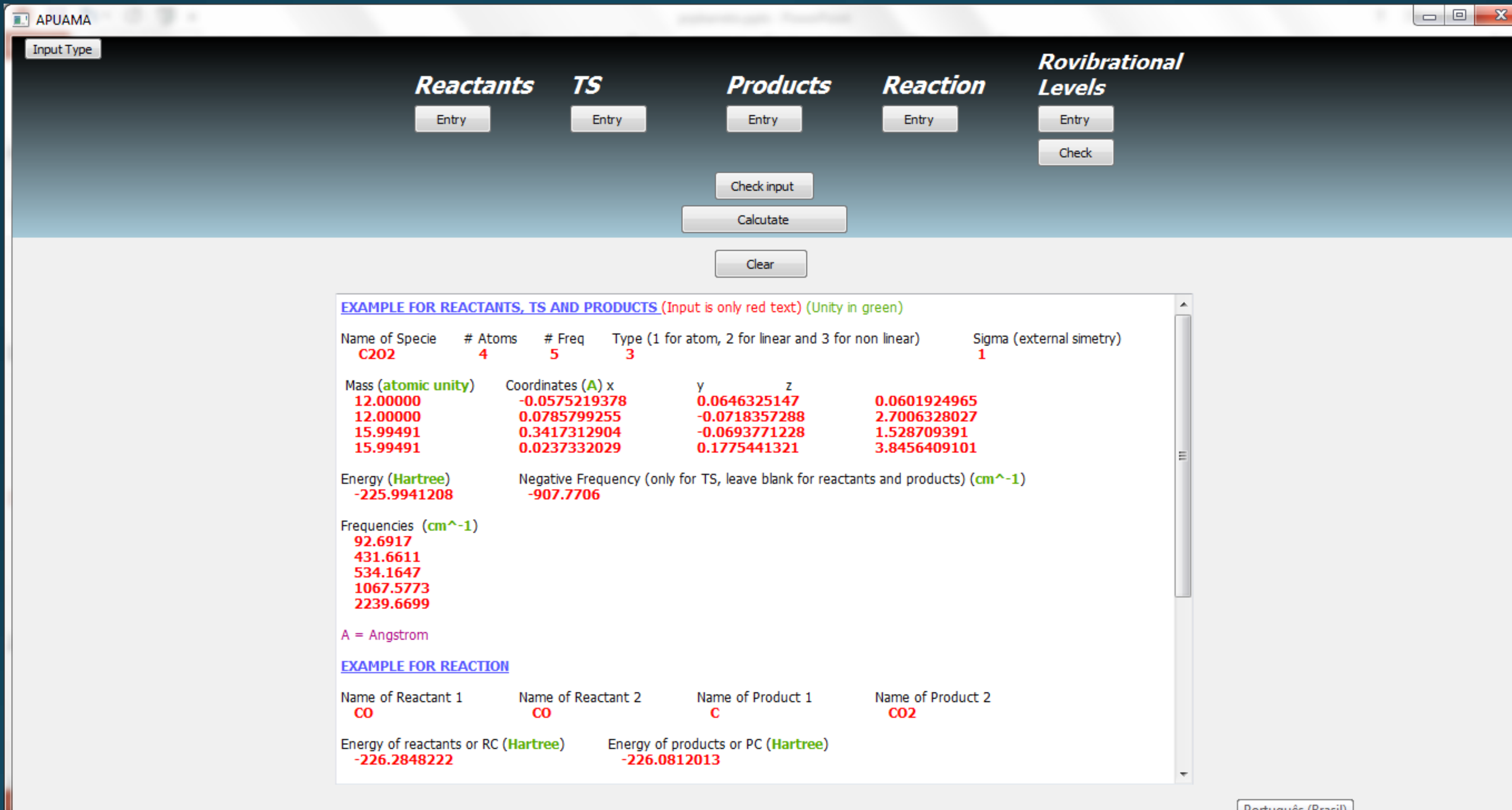
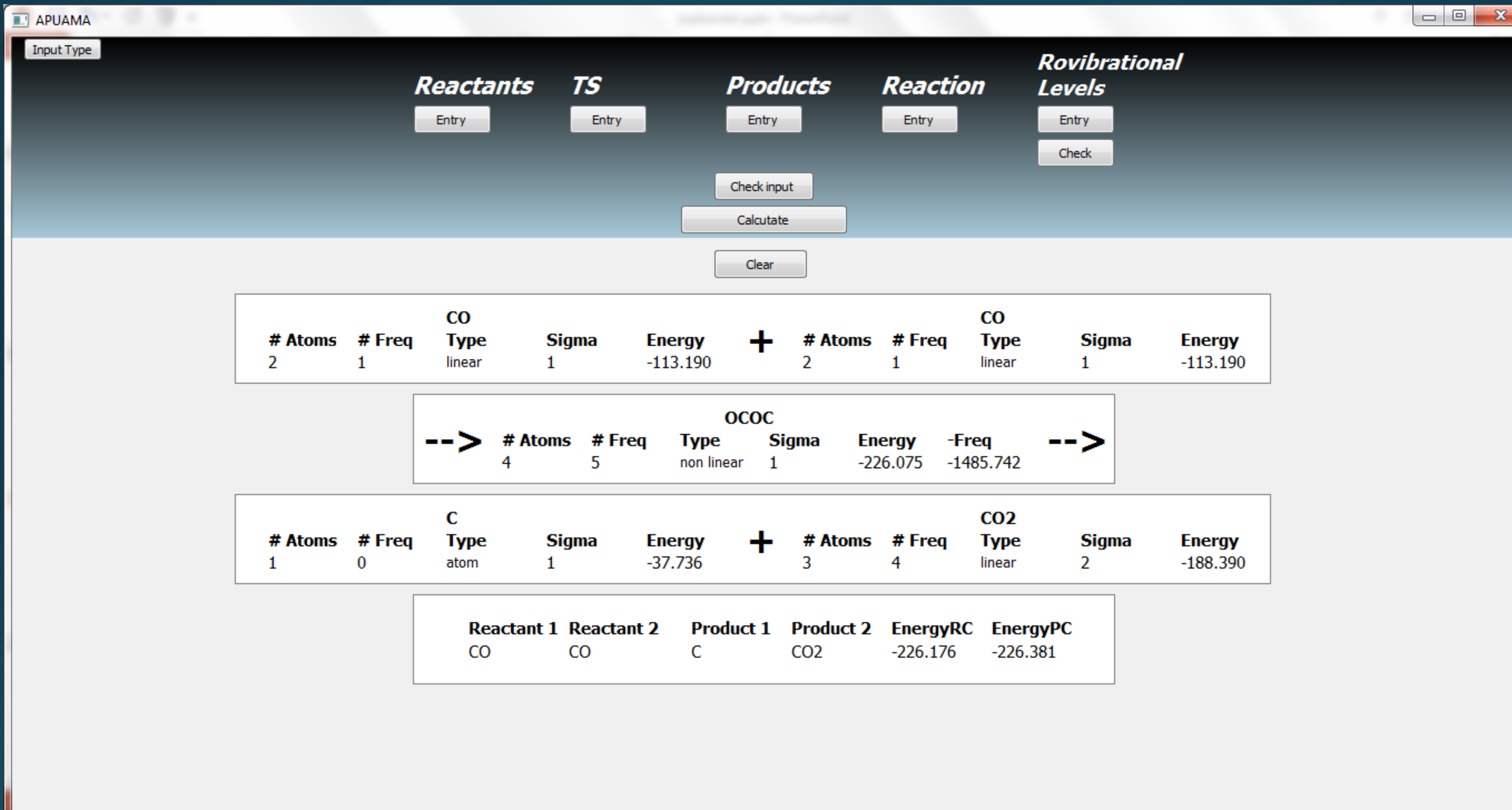
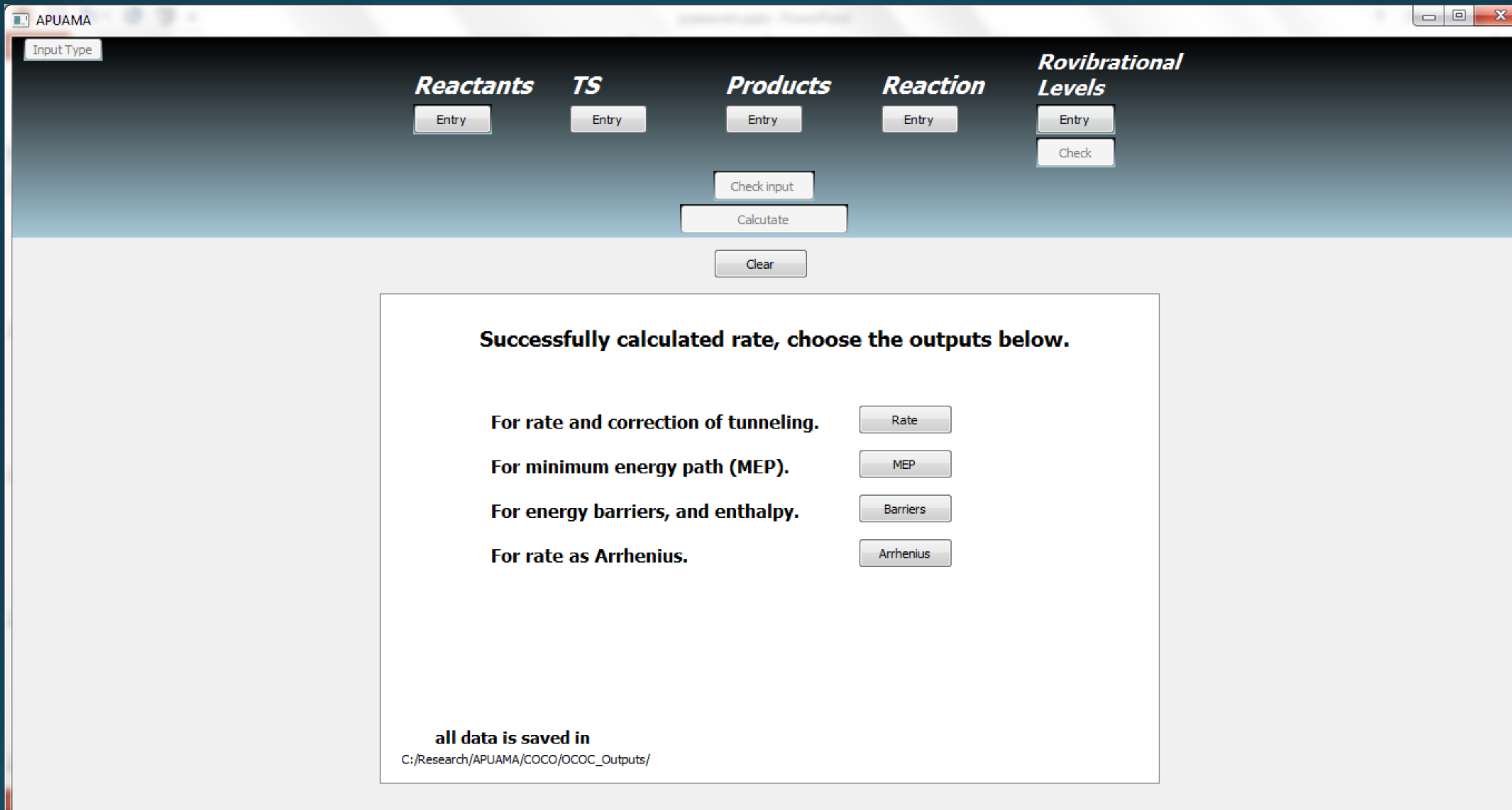
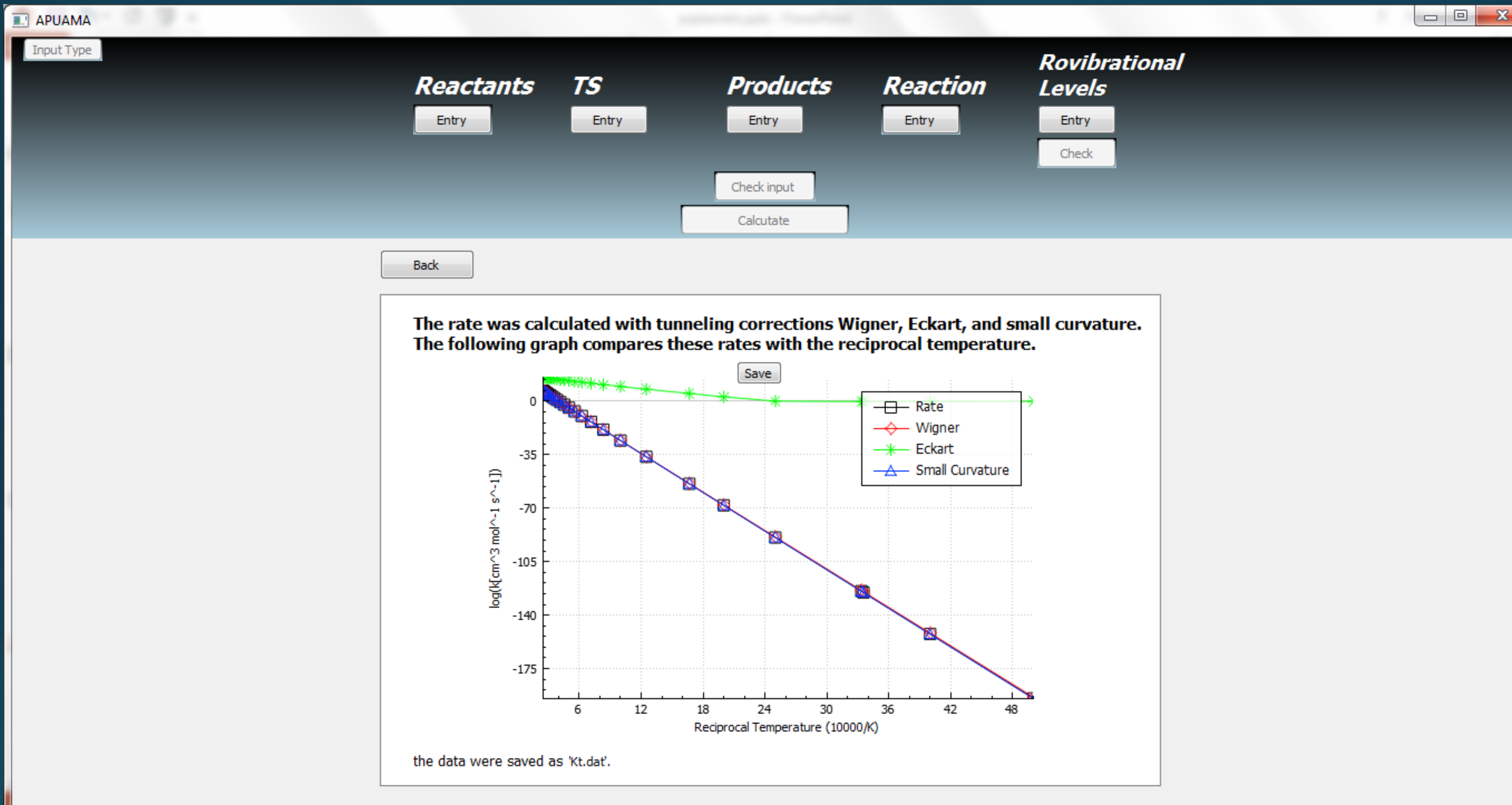
ABSTRACT: This work presents the rate constant for the gas-phase reaction BF_3 + BX, where X = H or N, over the temperature range of 200–4,000 K. Conventional transition state theory (TST) is used to study these reactions. Geometries, frequencies, and the potential energy for reactant, products, and saddle point are obtained from accurate electronic structure calculations performed with the GAUSSIAN 98 program. The reaction rate for these reactions are determined using a simple code developed for this task. Int J Quantum Chem 103: 685–694, 2005

