Experimental Characterization of Low-temperature Surface Reactions for Astrochemistry

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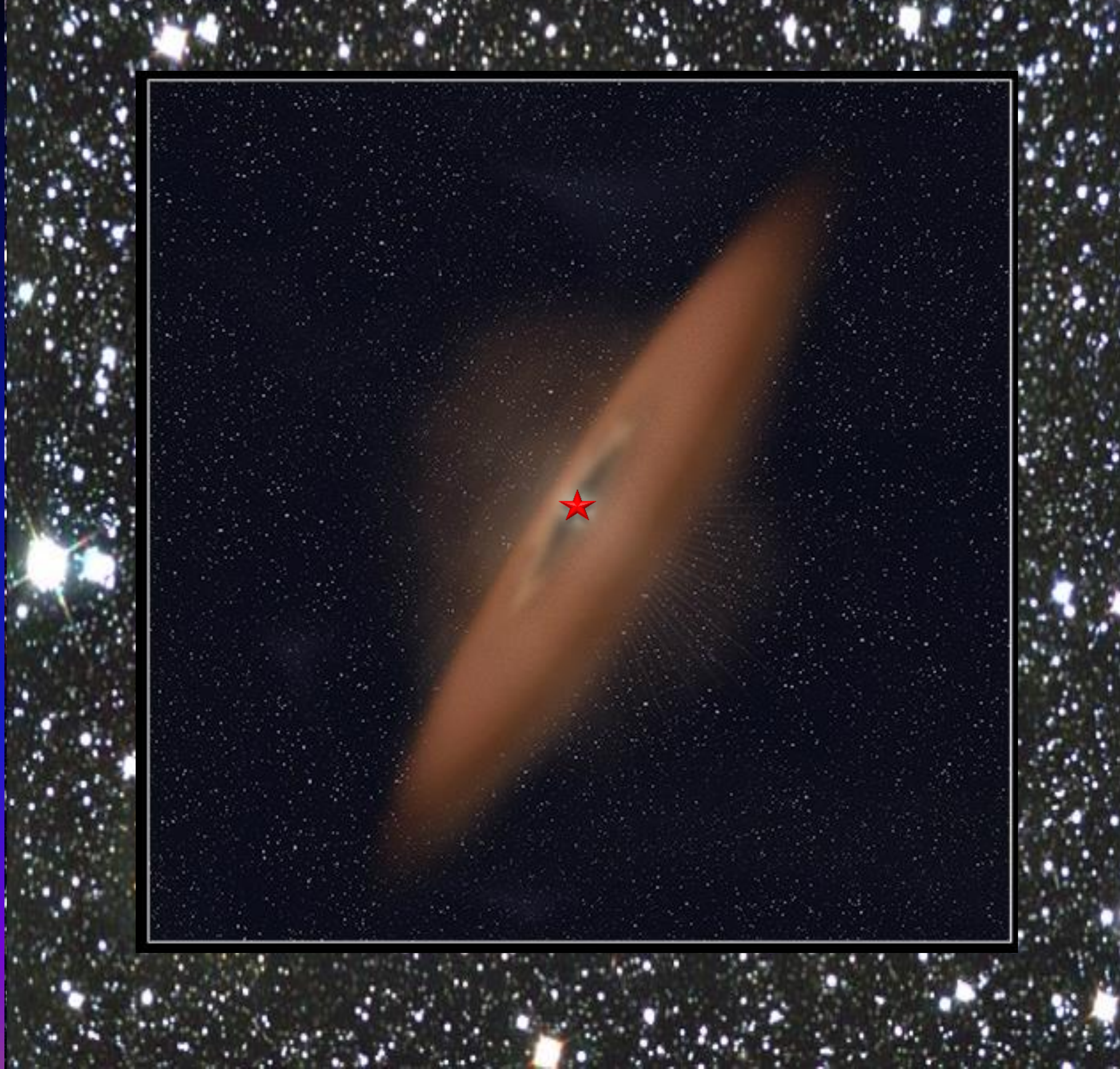
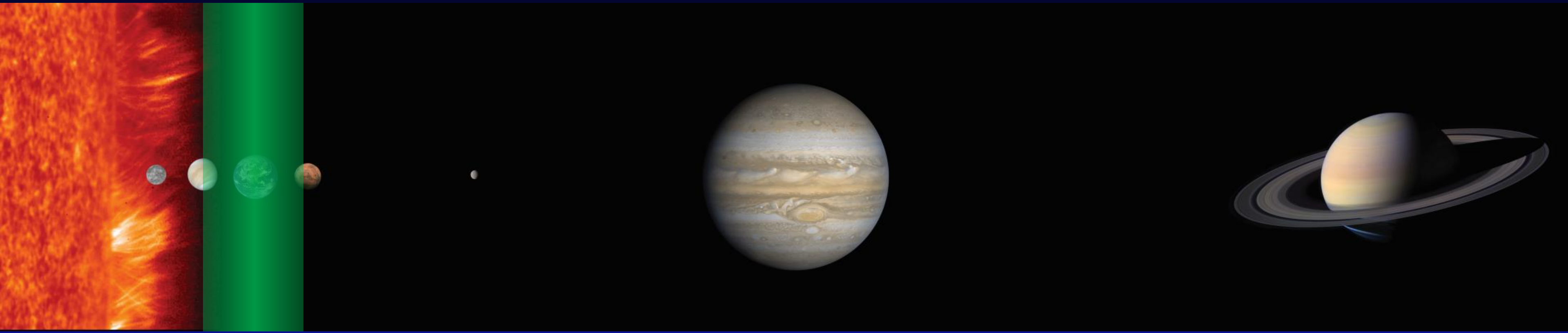
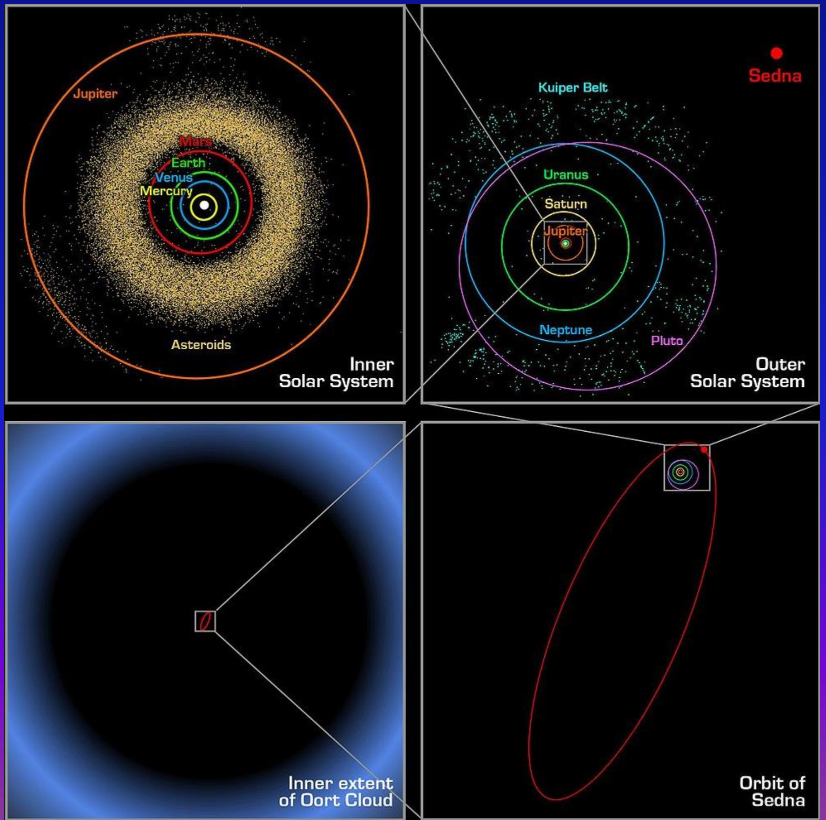
Dark molecular clouds T ~ 10 K



Volatiles in Habitable Planets



- No volatiles condense in the habitable zone
- Volatiles have to be delivered later
- They are likely delivered from the distant areas
- The delivery of pristine IS dust by meteorites and comets is expected
- Both meteorites and comets contain large quantities of organic and biological molecules



Dark molecular clouds T ~ 10 K

2 atoms	3 atoms	4 atoms	5 atoms	6 atoms	7 atoms	8 atoms	9 atoms	10 atoms	11 atoms	12 atoms	>12 atoms
H_2	C_3	c-C_3H	C_5	C_5H	C_6H	CH_3C_3N	CH_3C_4H	CH_3C_5N	HC_9N	c-C_6H_6	$HC_{11}N$
AlF	C_2H	l-C_3H	C_4H	l-H_2C_4	CH_2CHCN	$HC(O)OCH_3$	CH_3CH_2CN	$(CH_3)_2CO$	CH_3C_6H	n-C_3H_7CN	C_{60}
AlCl	C_2O	C_3N	C_4Si	C_2H_4*	CH_3C_2H	CH_3COOH	$(CH_3)_2O$	$(CH_2OH)_2$	C_2H_5OCHO	i-C_3H_7CN	C_{70}
C_2	C_2S	C_3O	l-C_3H_2	CH_3CN	HC_5N	C_7H	CH_3CH_2OH	CH_3CH_2CHO	$CH_3OC(O)CH_3$	$C_2H_5OCH_3$	C_{60}^+
CH	CH_2H_2	C_3S	c-C_3H_2	CH_3NC	CH_3CHO	C_6H_2	HC_7N	CH_3CHCH_2O			
CH^+	HCN	C_2H_2*	H_2CCN	CH_3OH	CH_3NH_2	CH_2OHCHO	C_8H				
CN	HCO	NH_3	CH_4	CH_3SH	c-C_2H_4O	l-HC_6H	$CH_3C(O)NH_2$				
CO	HCO^+	HCCN	HC_3N	HC_3NH^+	H_2CCHOH	CH_2CHCHO	C_8H^-				
CO^+	HCS^+	$HCNH^+$	HC_2NC	HC_2CHO	C_6H^-	CH_2CCHCN	C_3H_6				
CP	HOC^+	HNCO	HCOOH	NH_2CHO	CH_3NCO	H_2NCH_2CN	CH_3CH_2SH				
SiC	H_2O	HNCS	H_2CNH	C_5N	HC_5O	CH_3CHNH	CH_3NHCHO				
HCl	H_2S	$HOCO^+$	H_2C_2O	l-HC_4H		CH_3SiH_3					
KCl	HNC	H_2CO	H_2NCN	l-HC_4N							
NH	HNO	H_2CN	HNC_3	c-H_2C_3O							
NO	MgCN	H_2CS	SiH_4	H_2CCNH							
NS	MgNC	H_3O^+	H_2COH^+	C_5N^-							
NaCl	N_2H^+	c-SiC_3	C_4H^-	HNCHCN							
OH	N_2O	CH_3	HC(O)CN	SiH_3CN							
PN	NaCN	C_3N^-	HNCNH								
SO	OCS	PH_3	CH_3O								
SO^+	SO_2	HCNO	NH_4^+								
SiN	c-SiC_2	HOCN	H_2NCO^+								
SiO	CO_2	HSCN	$NCCNH^+$								
SiS	NH_2	H_2O_2	CH_3Cl								
CS	H_3^+	C_3H^+									
HF	SiCN	HMgNC									
HD	AlNC	HCCO									
FeO	SiNC										
O_2	HCP										
CF^+	CCP										
SiH	AlOH										
PO	H_2O^+										
AlO	H_2Cl^+										
OH^+	KCN										
CN^-	FeCN										

https://www.astro.uni-koeln.de/cdms/molecules

Surface reactions background

http://**kida**.obs.u-bordeaux1.fr
http://www.physics.ohio-state.edu:80/~eric/research_files/**osu**_09_2008

Gas-phase reactions — 4401
Surface reactions — 532
Only 37 species were considered to react with C atoms on the surface of dust grains

Information on surface reactions is often adopted from the gas-phase studies.

