Novel astrochemical aspects of cyanoacetylene-related molecules

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SAO Meeting, August 2008

Focus on:

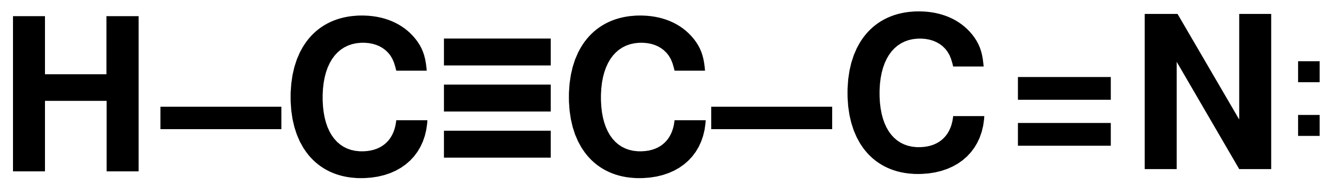
1. **Cyanovinylidene, the branched izomer of H-CC-CN**
2. **Cyanoacetylide, the anion produced from H-CC-CN**

INTERSTELLAR MOLECULES

2	3	4	5	6	7	8	9	10	11	12	13
H_2	C_2H	c-C_3H	C_5	C_5H	C_6H	CH_2C_3N	**HC_7N**	CH_3C_5N?	**HC_9N**	C_6H_6	**$HC_{11}N$**
AlF	C_2O	l-C_3H	C_4H	l-H_2C_4	CH_2CHCN	$HCOOCH_3$	CH_3CH_2CN	$(CH2)_2CO$			
AlCl	C_2S	C_3N	C_4Si	C_2H_4	CH_3C_2H	CH_2COOH?	$(CH_2)_2O$	NH_2CH_2COOH?			
C_2	CH_2	C_3O	l-C_3H_2	CH_3CN	**HC_5N**	C_7H	CH_3CH_2OH				
CH	**HCN**	C_3S	c-C_3H_2	CH_3NC	$HCOCH_3$	CH_2OHCHO	CH_3C_4H				
CH+	HCO	CH_2D+?	CH_2CN	CH_3OH	NH_2CH_3	HC_6H	C_8H				
CN	HCO+	HCCN	CH_4	CH_3SH	c-C_2H_4O						
CO	HCS+	HCNH+	**HC_3N**	HC_3NH+	CH_2CHOH						
CO+	HOC+	HNCO	HC_2NC	HC_2CHO							
CP	H_2O	HNCS	HCOOH	NH_2CHO							
CSi	H_2S	HOCO+	H_2CNH	HC_4H							
HCl	HNC	H_2CO	H_2C_2O								
KCl	HNO	H_2CN	H_2NCN								
NH	MgCN	H_2CS	HNC_3								
NO+	MgNC	H_3O+	SiH_4								
NS	N_2H+	NH_3	H_2COH^+								
NaCl	N_2O	SiC_3									
OH	NaCN	HC_2H									
PN	OCS										
SO	SO_2										
SO+	c-SiC_2										
SiN	CO_2										
SiO	NH_2										
SiS	SiCN										
CS	H_3+										
HF	C_3										
SH	AlNC										
FeO											