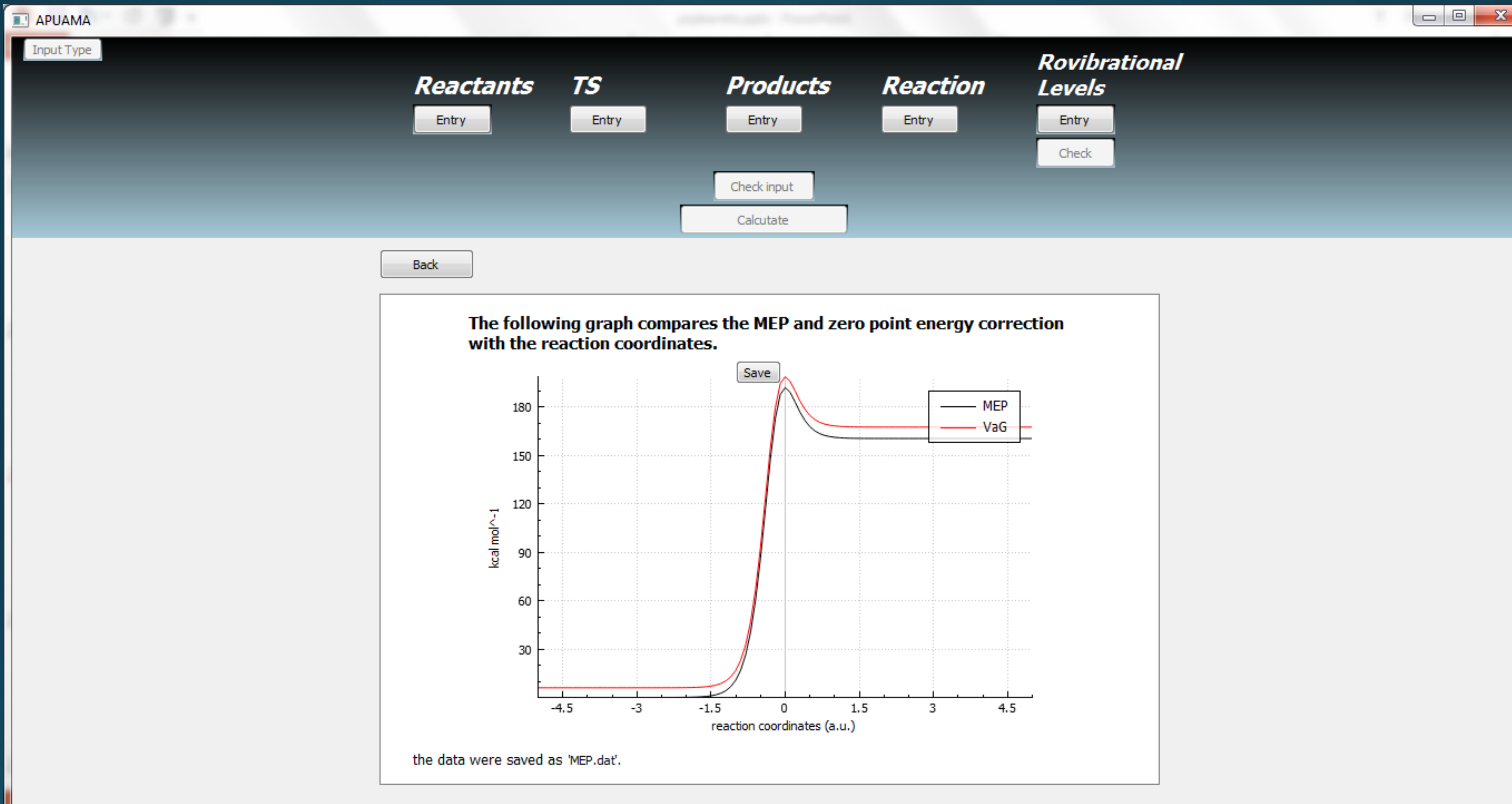

APUAMA
Input Type
Reactants
TS
Products
Reaction
Rovibrational Levels
Entry
Entry
Entry
Entry
Entry
Check
Check input
Calcutate
Clear
EXAMPLE FOR REACTANTS, TS AND PRODUCTS (Input is only red text) (Unity in green)
Name of Specie # Atoms # Freq Type (1 for atom, 2 for linear and 3 for non linear) Sigma (external simetry)
C2O2 4 5 3 1
Mass (atomic unity) Coordinates (A) x y z
12.00000 -0.0575219378 0.0646325147 0.0601924965
12.00000 0.0785799255 -0.0718357288 2.7006328027
15.99491 0.3417312904 -0.0693771228 1.528709391
15.99491 0.0237332029 0.1775441321 3.8456409101
Energy (Hartree) Negative Frequency (only for TS, leave blank for reactants and products) (cm^-1)
-225.9941208 -907.7706
Frequencies (cm^-1)
92.6917
431.6611
534.1647
1067.5773
2239.6699
A = Angstrom
EXAMPLE FOR REACTION
Name of Reactant 1 Name of Reactant 2 Name of Product 1 Name of Product 2
CO CO C CO2
Energy of reactants or RC (Hartree) Energy of products or PC (Hartree)
-226.2848222 -226.0812013
Português (Brasil)