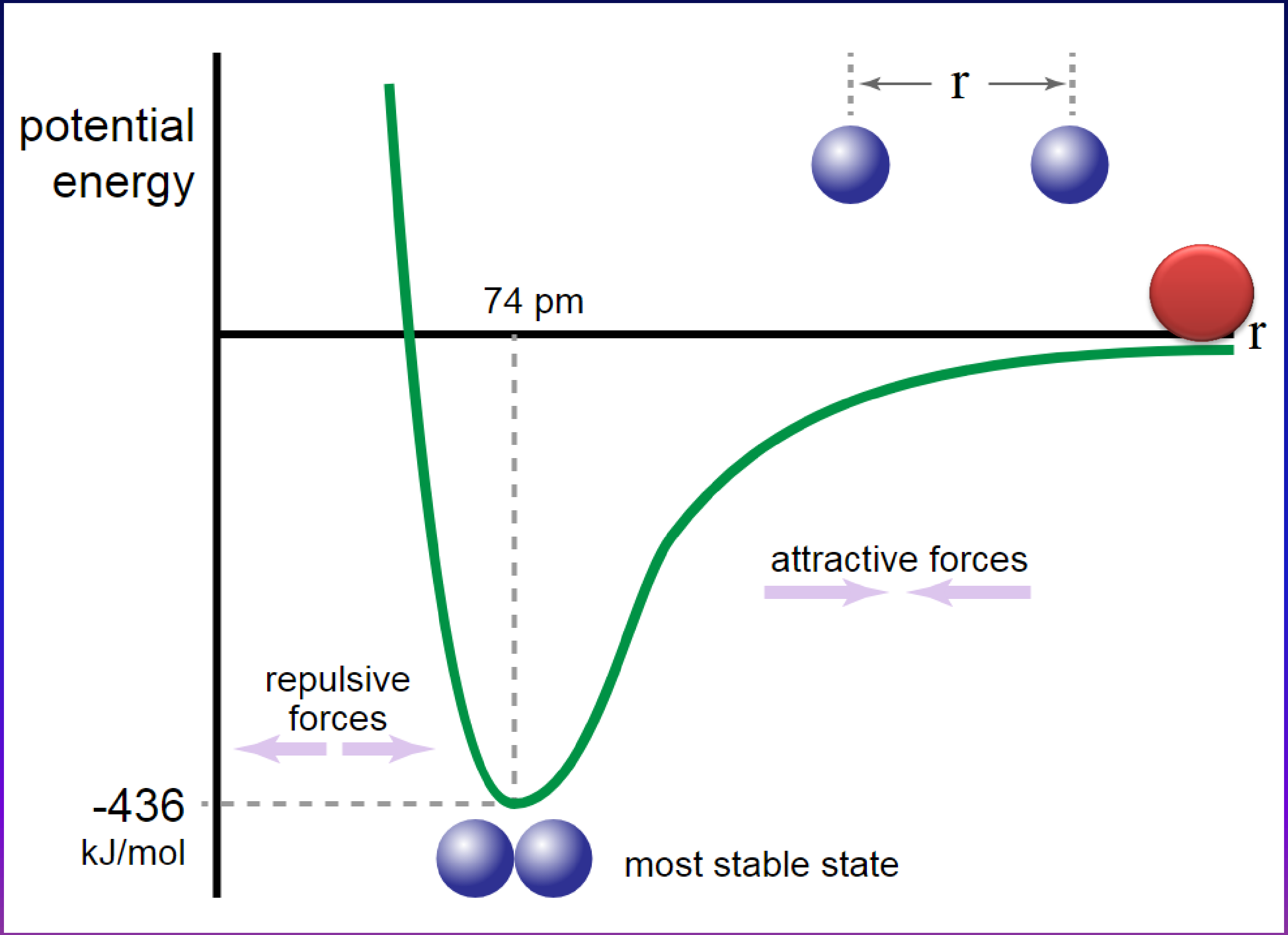
gC + gOH → gCO + gH gC + gOH → CO + H	No associative channel
gC + gH_2 → gCH_2	E_a = 2500K, No low-temperature reaction
gC + gC_2H_2 → gC + gNH_3 →	No surface reaction considered

Lack of solid experimental data on surface reactions

Surface reactions background

Surface reactions allow associative reactions

A + B → AB; (H + H → H_2 is efficient only on the surface)



Surface reactions background

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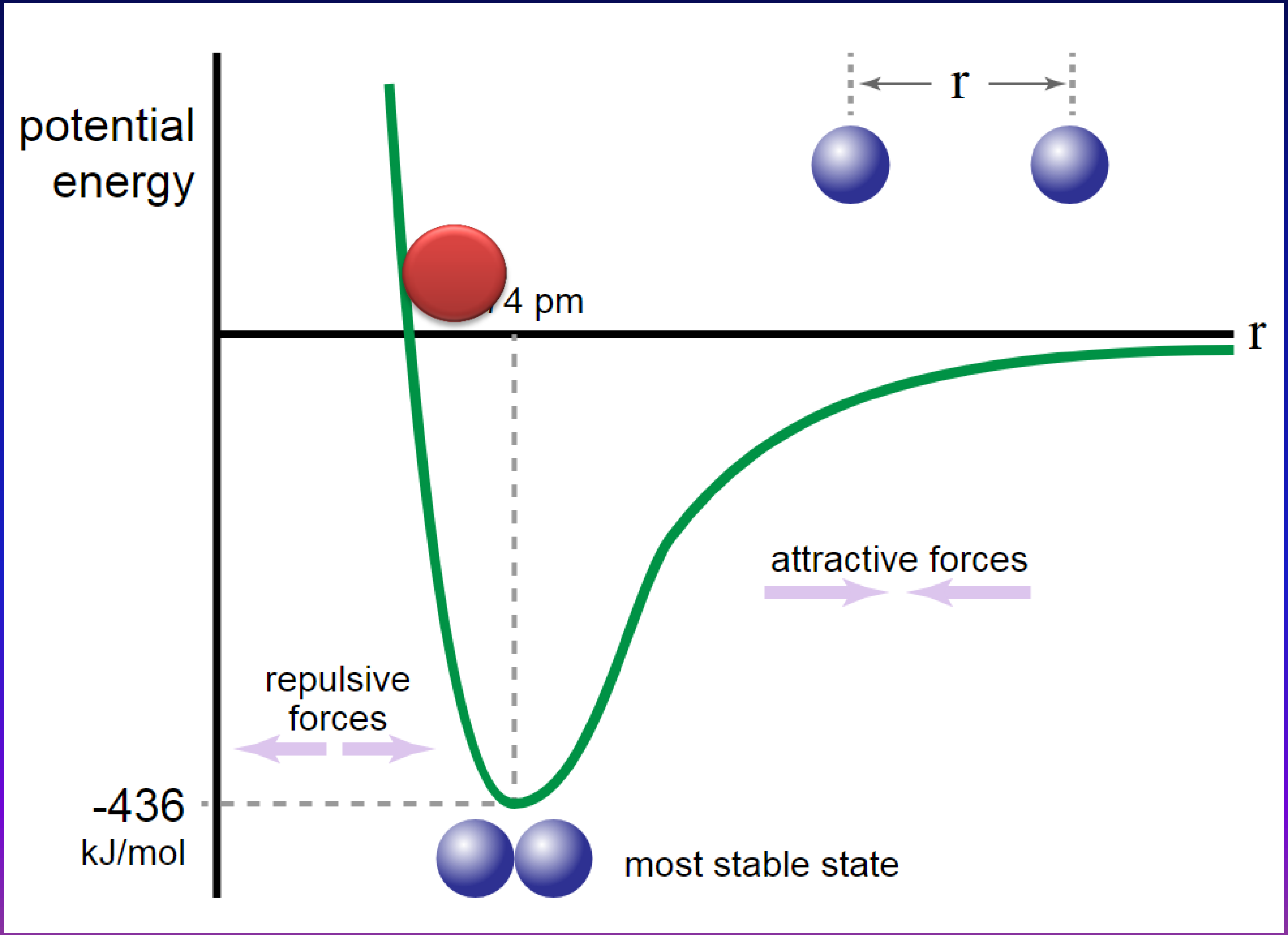