HCN

HNC



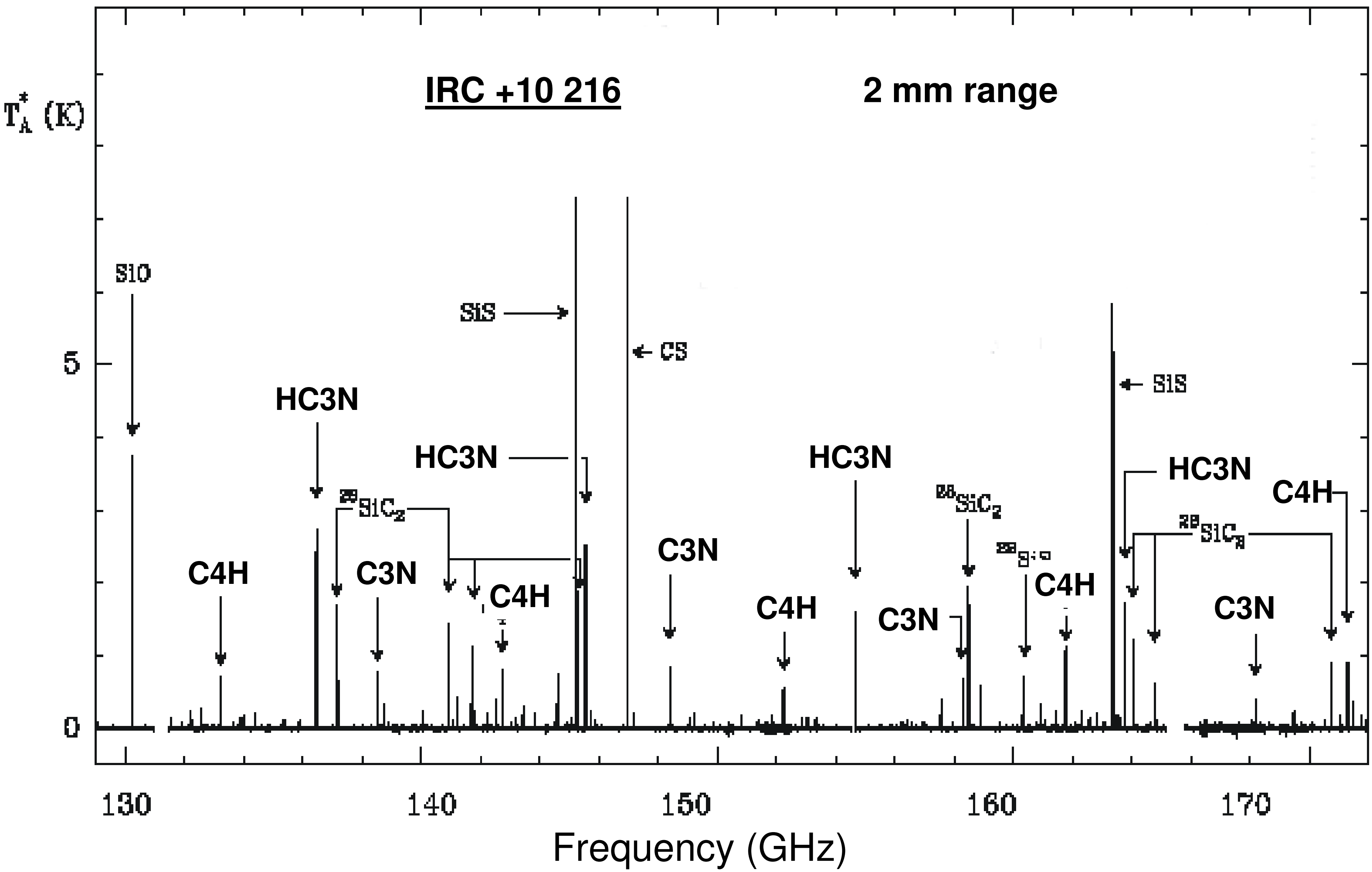
izonitrile

:C=C=C=N–H

imine

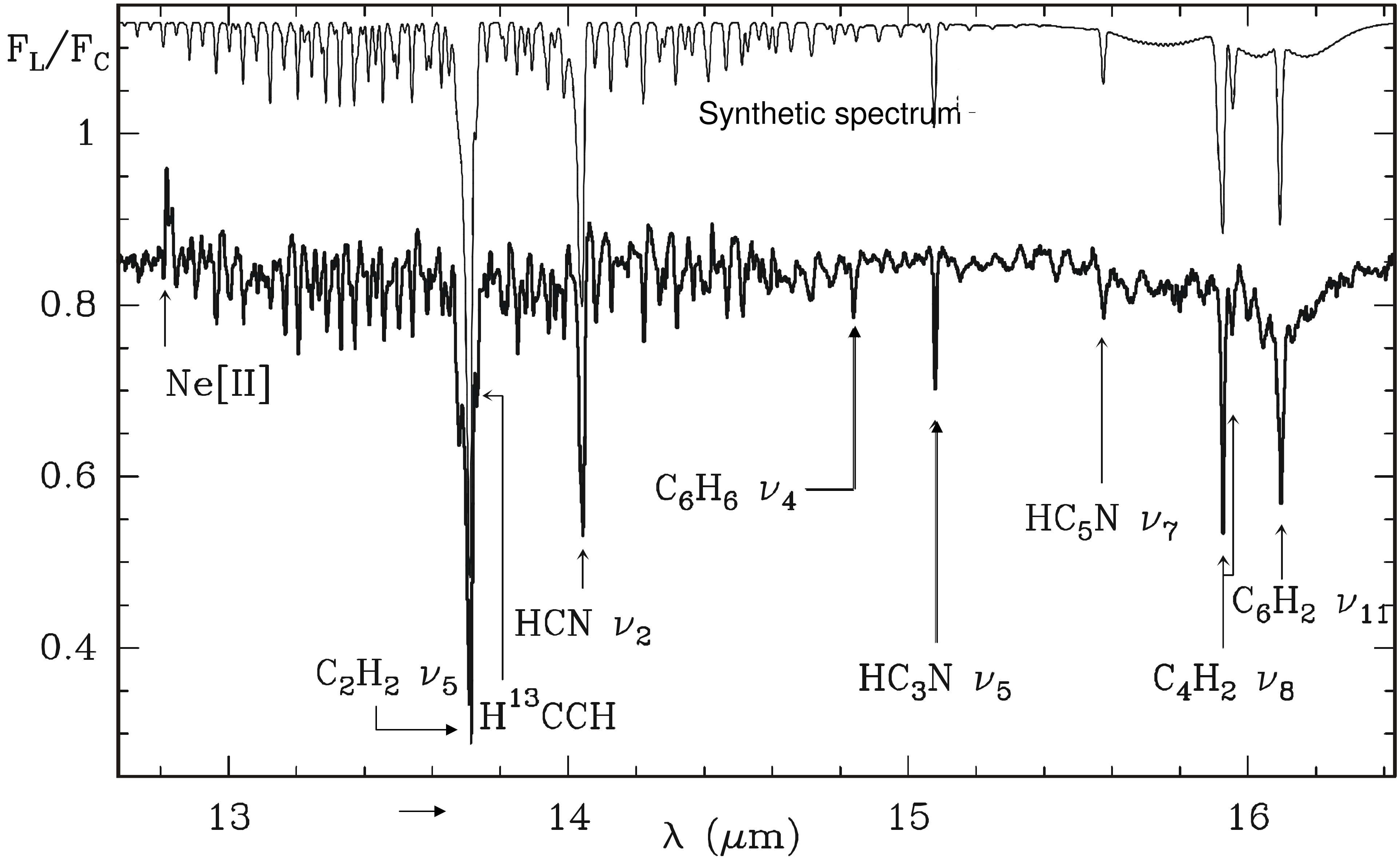
M