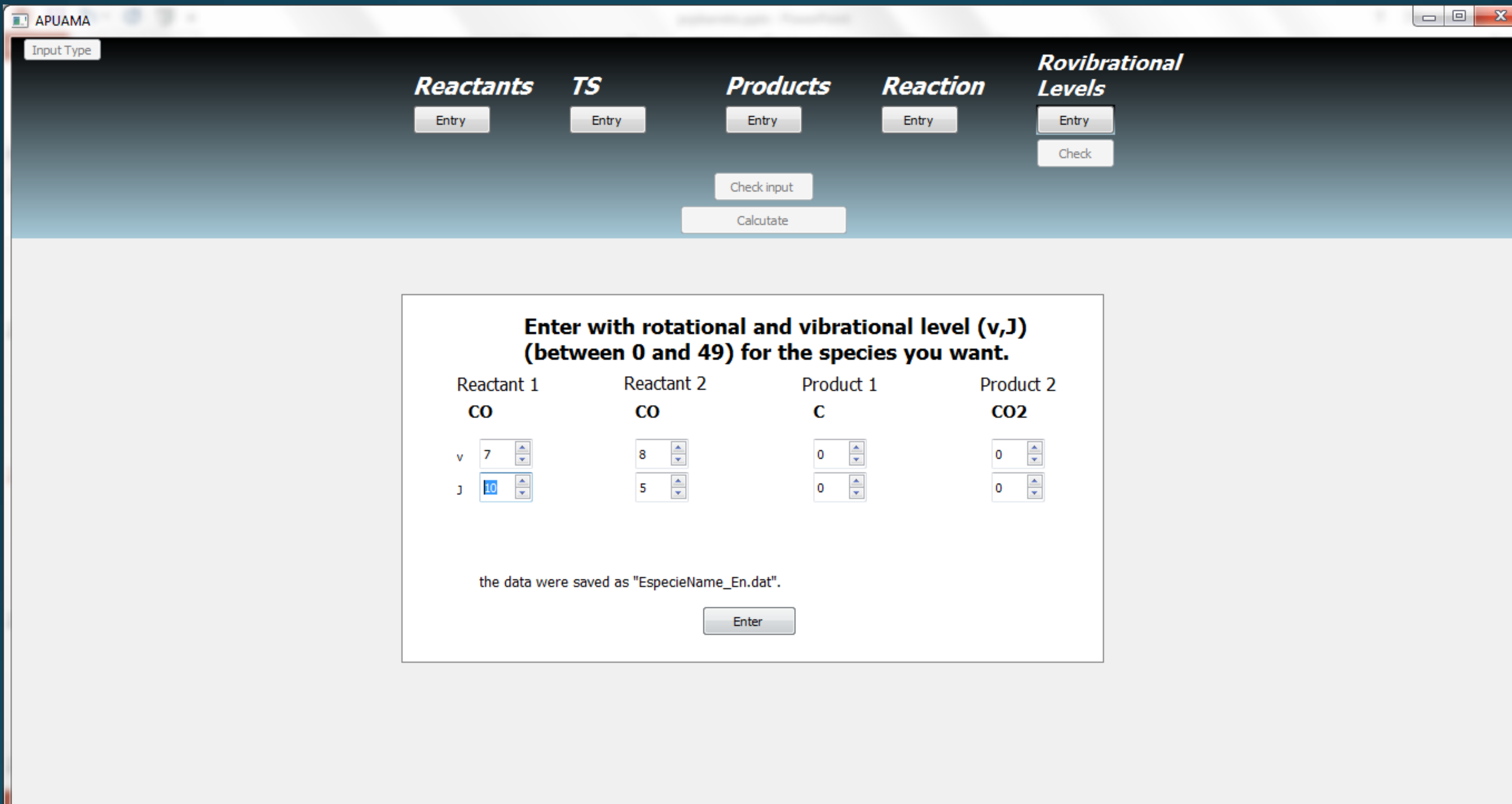

APUAMA
Input Type
Reactants
Entry
TS
Entry
Products
Entry
Reaction
Entry
Rovibrational Levels
Entry
Check
Check input
Calcutate
Clear
CO
Atoms # Freq Type Sigma Energy
2 1 linear 1 -113.190
+
CO
Atoms # Freq Type Sigma Energy
2 1 linear 1 -113.190
-->
OCOC
Atoms # Freq Type Sigma Energy -Freq
4 5 non linear 1 -226.075 -1485.742
-->
C
Atoms # Freq Type Sigma Energy
1 0 atom 1 -37.736
+
CO2
Atoms # Freq Type Sigma Energy
3 4 linear 2 -188.390
Reactant 1 Reactant 2 Product 1 Product 2 EnergyRC EnergyPC
CO CO C CO2 -226.176 -226.381