Surface reactions background

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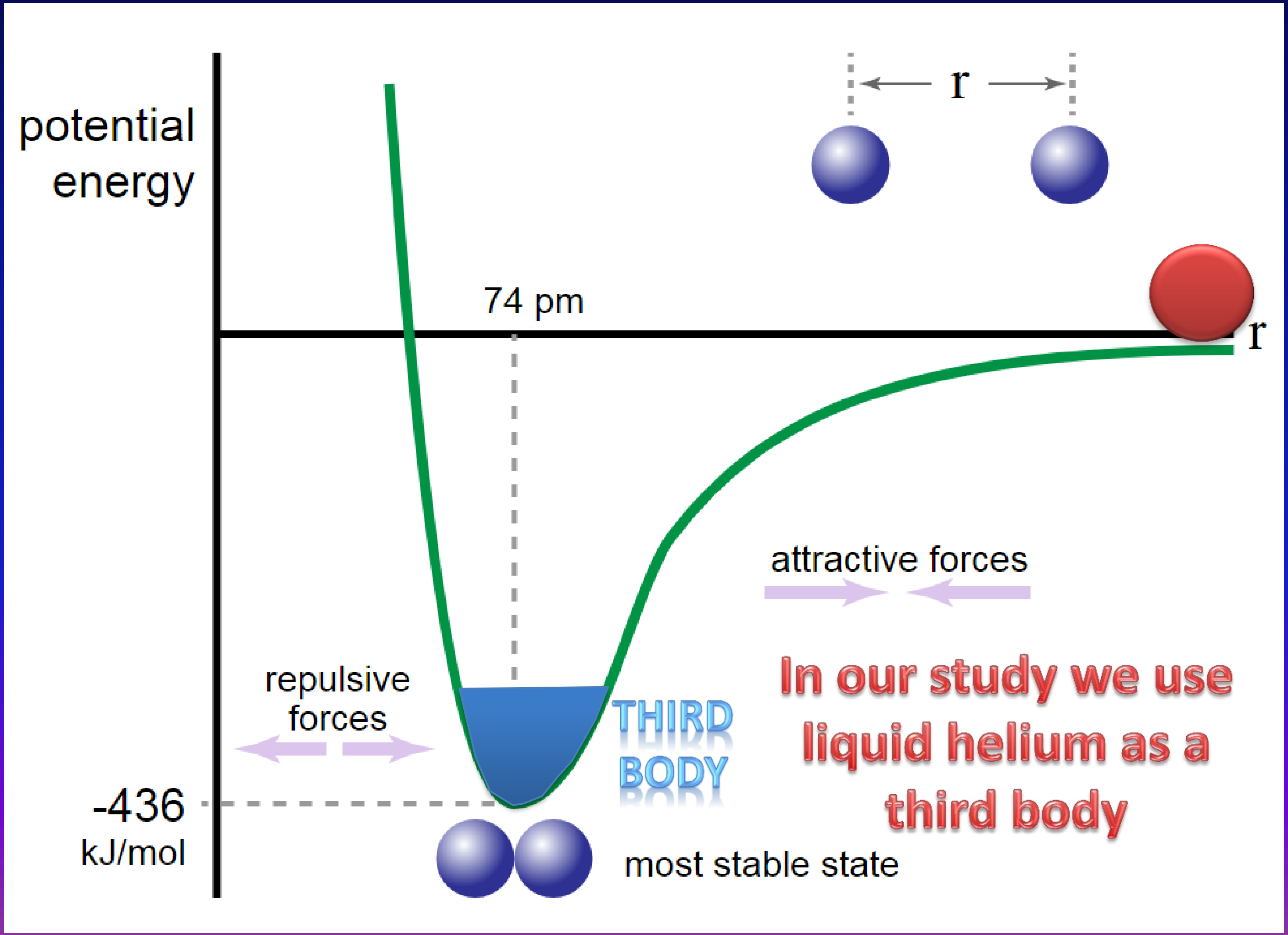
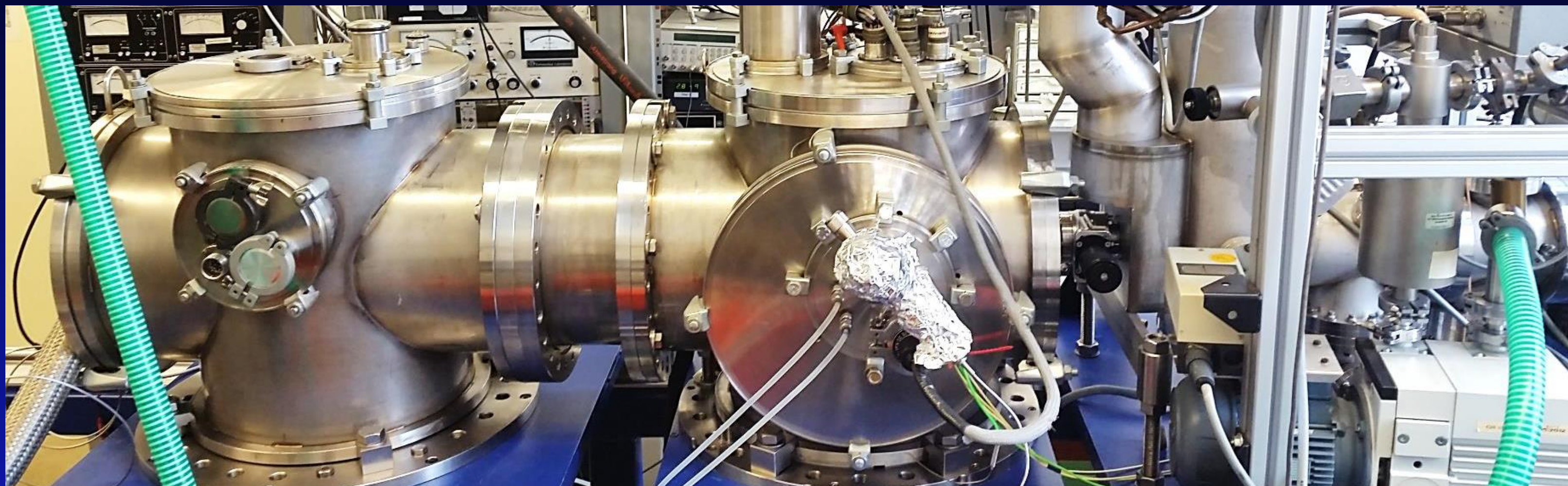
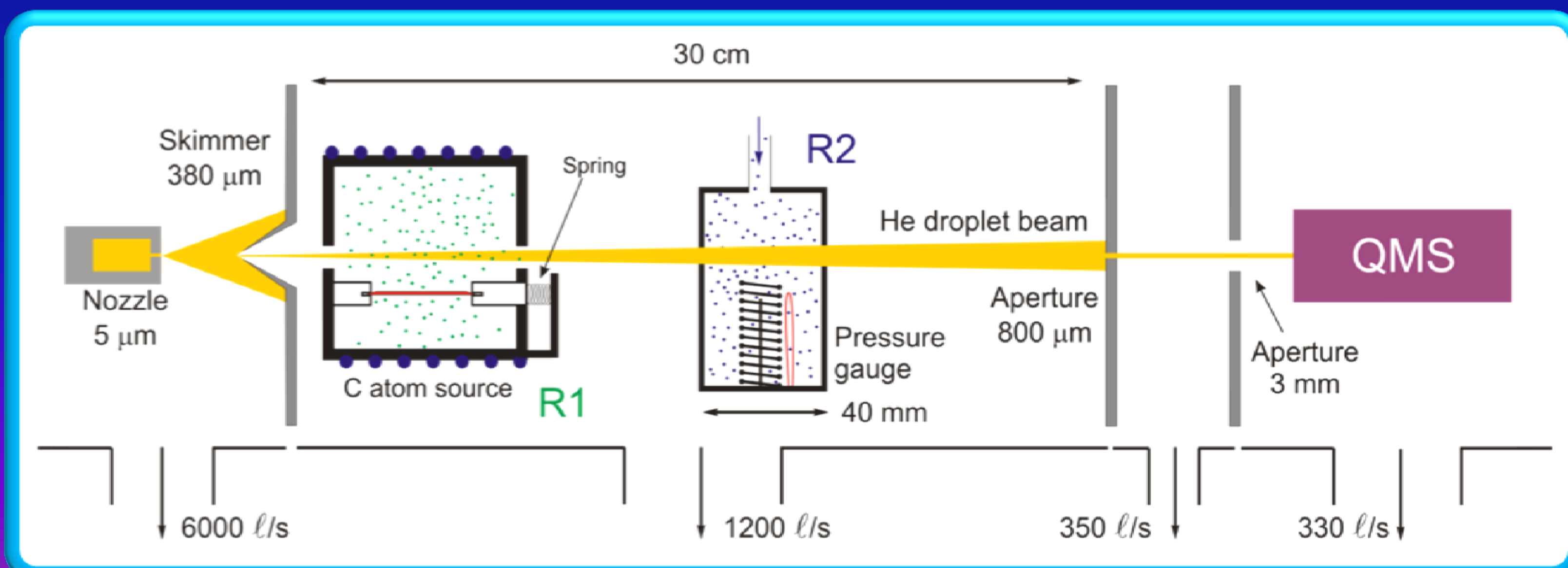