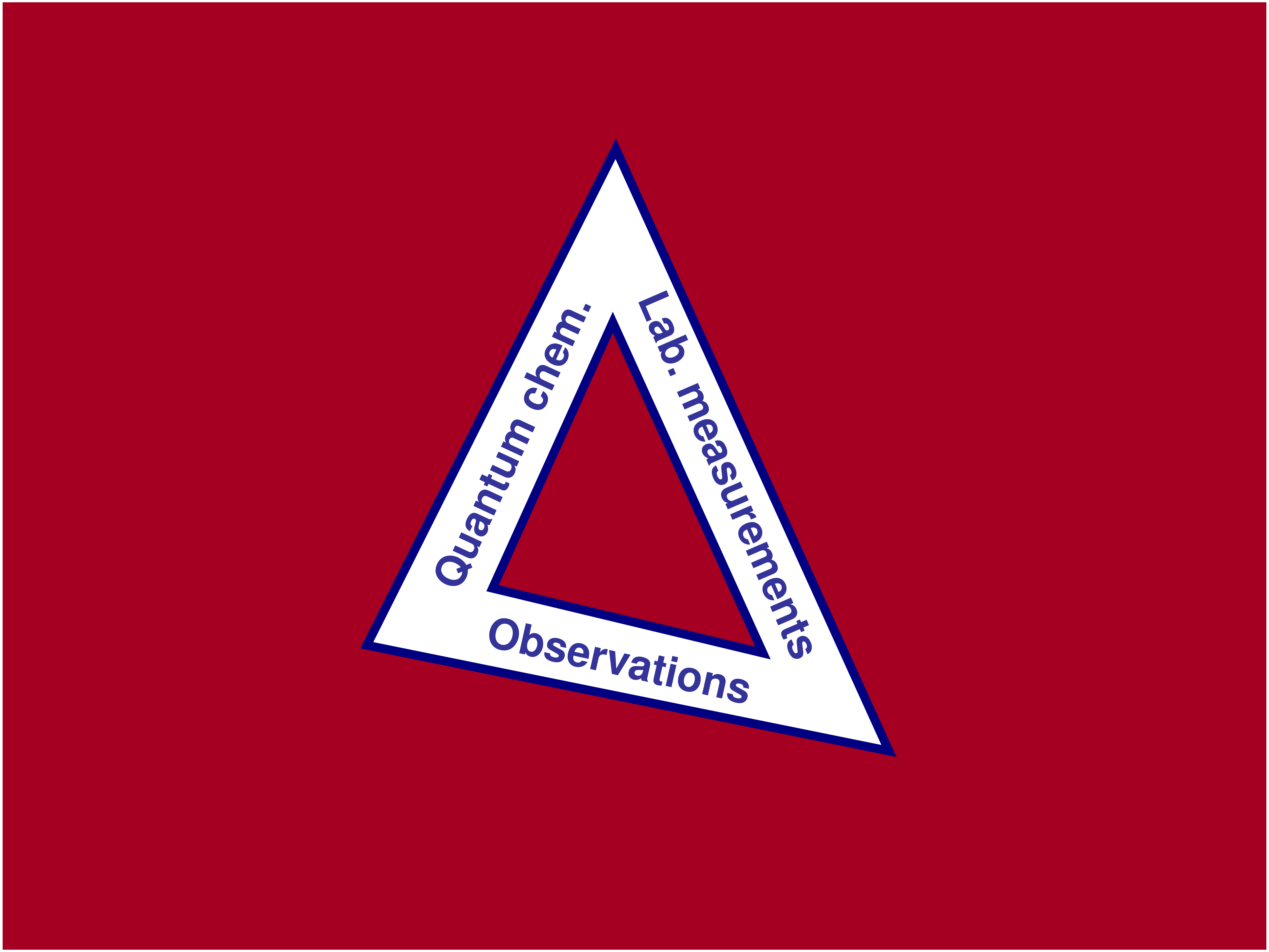
J. Cernicharo, M. Guelin , and C. Kahane; Astron. Astrophys. Suppl. Ser. 142, (2000) 181