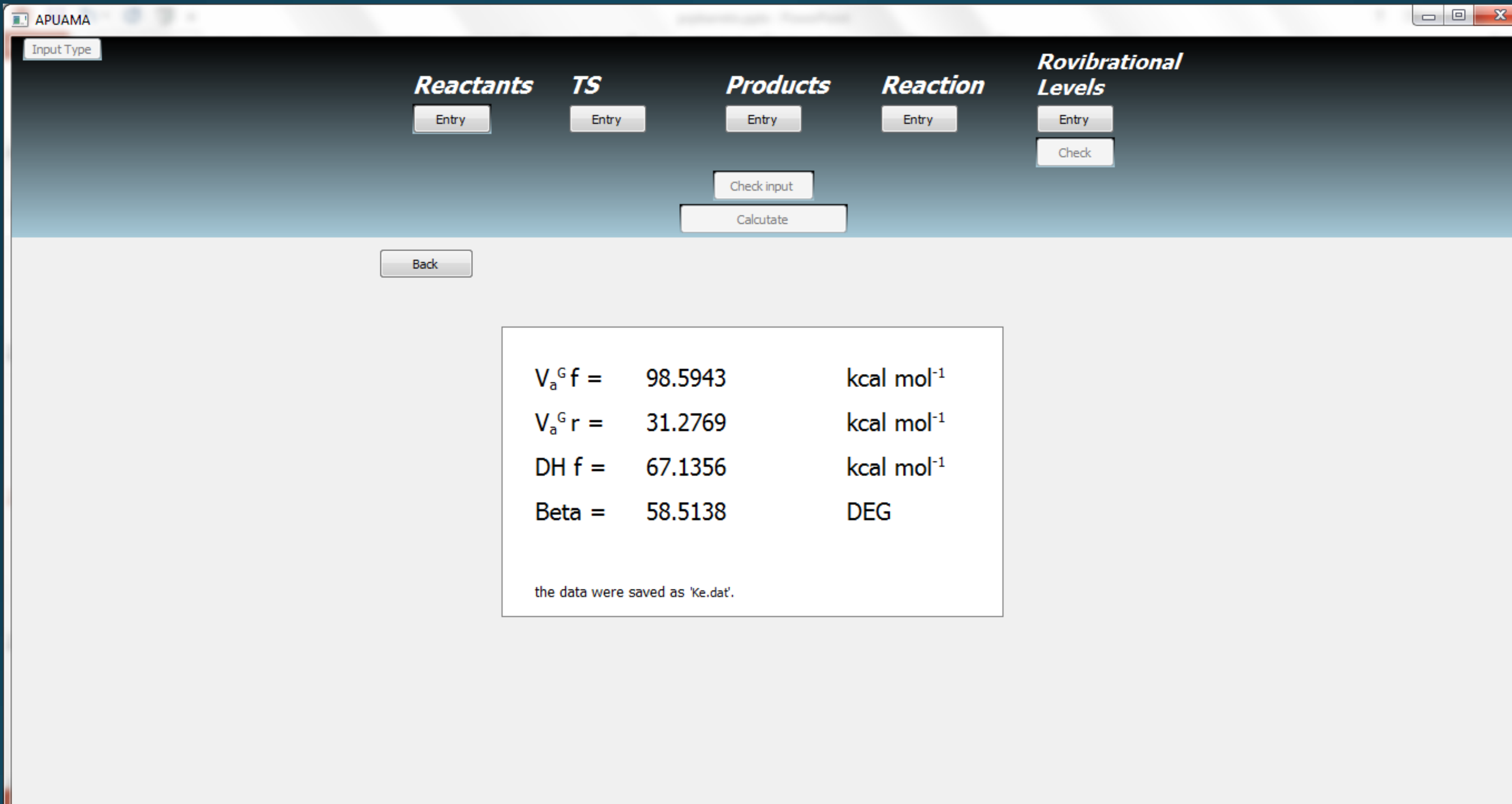


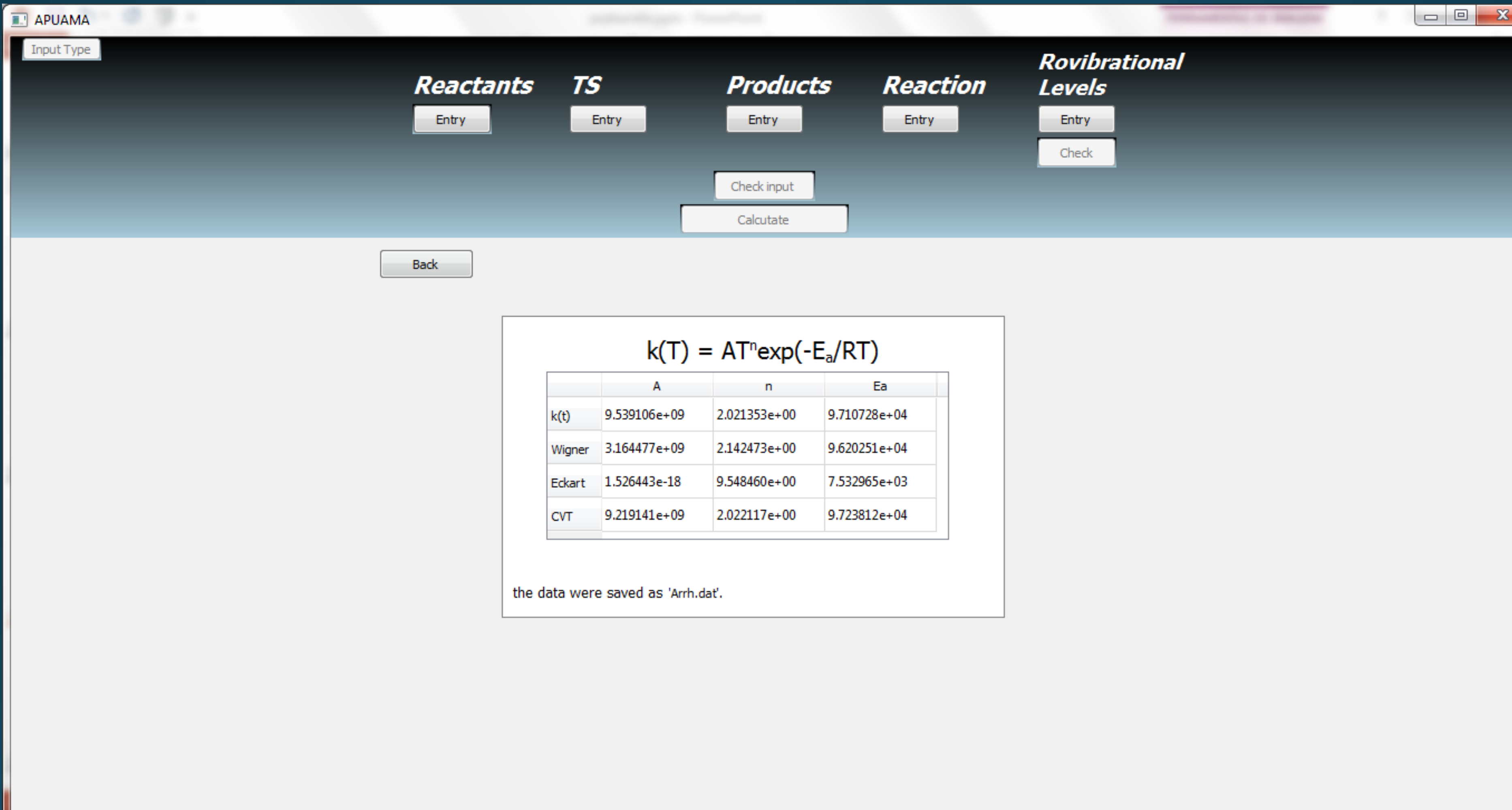
APUAMA
Input Type
Reactants
Entry
TS
Entry
Products
Entry
Reaction
Entry
Rovibrational Levels
Entry
Check
Check input
Calcutate
Clear
Successfully calculated rate, choose the outputs below.
For rate and correction of tunneling.
Rate
For minimum energy path (MEP).
MEP
For energy barriers, and enthalpy.
Barriers
For rate as Arrhenius.
Arrhenius
all data is saved in
C:/Research/APUAMA/COCO/OCOC_Outputs/


APUAMA
Input Type
Reactants
TS
Products
Reaction
Rovibrational Levels
Entry
Entry
Entry
Entry
Entry
Check
Check input
Calcutate
Back
The rate was calculated with tunneling corrections Wigner, Eckart, and small curvature.
The following graph compares these rates with the reciprocal temperature.
Save
Rate
Wigner
Eckart
Small Curvature
log(k[cm^3 mol^-1 s^-1])
0
-35
-70
-105
-140
-175
6
12
18
24
30
36
42
48
Reciprocal Temperature (10000/K)
the data were saved as 'Kt.dat'.


APUAMA
Input Type
Reactants
TS
Products
Reaction
Rovibrational Levels
Entry
Entry
Entry
Entry
Entry
Check
Check input
Calcutate
Back
The following graph compares the MEP and zero point energy correction with the reaction coordinates.
Save
MEP
VaG
kcal mol^-1
180
150
120
90
60
30
-4.5
-3
-1.5
0
1.5
3
4.5
reaction coordinates (a.u.)
the data were saved as 'MEP.dat'.


APUAMA
Input Type
Reactants
Entry
TS
Entry
Products
Entry
Reaction
Entry
Rovibrational Levels
Entry
Check
Check input
Calculate
Enter with rotational and vibrational level (v,J) (between 0 and 49) for the species you want.
Reactant 1
CO
Reactant 2
CO
Product 1
C
Product 2
CO2
v
J
7
10
8
5
0
0
0
0
the data were saved as "EspecieName_En.dat".
Enter

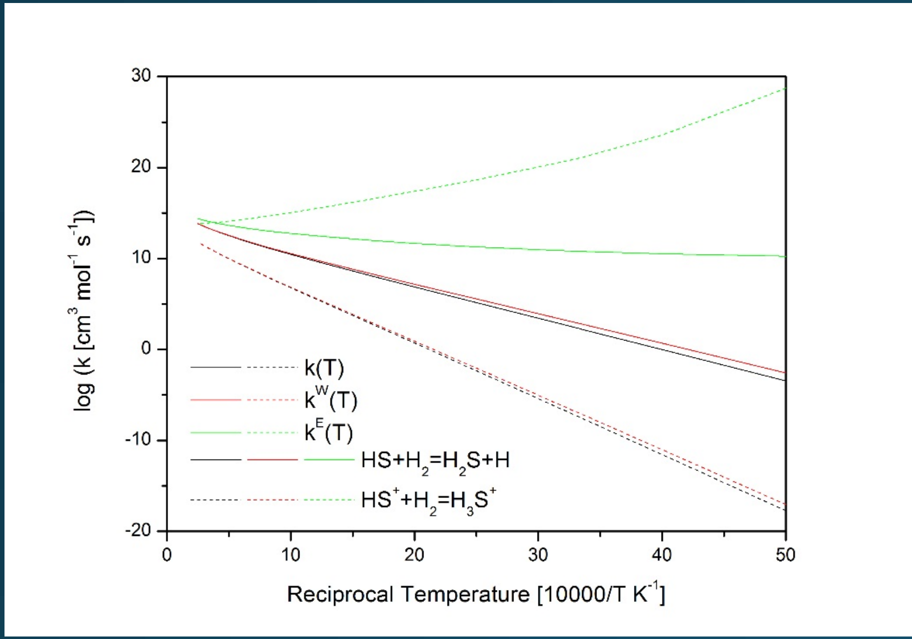

APUAMA
Input Type
Reactants
TS
Products
Reaction
Rovibrational Levels
Entry
Entry
Entry
Entry
Entry
Check
Check input
Calcutate
Back
$V_a^G f =$ 98.5943 kcal mol^{-1}
$V_a^G r =$ 31.2769 kcal mol^{-1}
DH f = 67.1356 kcal mol^{-1}
Beta = 58.5138 DEG
the data were saved as 'Ke.dat'.

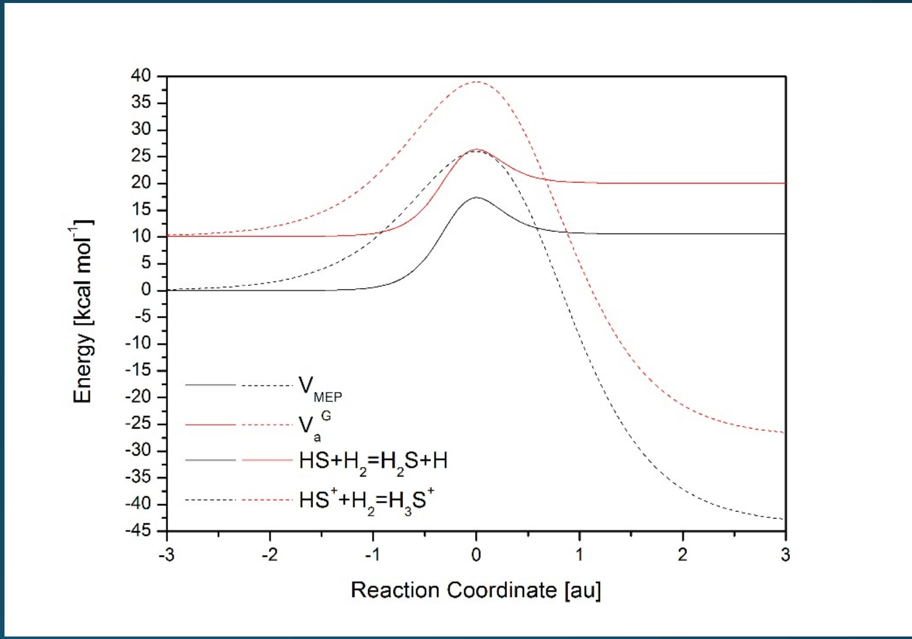


	A	n	Ea
k(t)	9.539106e+09	2.021353e+00	9.710728e+04
Wigner	3.164477e+09	2.142473e+00	9.620251e+04
Eckart	1.526443e-18	9.548460e+00	7.532965e+03
CVT	9.219141e+09	2.022117e+00	9.723812e+04