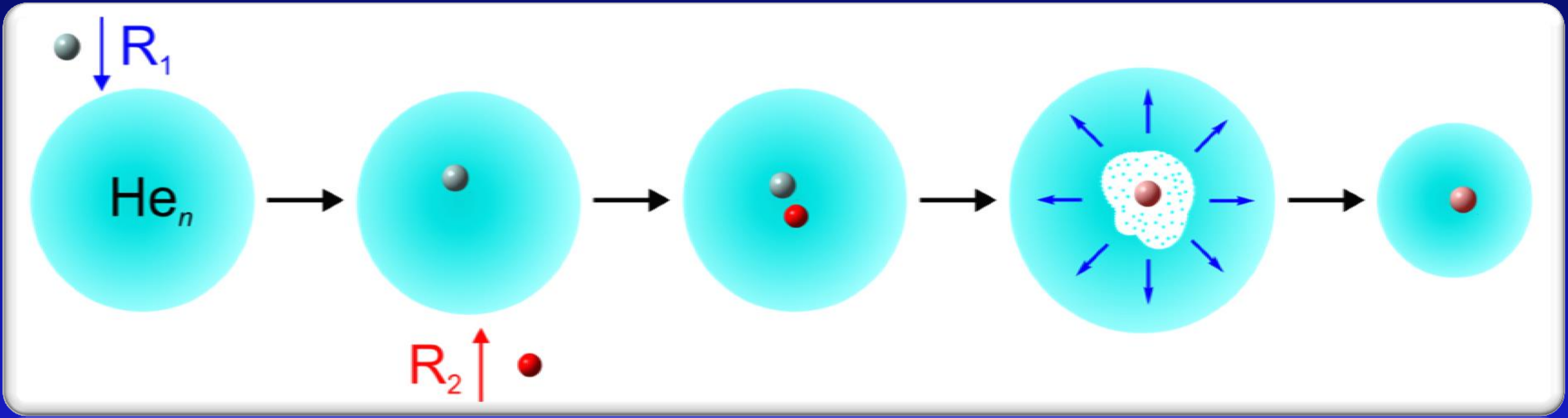
Helium droplet experimental setup



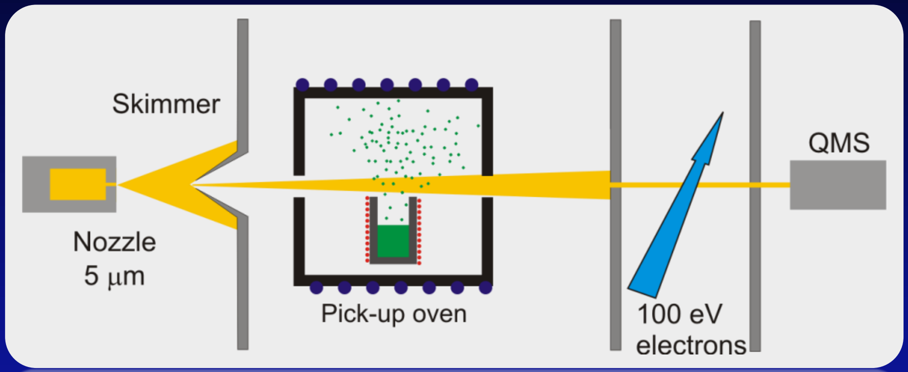


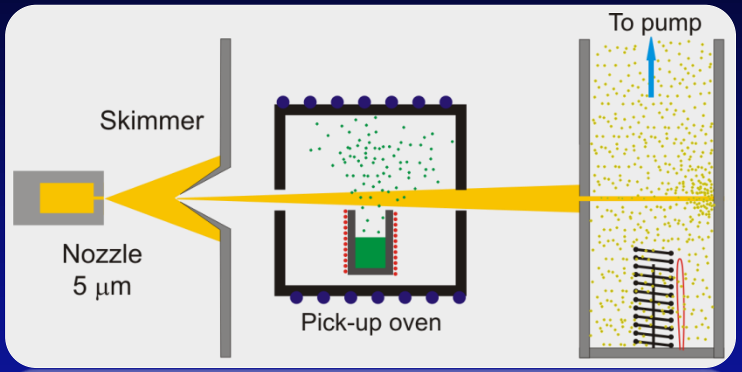
Experimental study of surface reactions

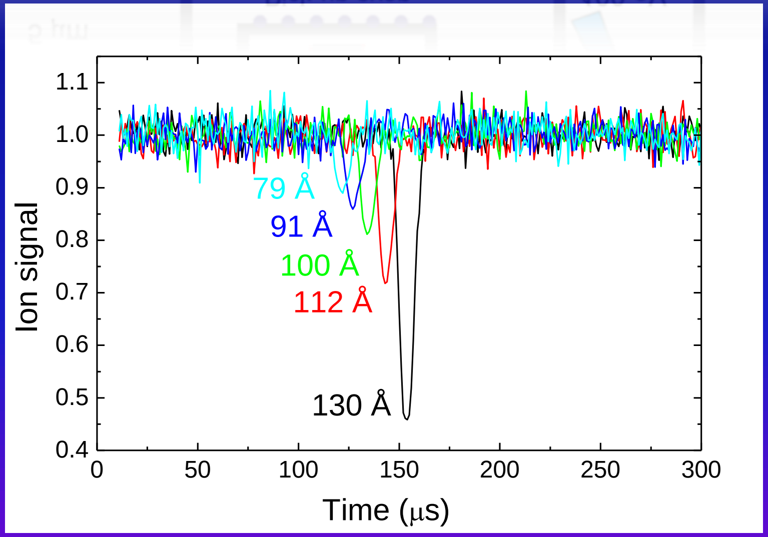
Liquid helium as a third body

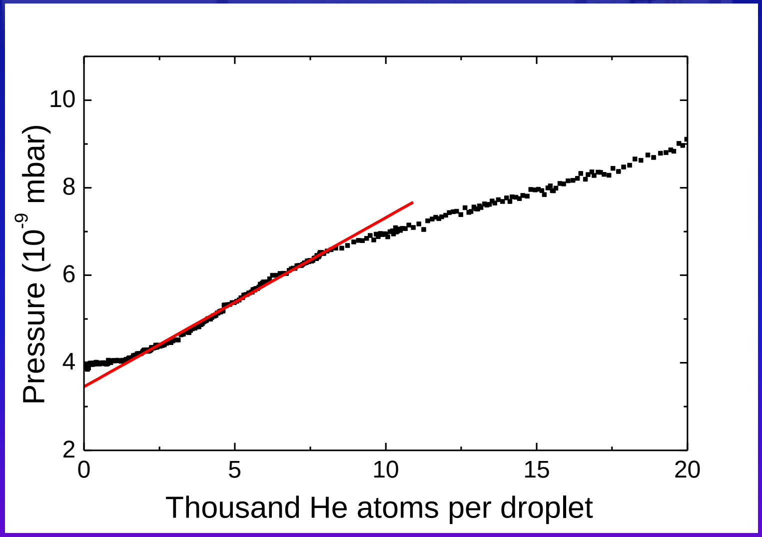


Measuring sizes of He droplets



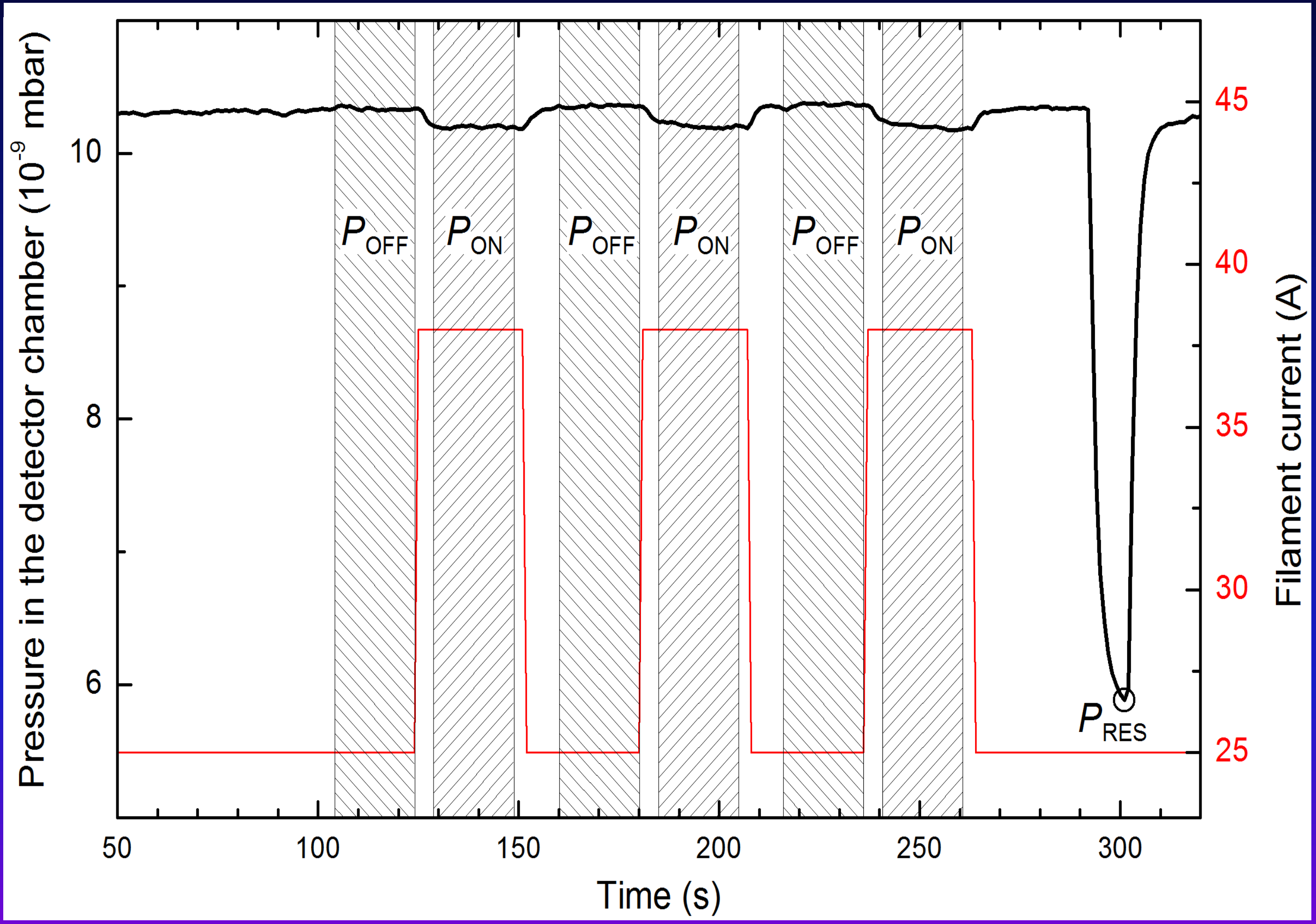




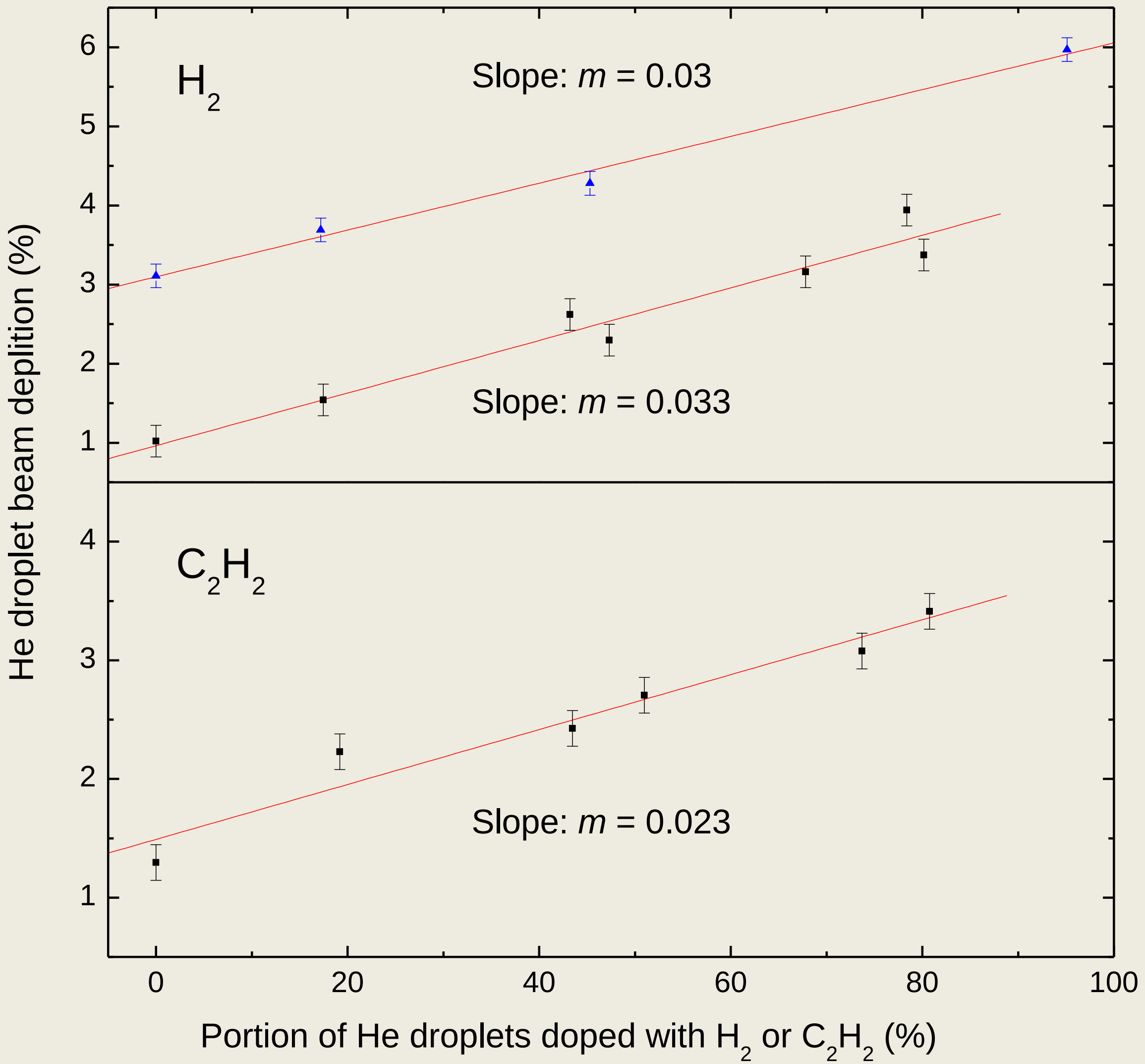


J. Phys. Chem. A, Vol. 114, No. 50, 2010

Measuring depletion caused by incorporation of one reactant



Ultra-low-temperature C + H_2 → HCH reaction

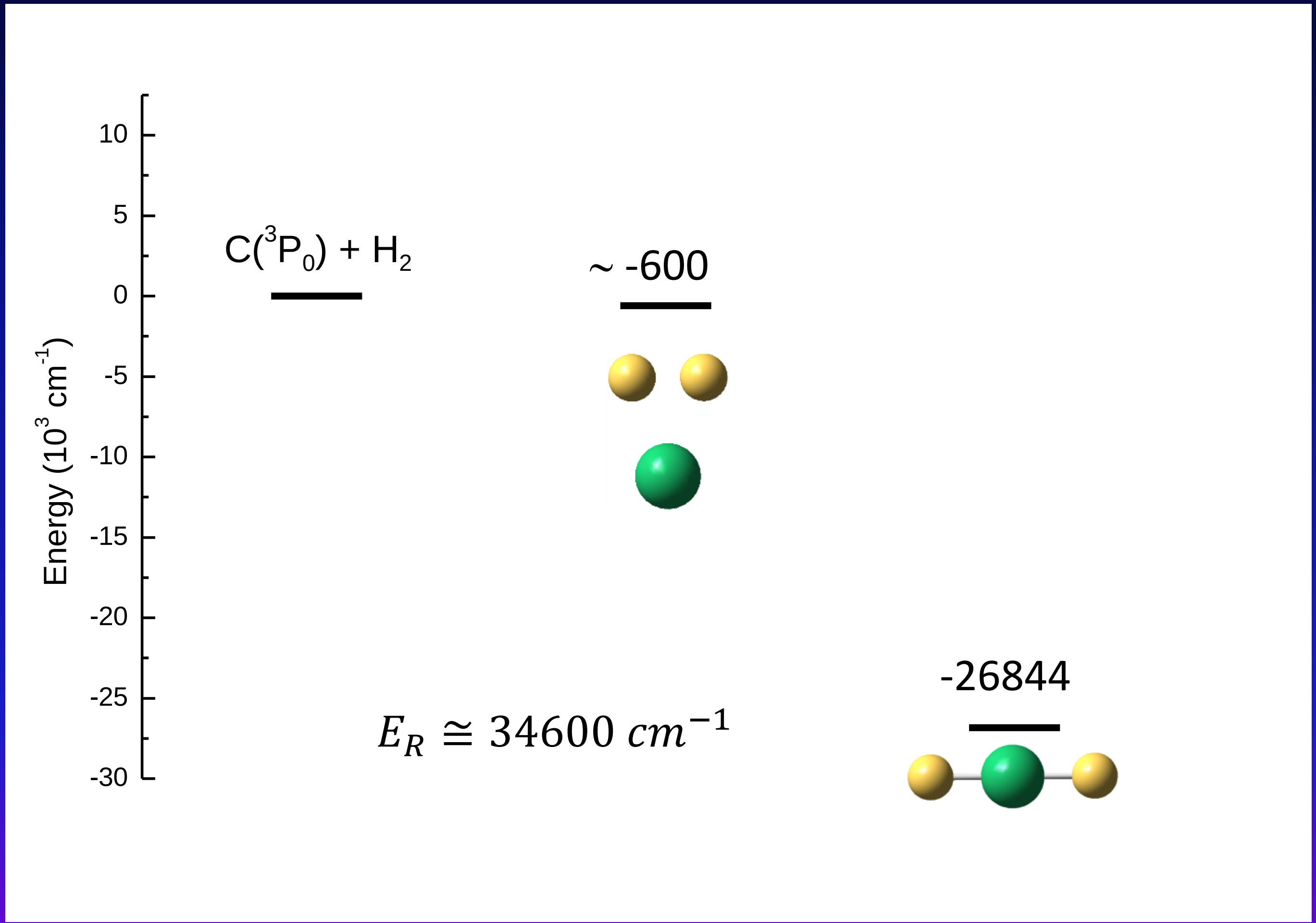