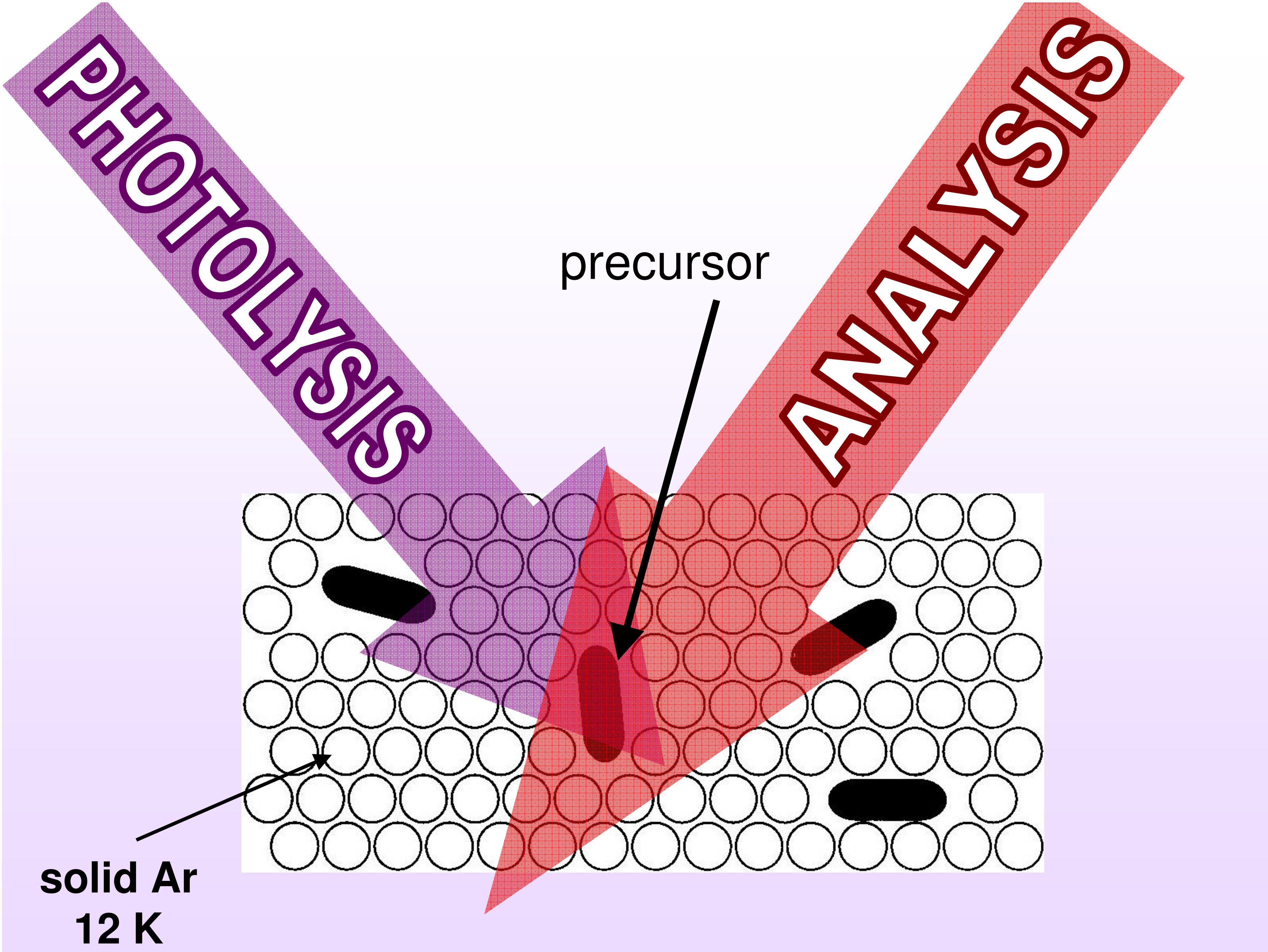


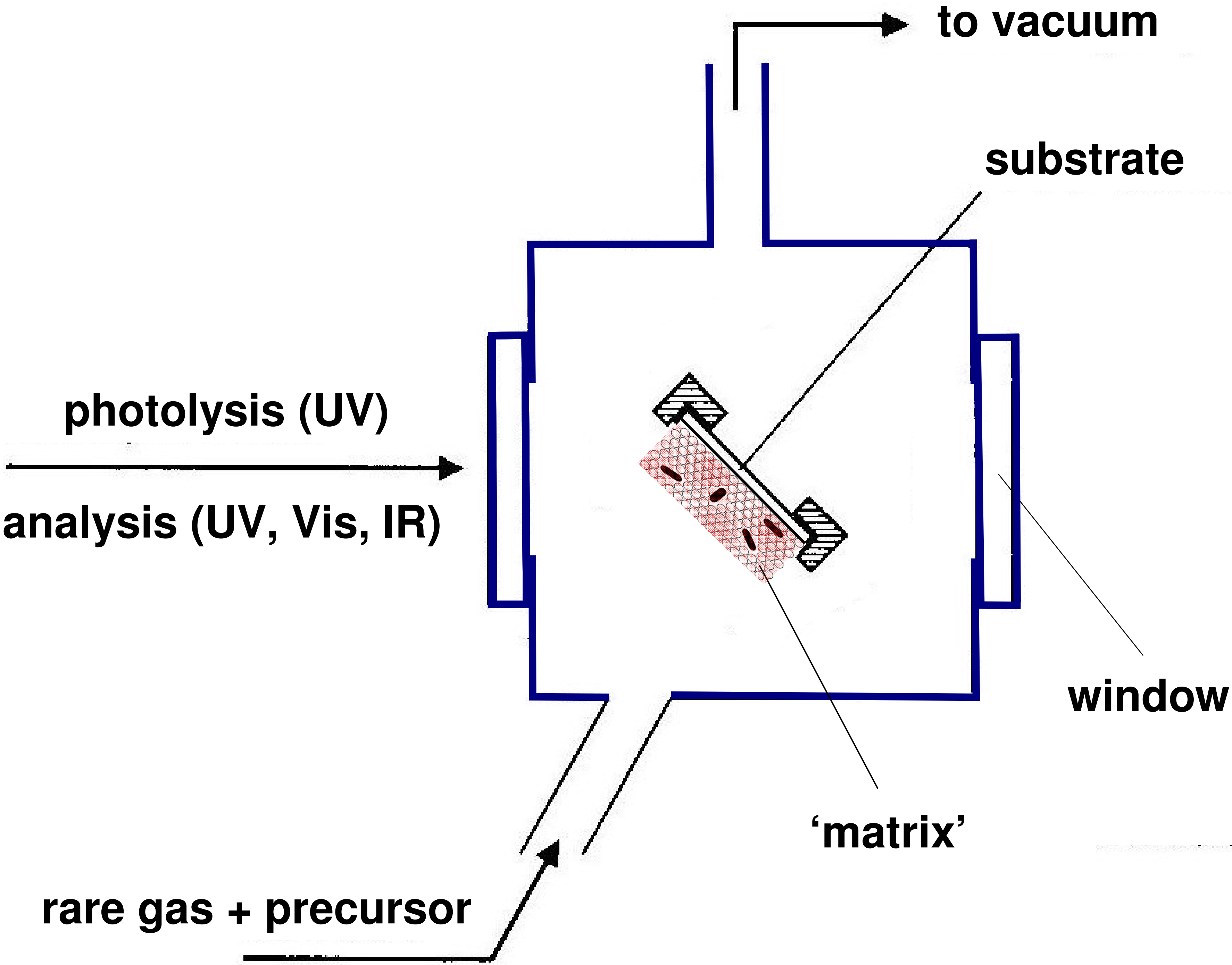
IR

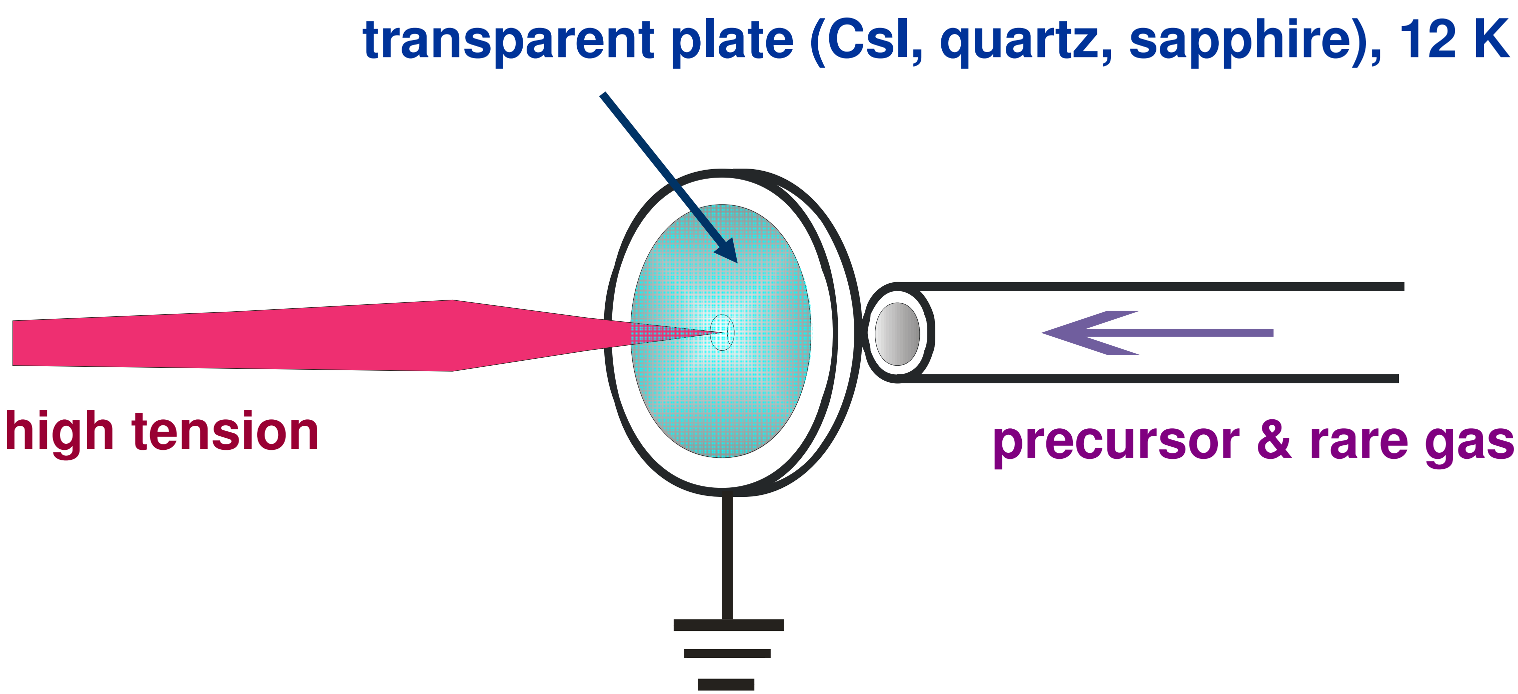
Cernicharo, J., Heras, A.M., Tielens, A.G.G.M., Pardo, J.R., Herpin, F., Guélin, M., and Waters, L.B.F.M.; 2001, *Ap. J.* 546, L123