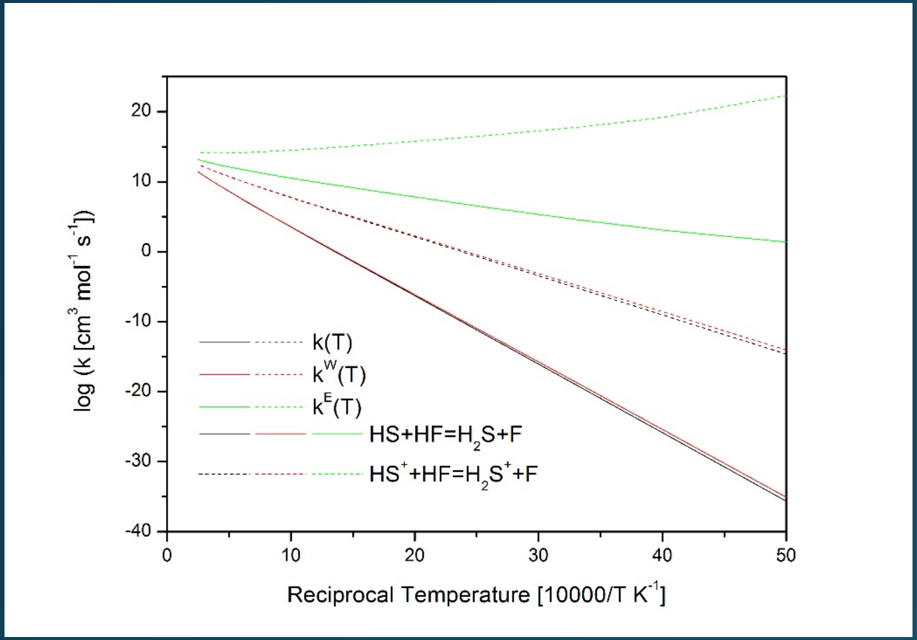
OCOC_(07,05)_(08,02)_Outputs
OCOC_(07,10)_(08,05)_Outputs
OCOC_(08,02)_(10,05)_Outputs
OCOC_(09,07)_(10,05)_Outputs
OCOC_(10,10)_(10,10)_Outputs
OCOC_Outputs
co.in.dat
produtos.dat
reacao.dat
reagentes.dat
ts1.dat