$$m = P_{R_1} \frac{E_R}{5N_{He}}$$

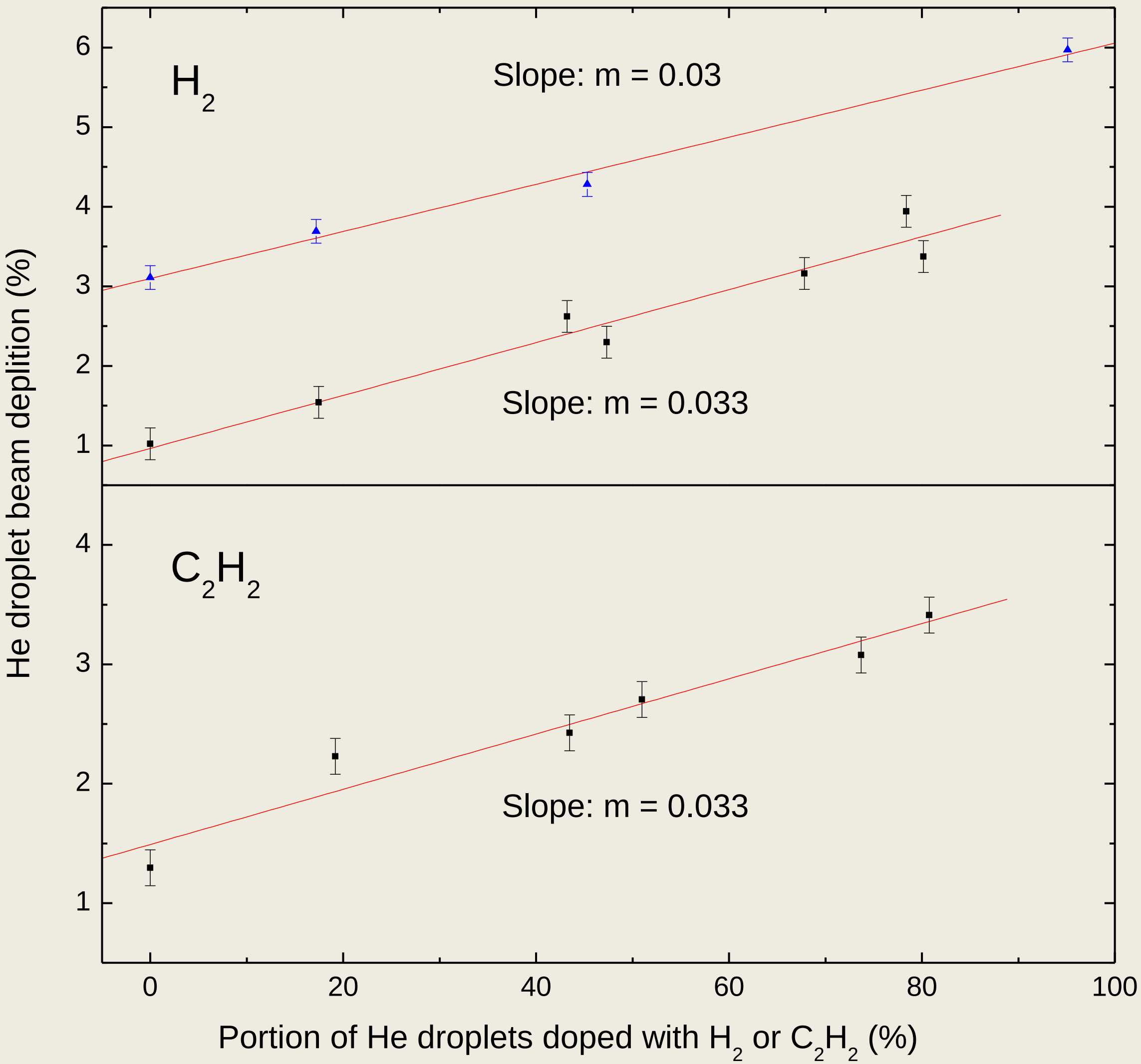
P_{R_1} is portion of He droplets doped with C atoms, E_R amount of released energy, and N_{He} is an initial size of He droplets

$$E_R \cong 34600\ cm^{-1}$$

Energy levels of the C + H_2 reaction



Ultra-low-temperature C + H_2 → HCH reaction



$$m = P_{R_1} \frac{E_R}{5N_{He}}$$

P_{R_1} is portion of He droplets doped with C atoms, E_R amount of released energy, and N_{He} is an initial size of He droplets

$$E_R = K_{cal} m$$

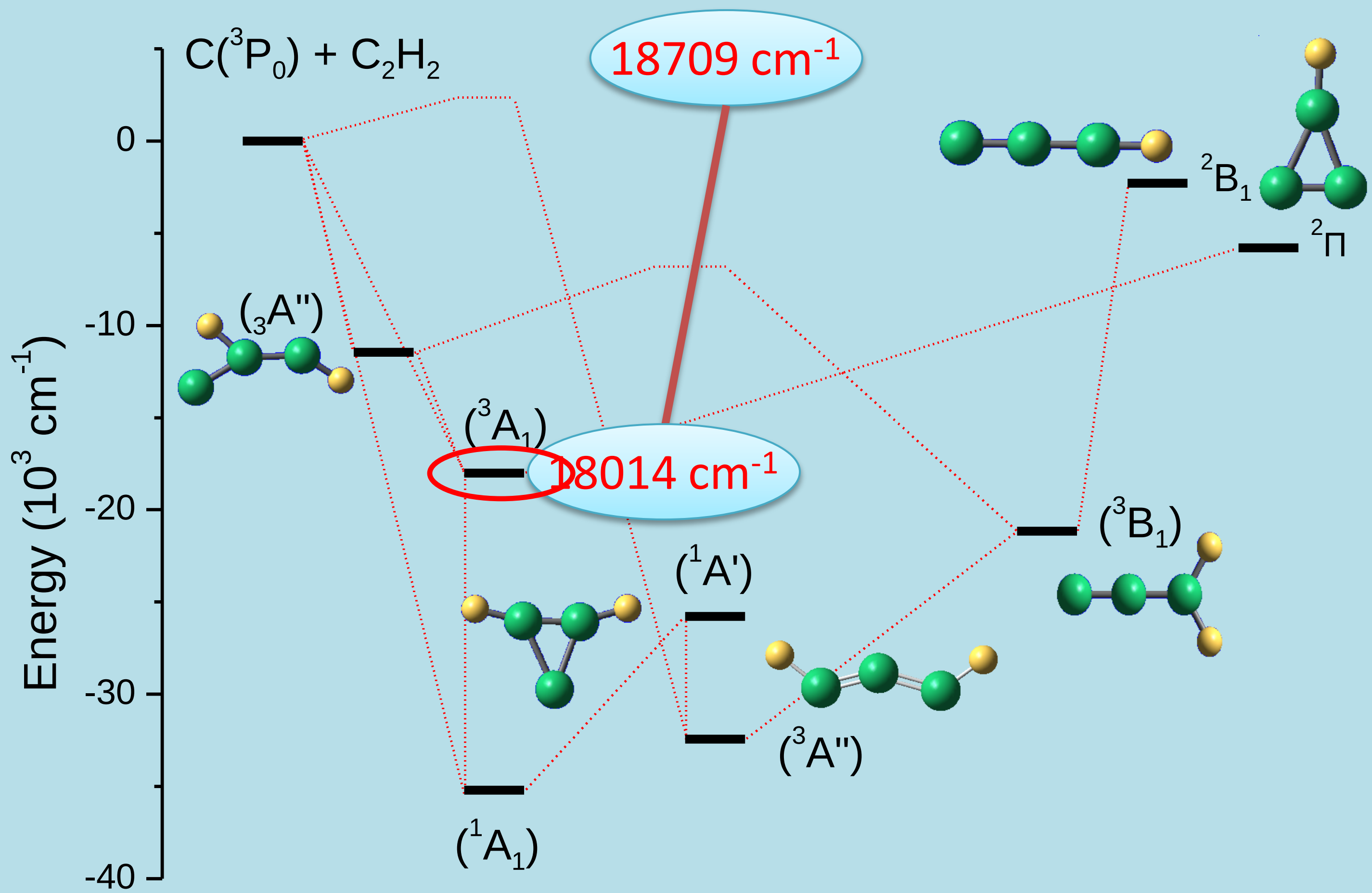
K_{cal} is calibration constant. Based on the energy release in C + H_2 reaction (26844 cm^{-1}).