Quantum chem.
Lab. measurements
Observations


PHOTOLYSIS
ANALYSIS
precursor
solid Ar
12 K


to vacuum
substrate
photolysis (UV)
analysis (UV, Vis, IR)
window
'matrix'
rare gas + precursor

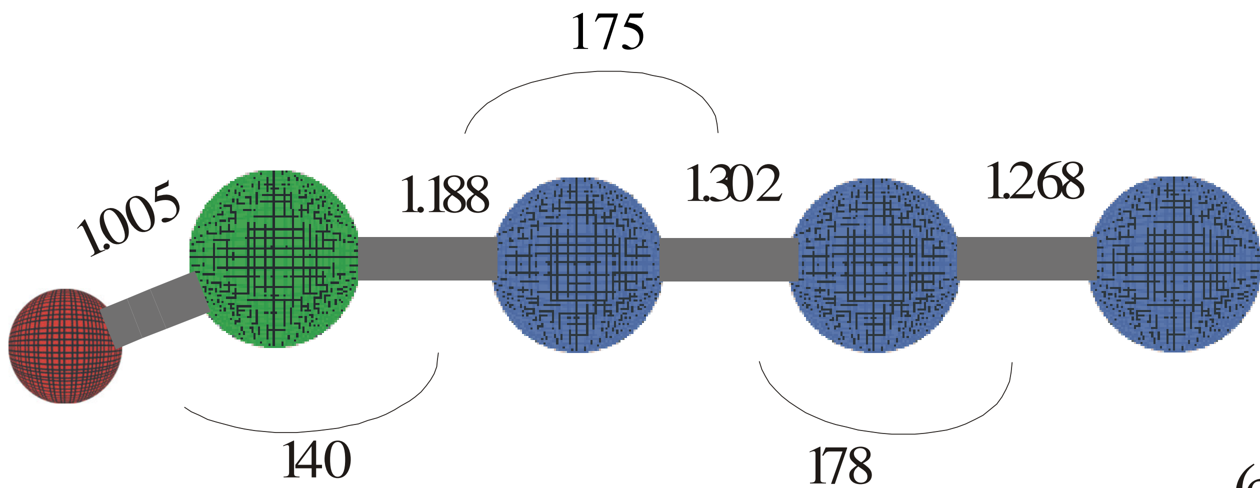


The Cold-Window-Radial-Discharge (CWRD)