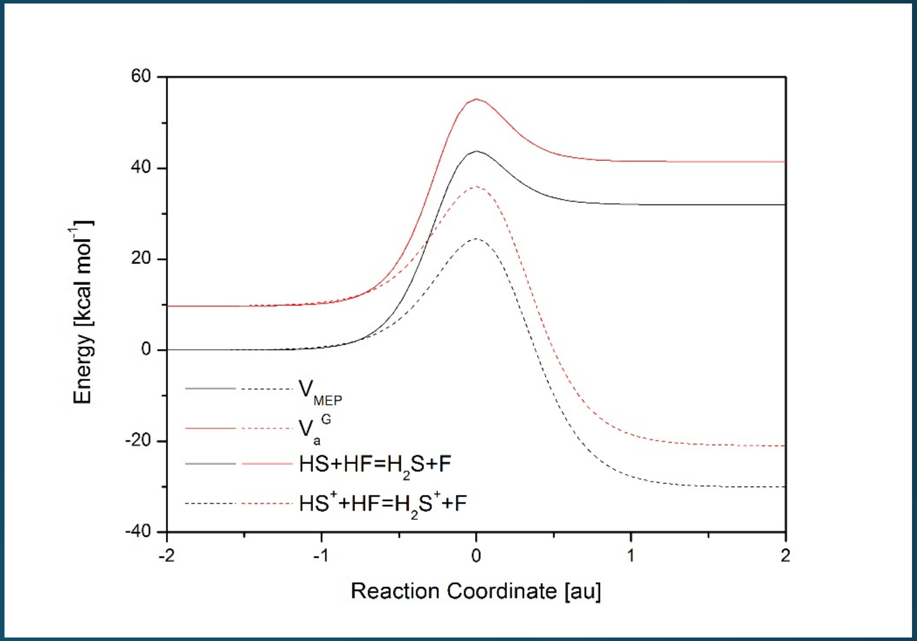
$HS+H_2=H_2S+H$ or $HS^++HF=H_3S^+$



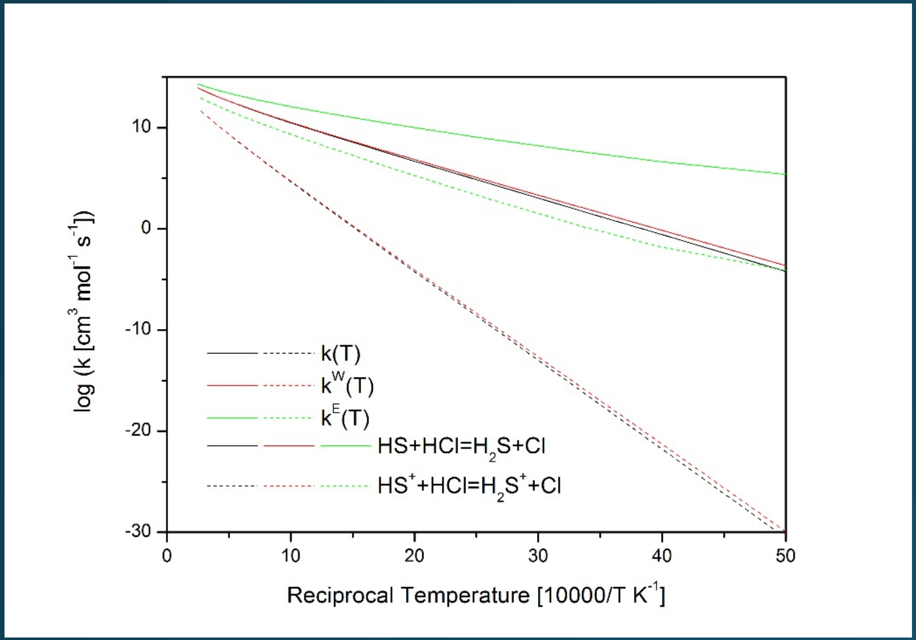


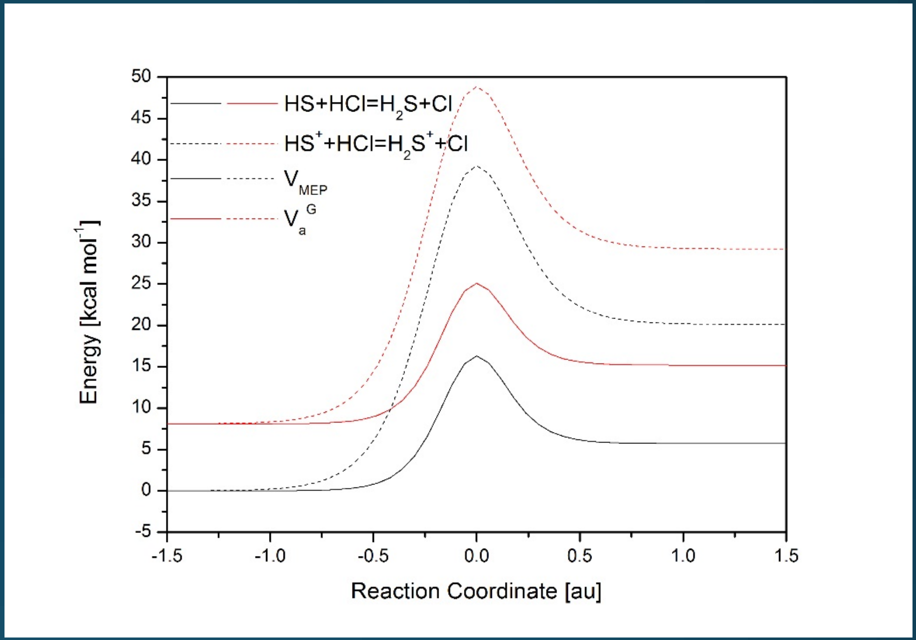
HS+HF=H_2S+F or HS^++H2=H_2S^++F



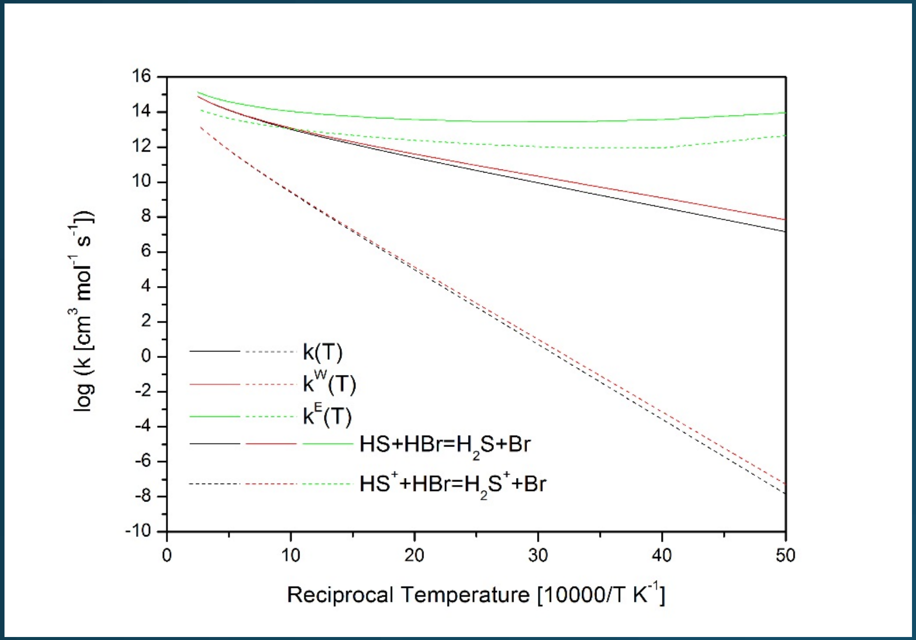


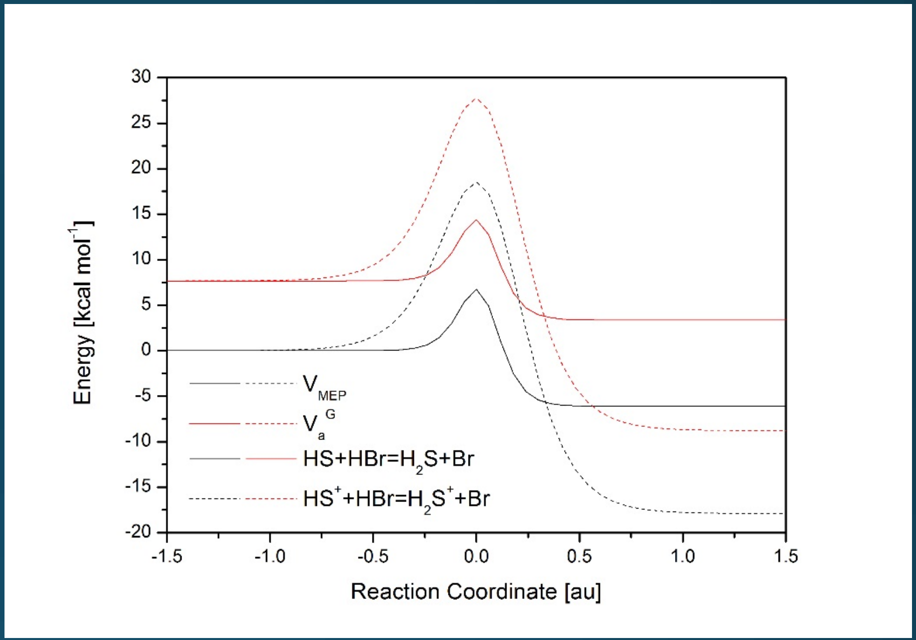
$HS+HCl=H_2S+Cl$ or $HS^{+}+HCl=H_2S^{+}+Cl$



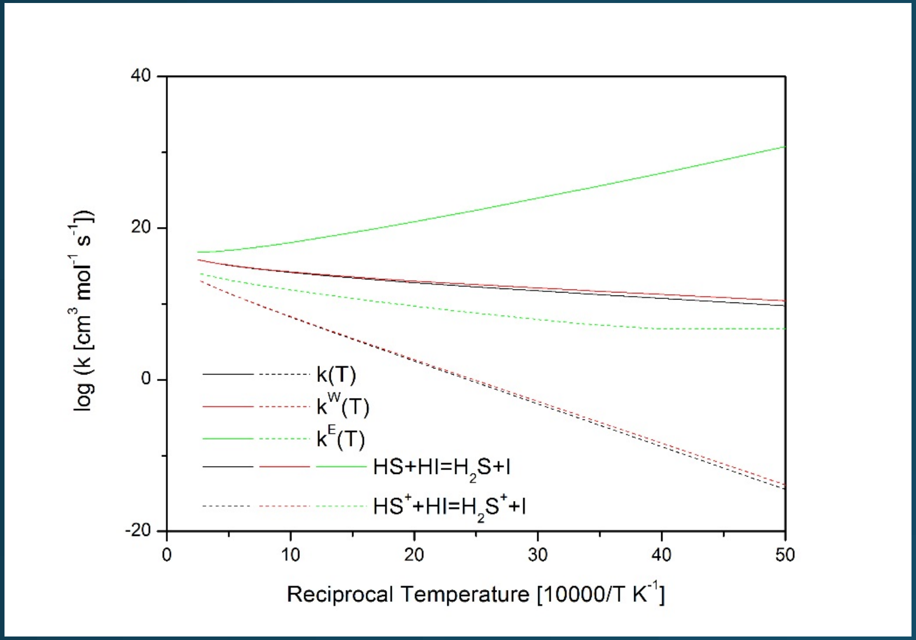


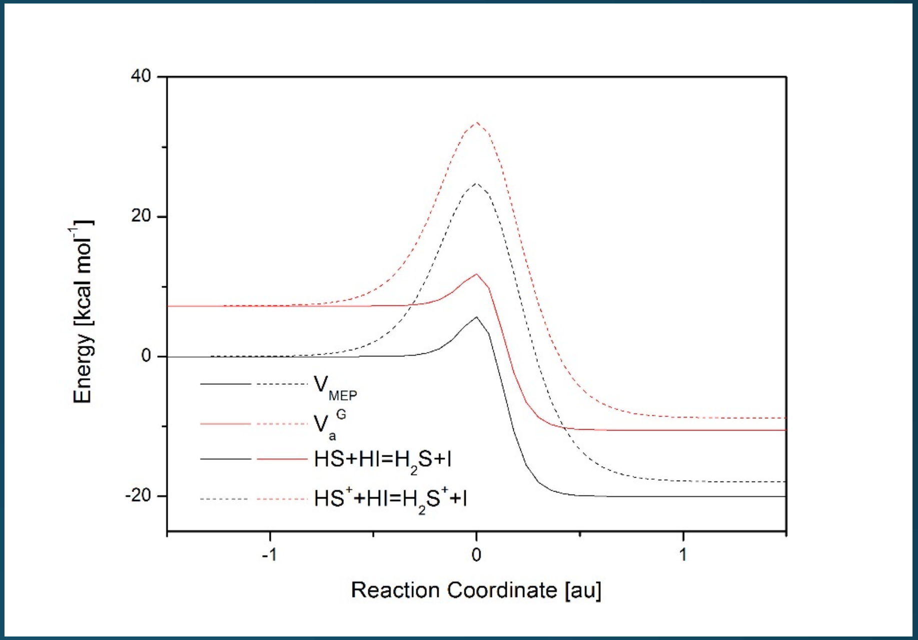
$HS+HBr=H_2S+Br$ or $HS^+ + HBr=H_2S^+ + Br$