$$K_{cal} = 813454\ cm^{-1}$$

Therefore, energy released in C + C_2H_2 reaction to be **18709 cm^{-1}**

T. Henning, and S. Krasnokutski
Nat. Astron. (2019)
doi: 10.1038/s41550-019-0729-8

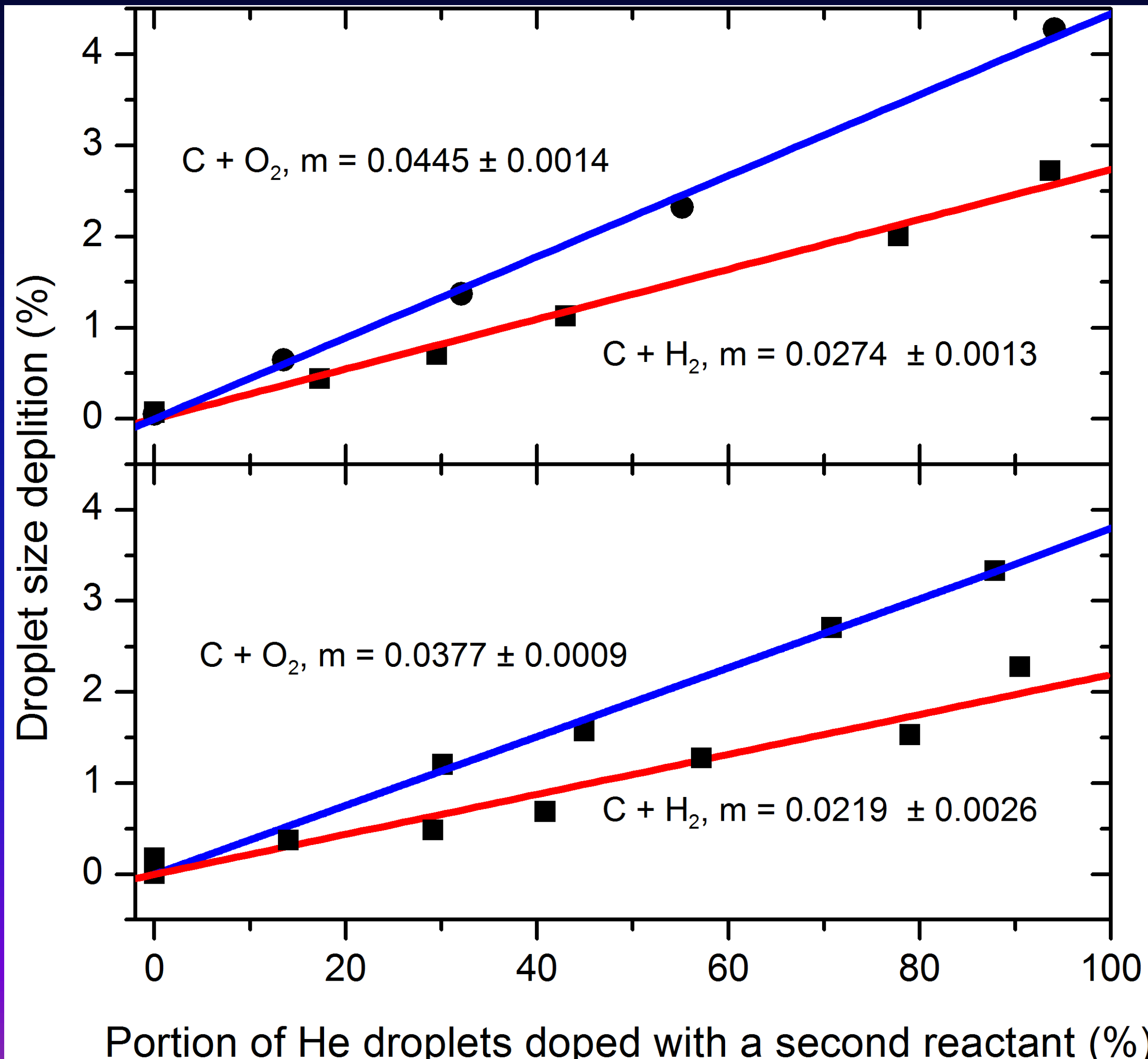
Energy levels of the C + C_2H_2 reaction



R. I. Kaiser, et. al., J. Chem. Phys. **106**, 1729 (1997)

J. Takahashi and K. Yamashita, J. Chem. Phys. **104**, 6613 (1996)

$C + O_2 \rightarrow CO + O$, $C + O_2 \rightarrow CO_2$ reactions

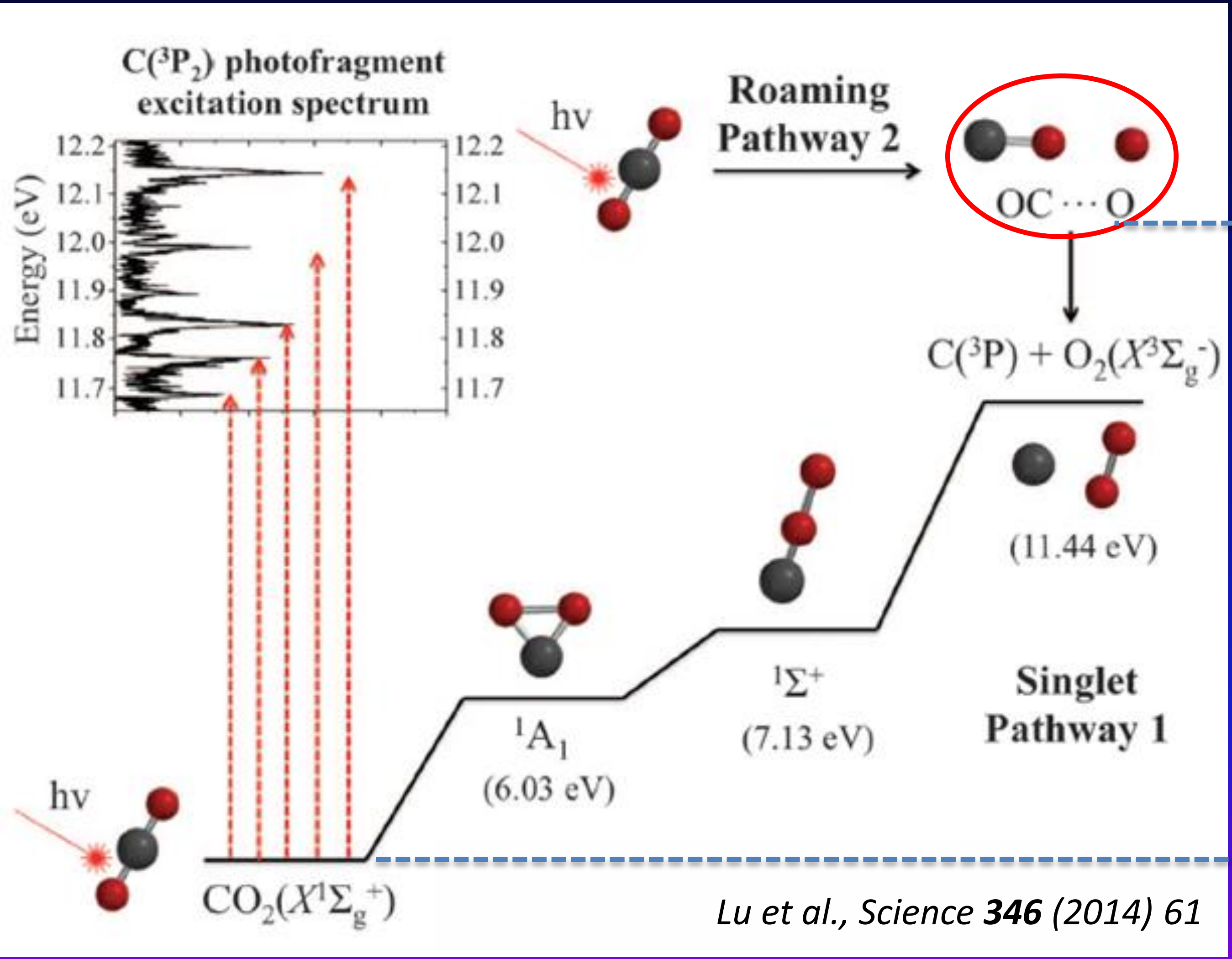


N_{He} = 20500
E_R = 45738 cm^{-1}

N_{He} = 145000
E_R = 44586 cm^{-1}

On platinum crystal:
$C + O_2 \rightarrow CO + O \rightarrow CO_2$
*Walker & King JCP **112** (2000) 1937*