R. Kołos; *Chem. Phys. Lett*. 247 (1995) 289

The Cold-Window-Radial-Discharge

R. Kołos,
Chem. Phys. Letters
247 (1995) 289



B_0=4668.5 MHz

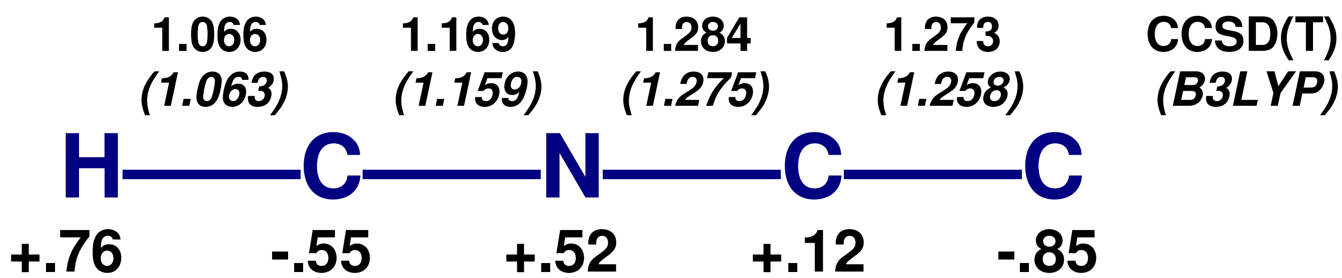
(exp.: 4668.3 MHz)

KOŁOS & SOBOLEWSKI, ***Chem.Phys.Letters*** **344 (2001) 625**

HNCCC IDENTIFICATION in IR

	Mode	Theory B3LYP/6-311++G** (scaled with 0.96)		Experimental (in solid Ar)	
		cm^{-1}	km/mol	cm^{-1}	relat. int.
$^{1}H^{14}NCCC$	ν_1	3567	448	3562	0.4
	ν_2	2202	1590	2205	1
	ν_3	1880	27	1905	0.06
$^{2}H^{14}NCCC$	ν_1	2658	560	[illegible]	0.5
	ν_2	2171	1408	[illegible]	1
	ν_3	1855	12	[illegible]	[illegible]
$^{1}H^{15}NCCC$	ν_1	3557	435	3552	[illegible]
	ν_2	2193	1591	2195	1
	ν_3	1869	17	1895	

KOŁOS & SOBOLEWSKI, *Chem.Phys.Letters* 344 (2001) 625

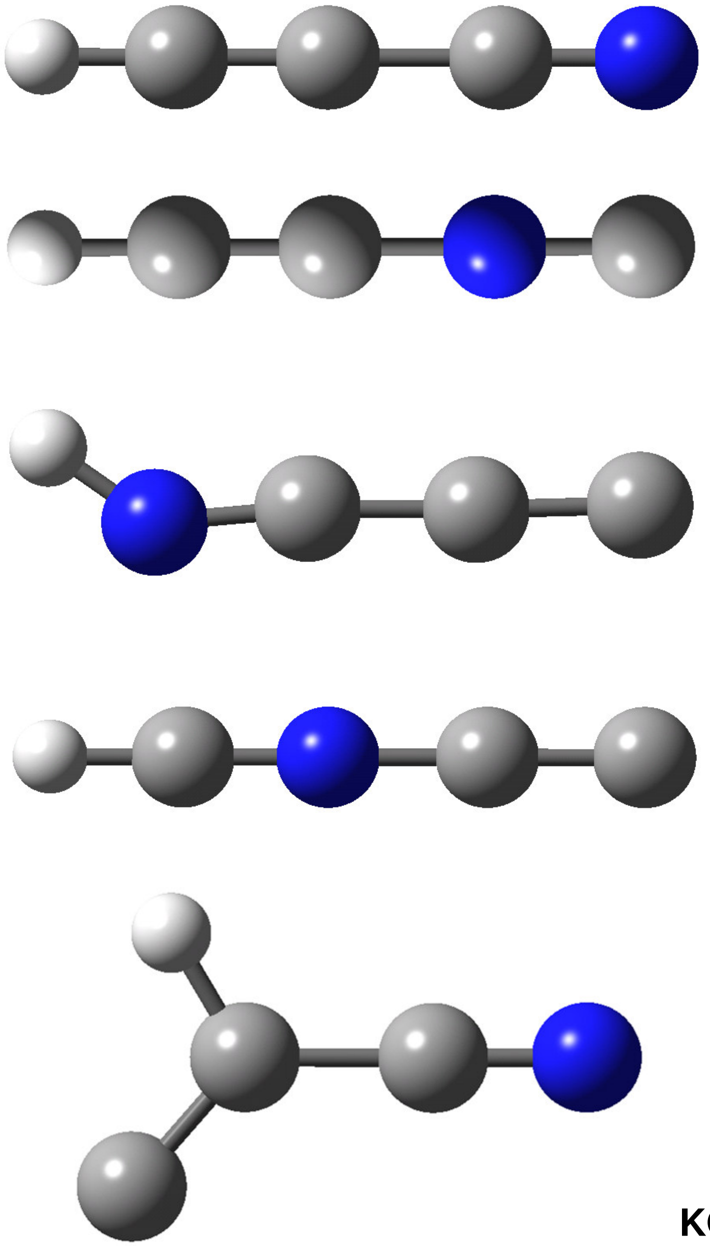


B_e = 4992 MHz

μ = 8.1 D (CCD/aug-cc-pVTZ)

KOŁOS & DOBROWOLSKI;
Chem. Phys. Letters **369 (2003) 75**

HC_3N isomers



CCSD(T)/aug-cc-pVTZ

species	Rel. energy (kcal/mol)	SPACE	LAB
HCCCN	0	+	+
HCCNC	26.6	+	+
CCCNH	50.9	+	+
HCNCC	77.6	-	+
CC(H)CN	48.6	-	-