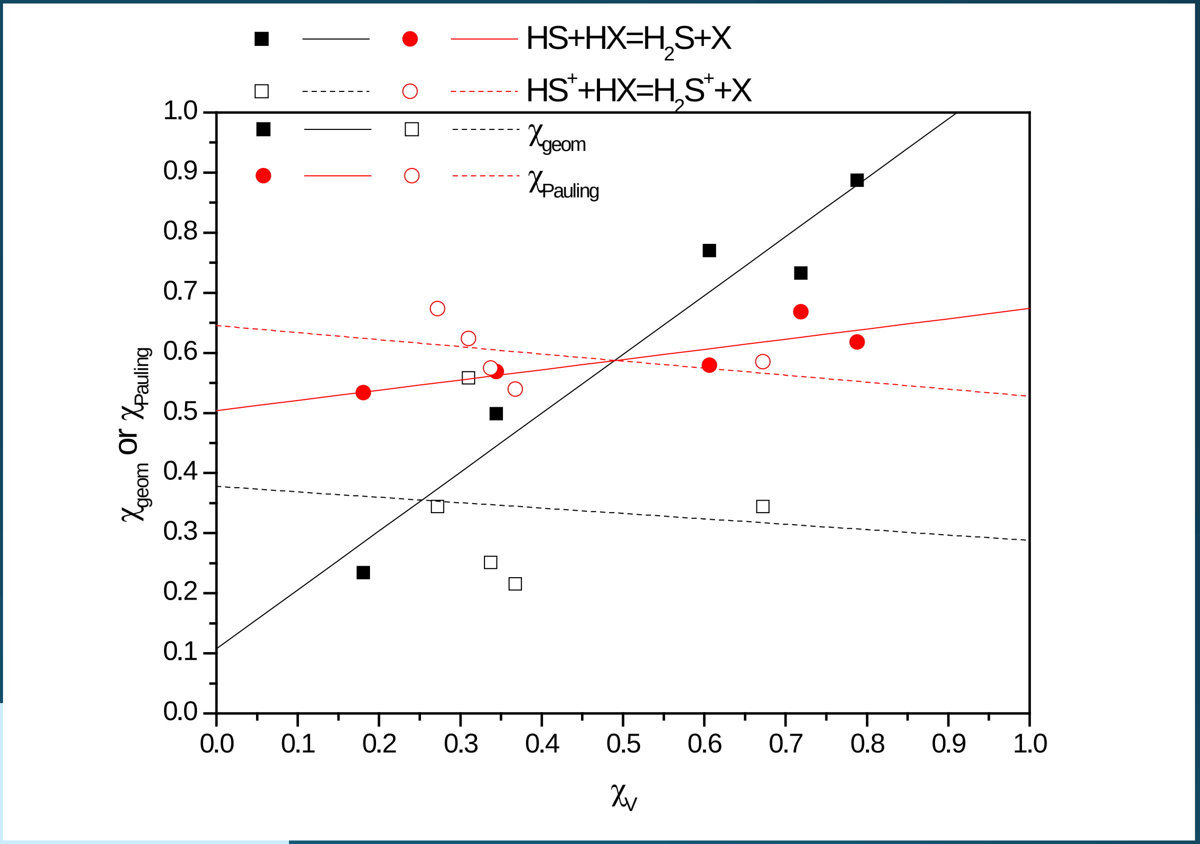


$HS+HI=H_2S+I$ or $HS^++HI=H_2S^++I$





Hammond's Postulate



$$\chi(V) = \frac{V_f^+}{V_f^+ + V_r^+}$$

$$\chi(geom) = \frac{\left(r_1 - r_{1,eq}\right)_b}{\left(r_1 - r_{1,eq}\right)_b + \left(r_2 - r_{2,eq}\right)_m}$$

$$\chi(Pauling) = \frac{n_m}{n_m + n_b}, \qquad n = \exp\left[-\beta\left(r - r_{eq}\right)\right]$$

Arrheius rate

	Conventional			Wigner			Eckart		
TS	A	n	Ea	A	n	Ea	A	n	Ea
$HS-H_2$	6.16E+08	1.61	14473.00	2.22E+08	1.72	13474.00	3.85E+05	2.47	1143.00
HS-HF	3.71E+09	1.17	43691.00	1.25E+09	1.29	42976.00	4.59E+06	1.95	9343.60
HS-HCl	3.11E+09	1.47	15548.00	1.06E+09	1.59	14847.00	1.86E+07	2.07	6354.20
HS-HBr	2.06E+09	1.63	5342.90	6.71E+08	1.75	4512.10	7.49E+06	2.28	-1408.60
HS-HI	3.01E+09	1.82	3589.20	9.83E+08	1.95	2771.40	4.59E+07	2.31	-16085.00
$HS-H_2^+$	1.11E+10	0.89	27110.00	3.63E+09	1.01	26291.00	7.58E+02	2.83	-16214.00
$HS-HF^+$	3.71E+09	1.17	24460.00	1.25E+09	1.29	23745.00	2.07E+05	2.32	-9770.10
$HS-HCl^+$	1.48E+09	1.35	39102.00	4.88E+08	1.48	38347.00	8.31E+04	2.50	14353.00
$HS-HBr^+$	2.37E+09	1.36	18528.00	8.14E+08	1.48	17842.00	1.74E+06	2.21	-635.64
$HS-HI^+$	3.30E+09	1.40	24825.00	1.10E+09	1.52	24085.00	7.07E+04	2.66	4929.70

	A	n	Ea	Ref	Ti	Tf
SH + HBr = Br + H2S	**2.65E+12**		**971.00**	**92NIC/KRE**	**299.00**	**423.00**
Br + H2S = HBr + SH	8.43E+12		2750.00	97DEM/SAN	200.00	300.00
	8.55E+12		2752.00	92NIC/KRE	319.00	431.00
F + H2S = HF + SH	7.71E+13			87SCH/RAH	298.00	00
Cl + H2S = HCl + SH	2.23E+13		-210	97DEM/SAN	200	300
	2.23E+13		-208	97ATK/BAU2	200	430
	2.22E+13		-208	95NIC/WAN	202	430
	6.32E+13			86LU/IYE	232	359
	3.78E+13			85NAV/BRO	211	353
	3.07E+13			84CLY/MAC	296	
	2.41E+13			83CLY/ONO	298	
	4.40E+13			80NES/LEO	298	
	3.61E+13			78BRA/LEO	296	
H + H2S = H2 + SH	1.18E+07	2.1	352	92YOS/KOS	293	2237
	4.46E+11			83CLY/ONO	298	8
	1.08E+13		1500	82ROT/LOH	1965	2560
	5.18E+11			80HUS/SLA	300	
	4.82E+11			79WOJ/BAJ	298	
	5.00E+11			79NIC/AMO	295	
	2.75E+13		330	77PRA/ROG	808	937
	9.04E+12		855	73SCH2	190	500
	5.00E+11			73BRA/TRU	298	298
	2.29E+11			72ROM/SCH	298	
	7.76E+12		860	71KUR/PET	190	464
	1.02E+13		845	70MIH/SCH	243	368
	1.93E+12			70CUP/GLA	295	
	7.69E+11			69PER/FRA	298	

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FAPESP

CAPES

CNPq

Thank you

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