Energy levels diagram of the C + O_2 reaction



C + O_2 → CO + O
+ 48346 cm^{-1}

E_R = 45738 cm^{-1}

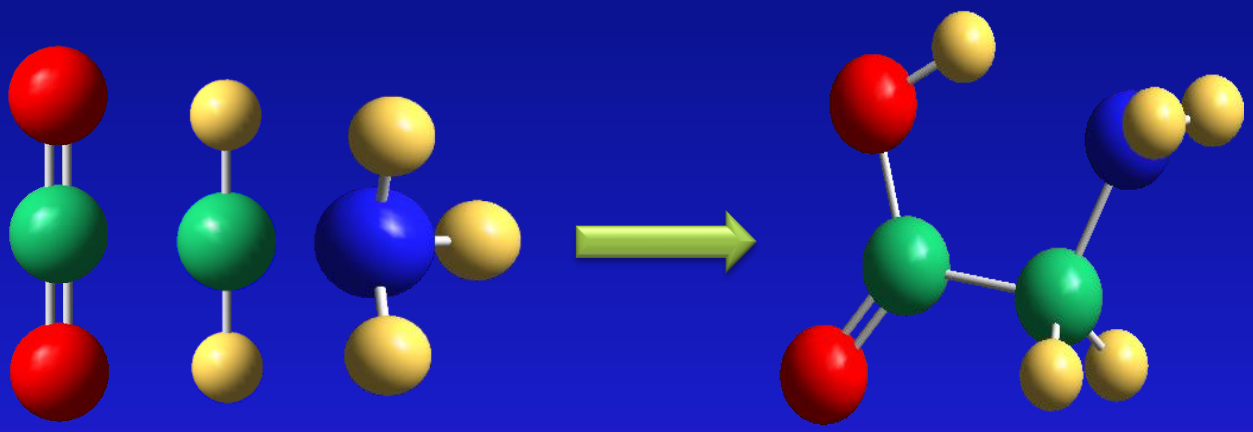
C + O_2 → OCO
+ 92328.5 cm^{-1}

On platinum crystal: C + O_2 → CO + O → CO_2

*Walker & King JCP **112** (2000) 1937*

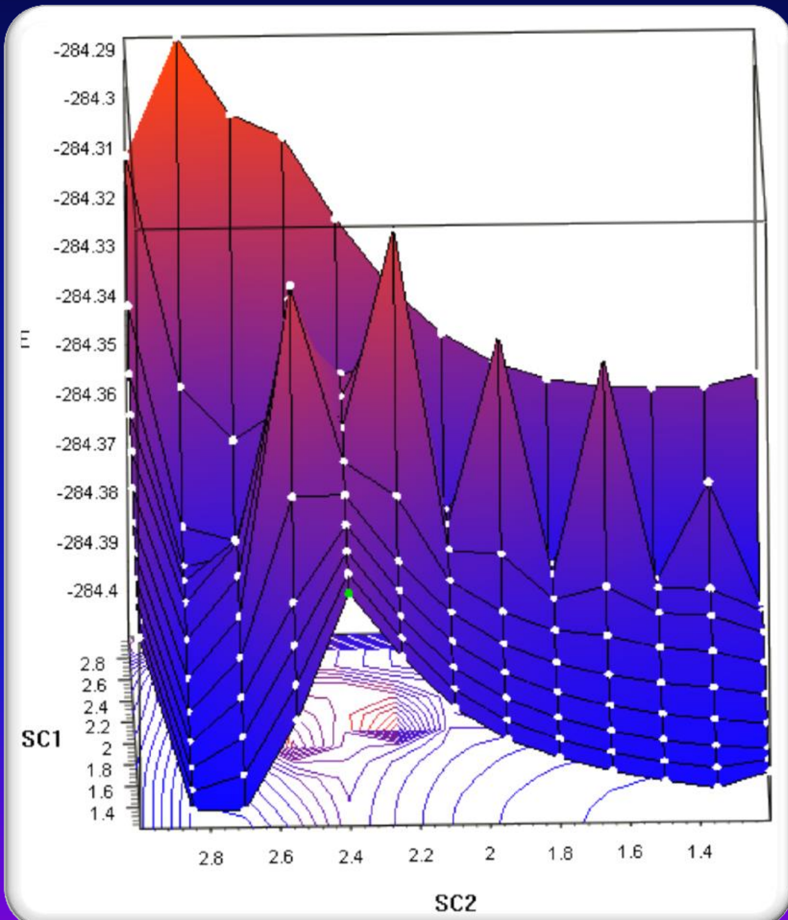
Glycine formation pathway

$C + H_2 \rightarrow HCH$

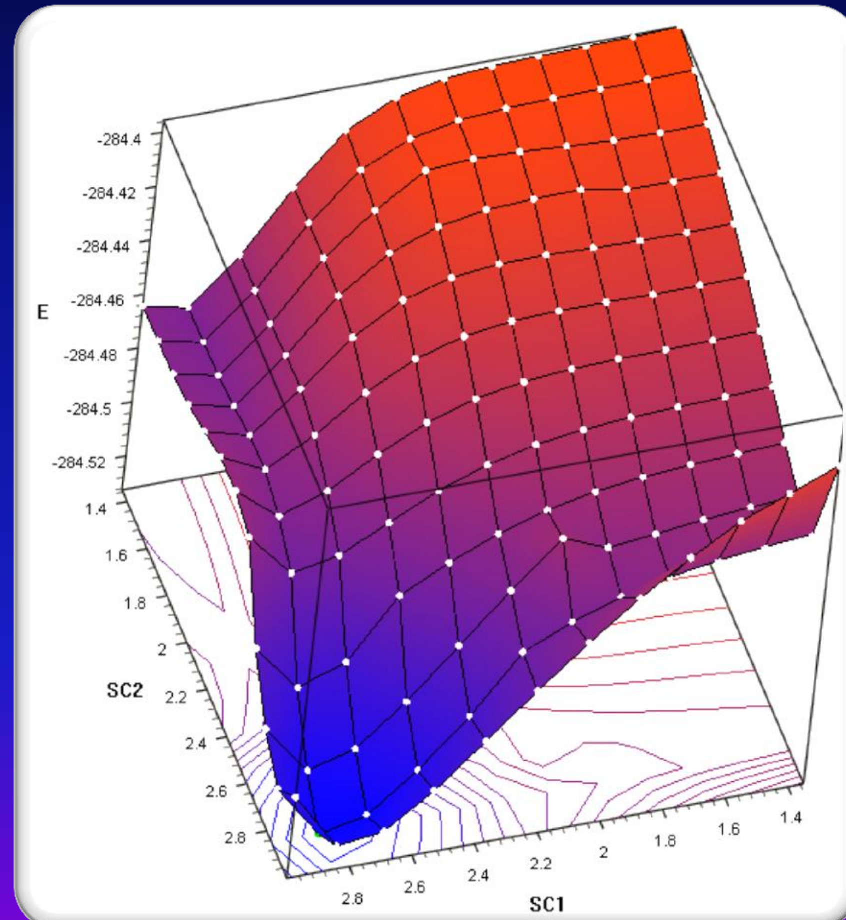


Potential energy surface of HCH + CO_2 + NH_3 reaction

Triplet channel



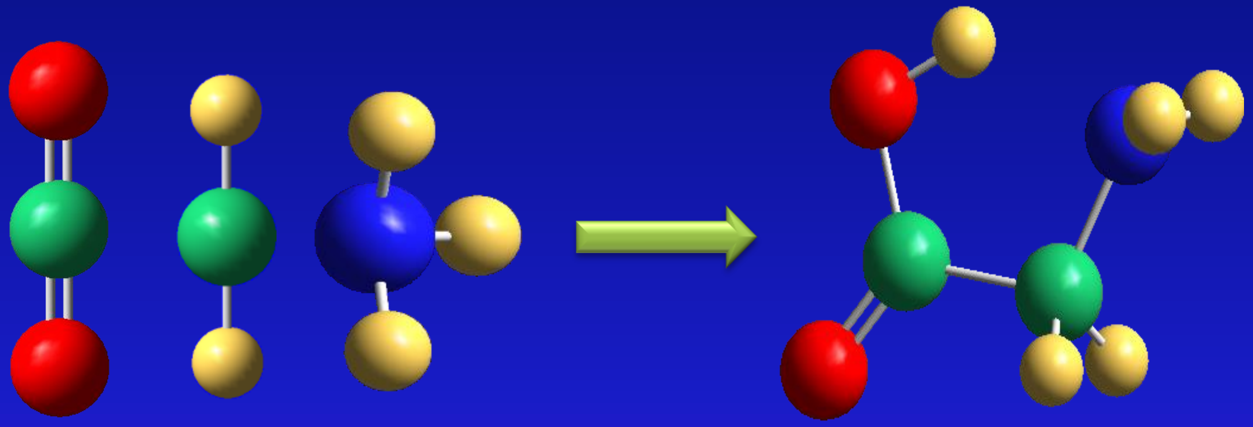
Singlet channel



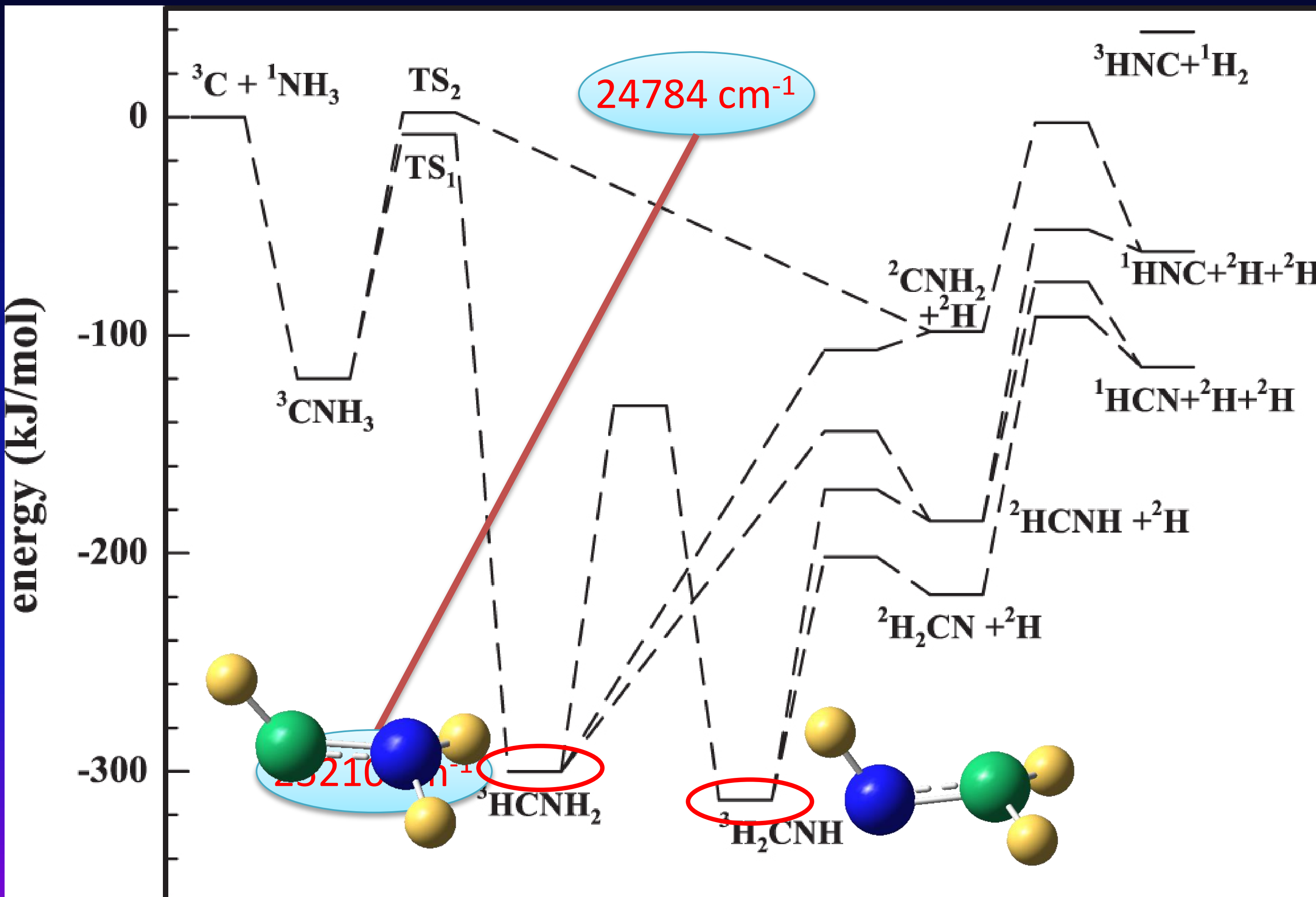
MP2/6-311G+(d,p)