KOŁOS & DOBROWOLSKI; *Chem. Phys. Letters* 369 (2003) 75

INTERSTELLAR MOLECULES

2	3	4	5	6	7	8	9	10	11	12	13
H_2	C_2H	$c\text{-}C_3H$	C_5	C_5H	C_6H	CH_2C_3N	**HC_7N**	CH_3C_5N?	**HC_9N**	C_6H_6	**$HC_{11}N$**
AlF	C_2O	$l\text{-}C_3H$	C_4H	$l\text{-}H_2C_4$	CH_2CHCN	$HCOOCH_3$	CH_3CH_2CN	$(CH2)_2CO$			
AlCl	C_2S	C_3N	C_4Si	C_2H_4	CH_3C_2H	CH_2COOH?	$(CH_2)_2O$	NH_2CH_2COOH?			
C_2	CH_2	C_3O	$l\text{-}C_3H_2$	CH_3CN	**HC_5N**	C_7H	CH_3CH_2OH				
CH	**HCN**	C_3S	$c\text{-}C_3H_2$	CH_3NC	$HCOCH_3$	CH_2OHCHO	CH_3C_4H				
CH+	HCO	CH_2D+?	CH_2CN	CH_3OH	NH_2CH_3	HC_6H	C_8H				
CN	HCO+	HCCN	CH_4	CH_3SH	$c\text{-}C_2H_4O$						
CO	HCS+	HCNH+	**HC_3N**	HC_3NH+	CH_2CHOH						
CO+	HOC+	HNCO	HC_2NC	HC_2CHO							
CP	H_2O	HNCS	HCOOH	NH_2CHO							
CSi	H_2S	HOCO+	H_2CNH	HC_4H							
HCl	HNC	H_2CO	H_2C_2O								
KCl	HNO	H_2CN	H_2NCN								
NH	MgCN	H_2CS	HNC_3								
NO+	MgNC	H_3O+	SiH_4								
NS	N_2H+	NH_3	H_2COH^+								
NaCl	N_2O	SiC_3									
OH	NaCN	HC_2H									
PN	OCS										
SO	SO_2										
SO+	$c\text{-}SiC_2$										
SiN	CO_2										
SiO	NH_2										
SiS	SiCN										
CS	H_3+										
HF	C_3										
SH	AlNC										
FeO											

H-C≡C-C≡C-C≡N

1975:

DETECTION OF THE HEAVY INTERSTELLAR MOLECULE CYANODIACETYLENE

L. W. AVERY, N. W. BROTEN, J. M. MACLEOD, AND T. OKA
Herzberg Institute of Astrophysics, National Research Council of Canada, Ottawa, Ontario, Canada

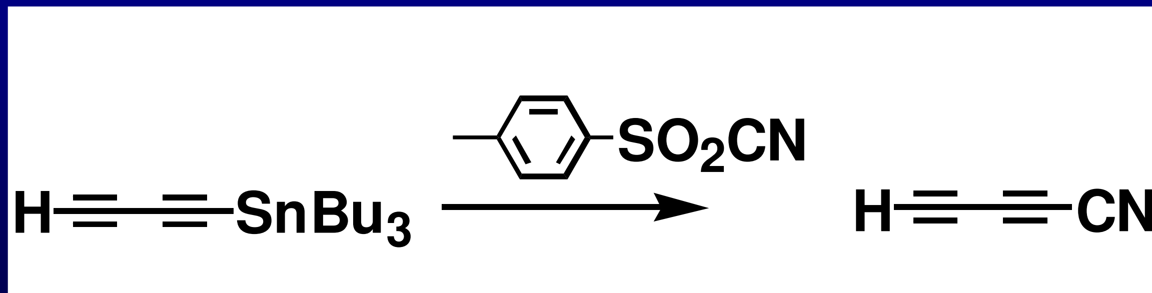
AND

H. W. KROTO
School of Molecular Sciences, University of Sussex, Brighton, England
Received 1975 December 10; revised 1976 January 29