Glycine formation pathway

$C + H_2 \rightarrow HCH$

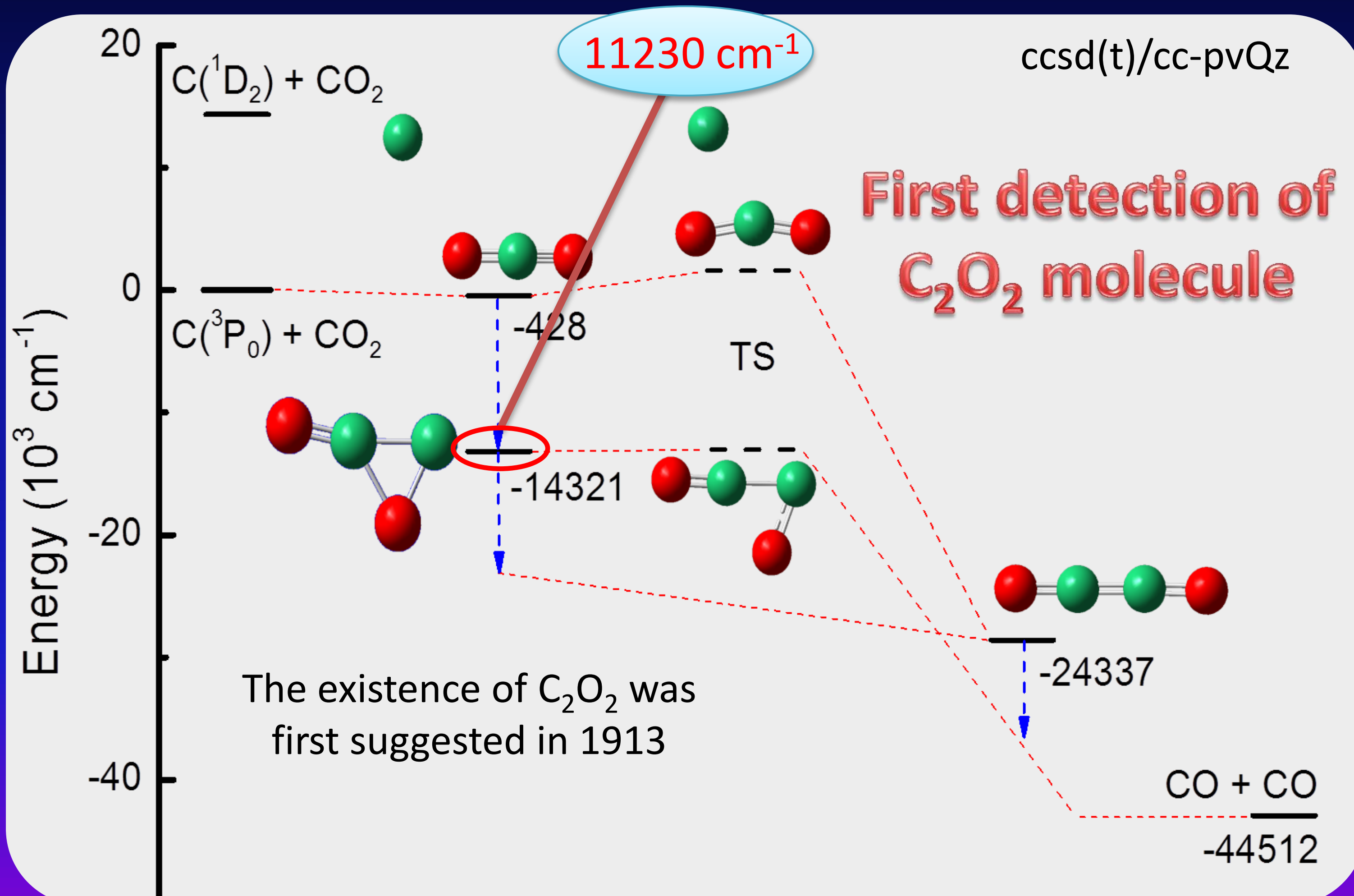


Energy levels diagram of the C + NH_3 reaction



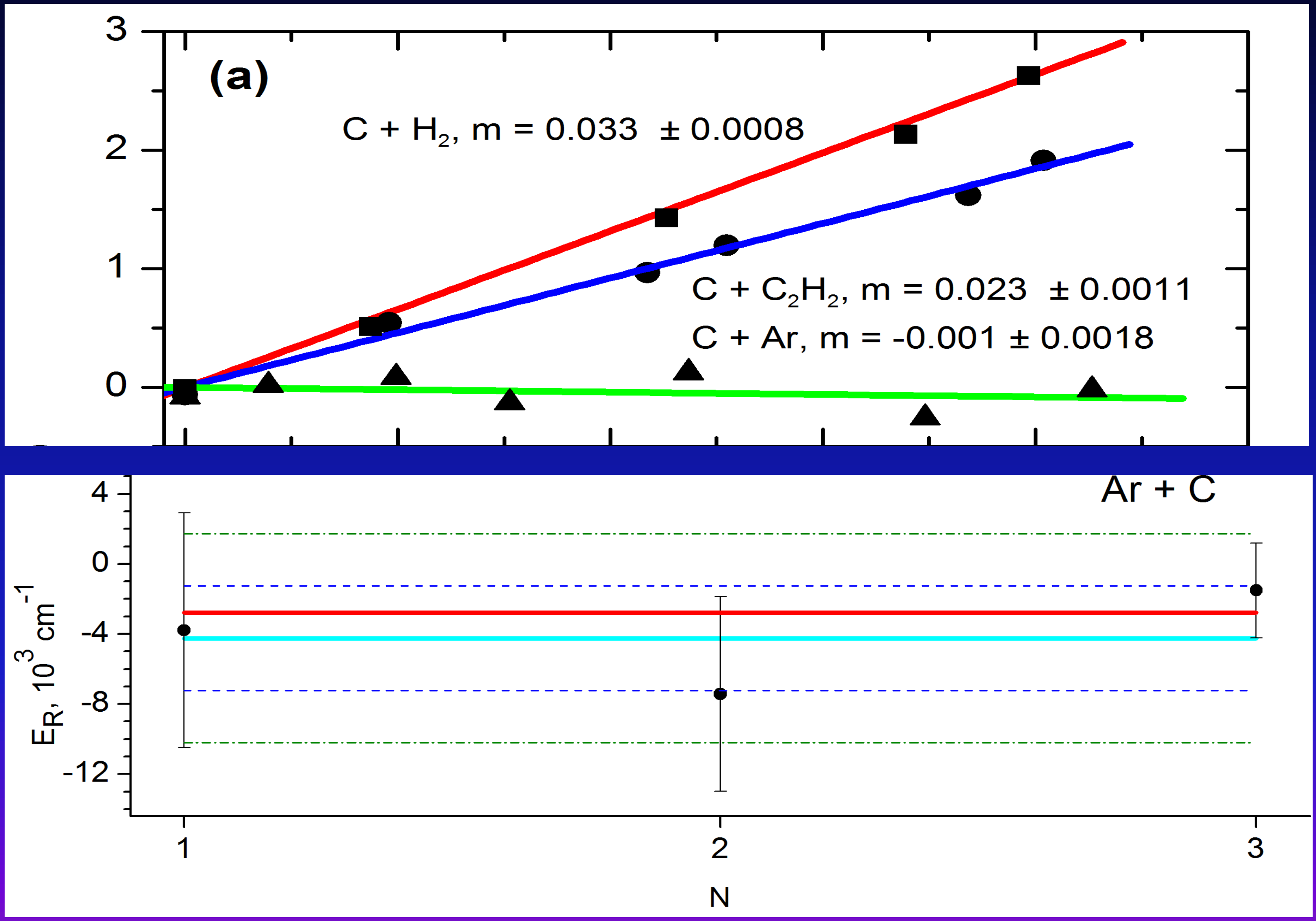
APJ, 812:106, 2015

Energy levels diagram of the C + CO_2 reaction

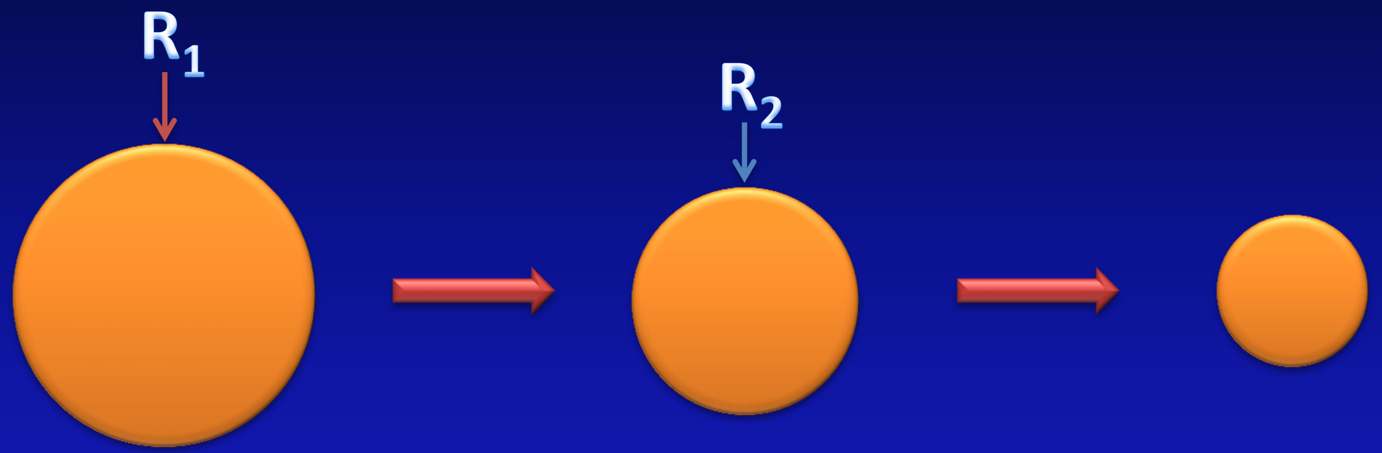


S. Krasnokutski, et.al. PCCP (2019) doi:10.1039/C9CP01616C

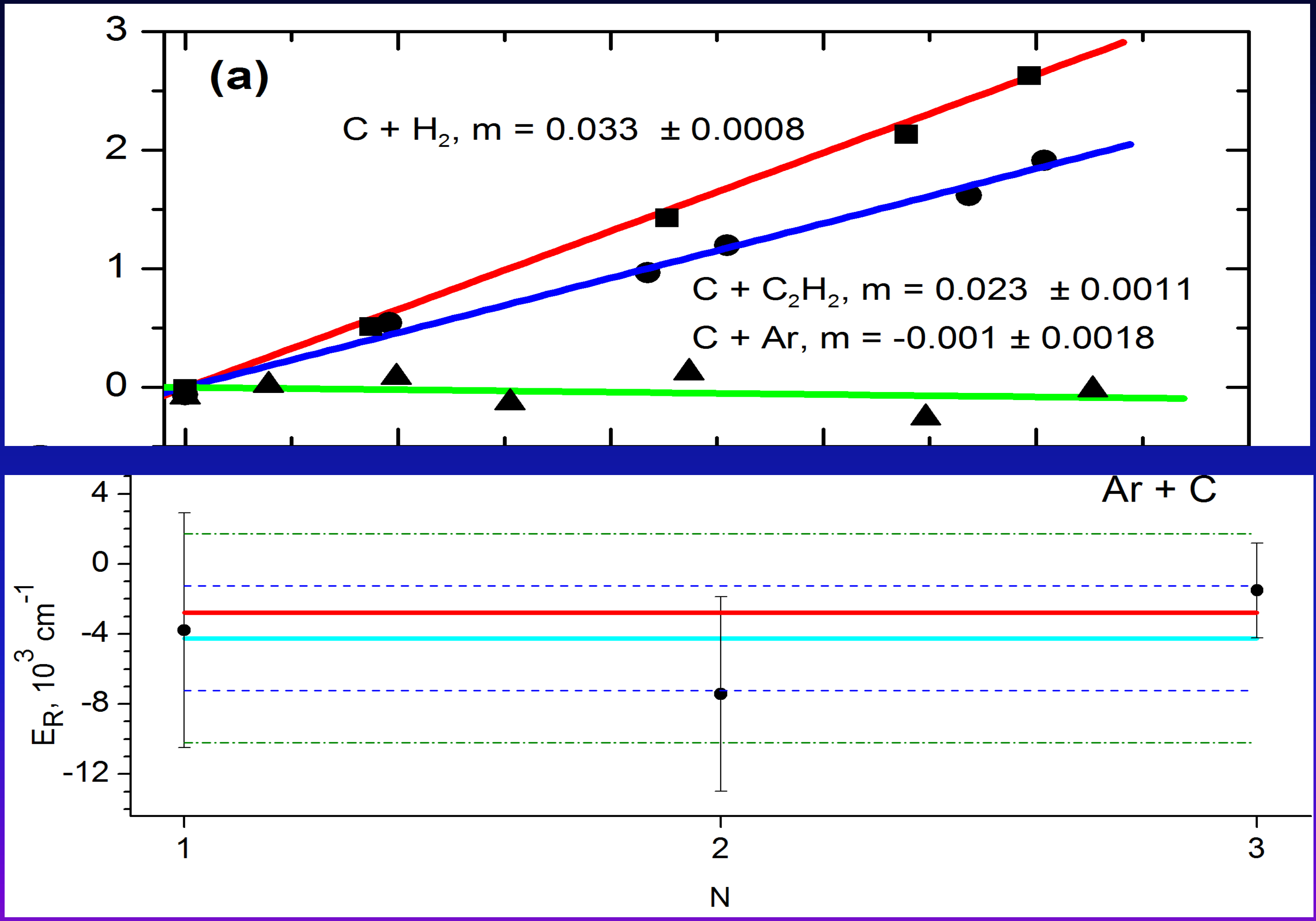
Negative slope of C + Ar reaction



Origin of negative slope



Negative slope of C + Ar reaction



Conclusions

- The experimental technique, which can be used to measure the energy released in reactions of a single pair of reactants was developed.
- These data can be directly compared with the results of quantum chemical computations leading to unequivocal conclusions regarding the reaction pathways, the presence of energy barriers, and the final reaction products.
- The ground reactions $C + H_2 \rightarrow HCH$ and $C + C_2H_2 \rightarrow C_3H_2$ are barrierless, and therefore should be considered in the modeling of the chemistry of the ISM.
- The barrierless formation of $CHNH_2$, which is one of the key molecules of Strecker type synthesis, was found, suggesting an efficient formation of prebiotic molecules during condensation of C atoms on the surfaces of dust grains.
- After almost a hundred years of unsuccessful trials, we finally managed to detect an elusive molecule ethylenedione (C_2O_2).