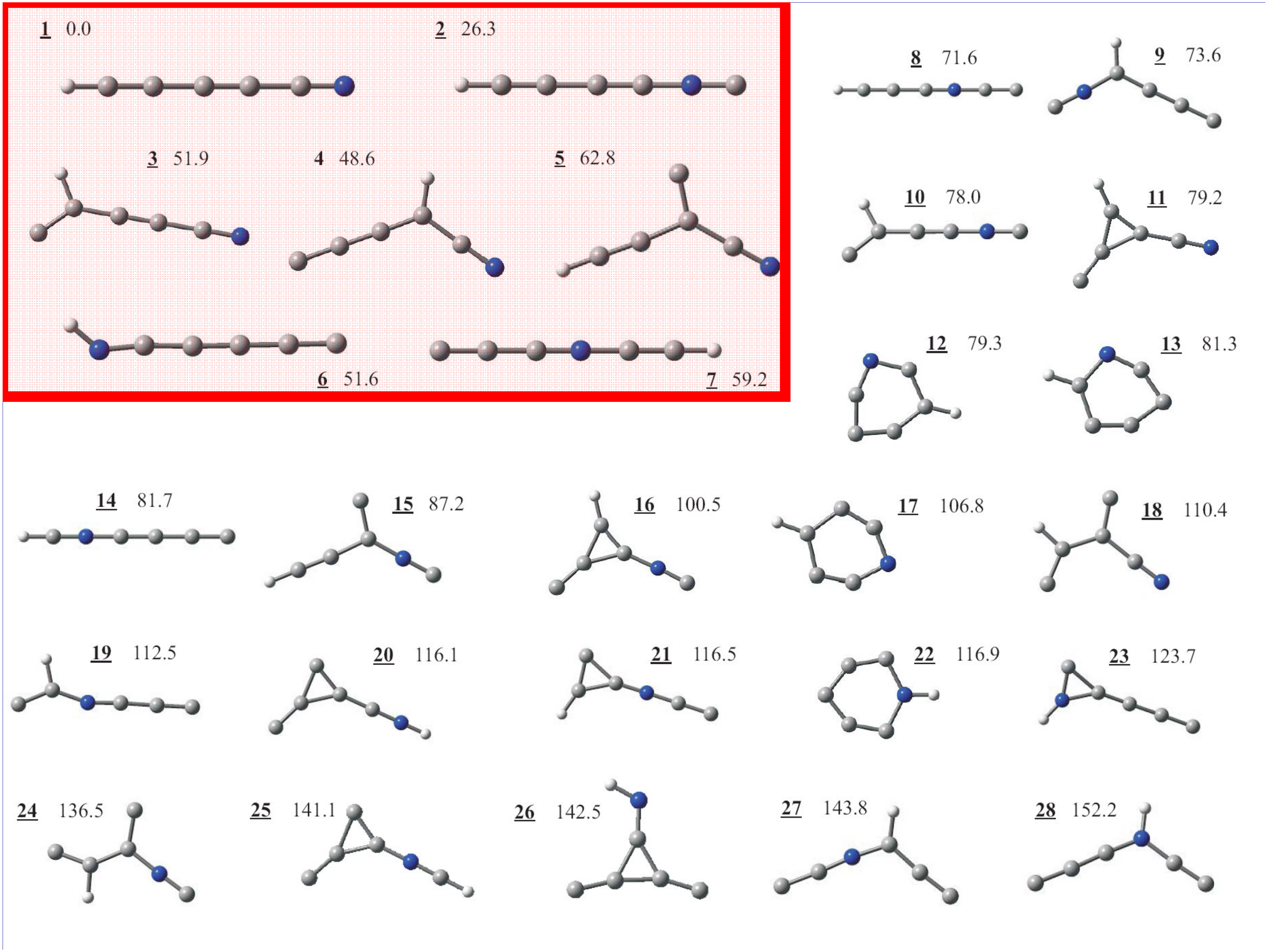
ABSTRACT

The $J = 4 \rightarrow 3$ rotational emission line of cyanodiacetylene H—C≡C—C≡C—C≡N has been detected in Sgr B2. If the molecules are assumed to be in thermal equilibrium at a temperature of 30 K, a column density of 1.5×10^{14} cm^{-2} is obtained. This observation provides further evidence that heavy polyatomic molecules exist in abundance in Sgr B2.

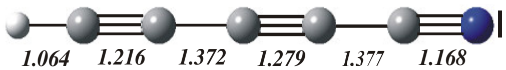
2005:



Trolez & Guillemin, *Angew. Chem. Int. Ed.*, 55 (2005) 2

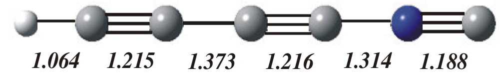

1 0.0
2 26.3
3 51.9
4 48.6
5 62.8
6 51.6
7 59.2
8 71.6
9 73.6
10 78.0
11 79.2
12 79.3
13 81.3
14 81.7
15 87.2
16 100.5
17 106.8
18 110.4
19 112.5
20 116.1
21 116.5
22 116.9
23 123.7
24 136.5
25 141.1
26 142.5
27 143.8
28 152.2

1 98
120



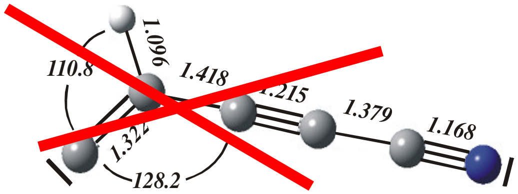
0 kcal/mol

2 140
120
72



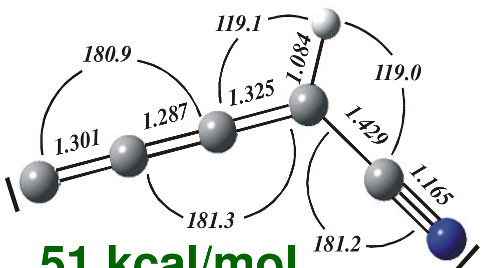
27 kcal/mol

3 95
89
51



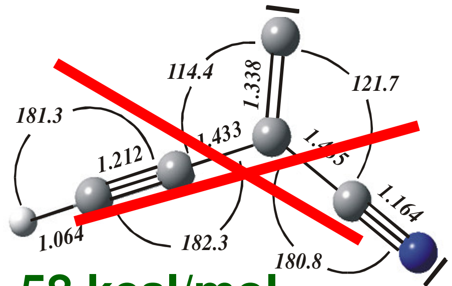
49 kcal/mol

4 1010



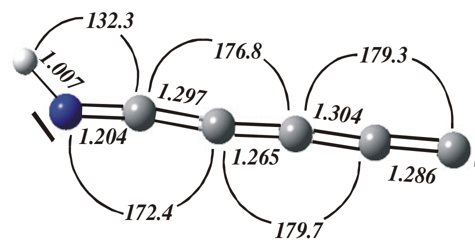
51 kcal/mol

5 81



58 kcal/mol

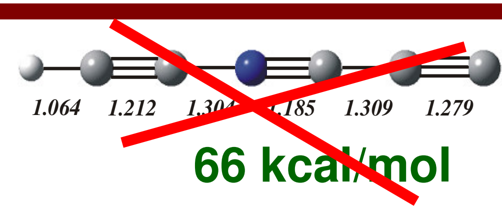
6 3890
580
500
460



61 kcal/mol

Predicted IR intensities higher than 50 km/mol

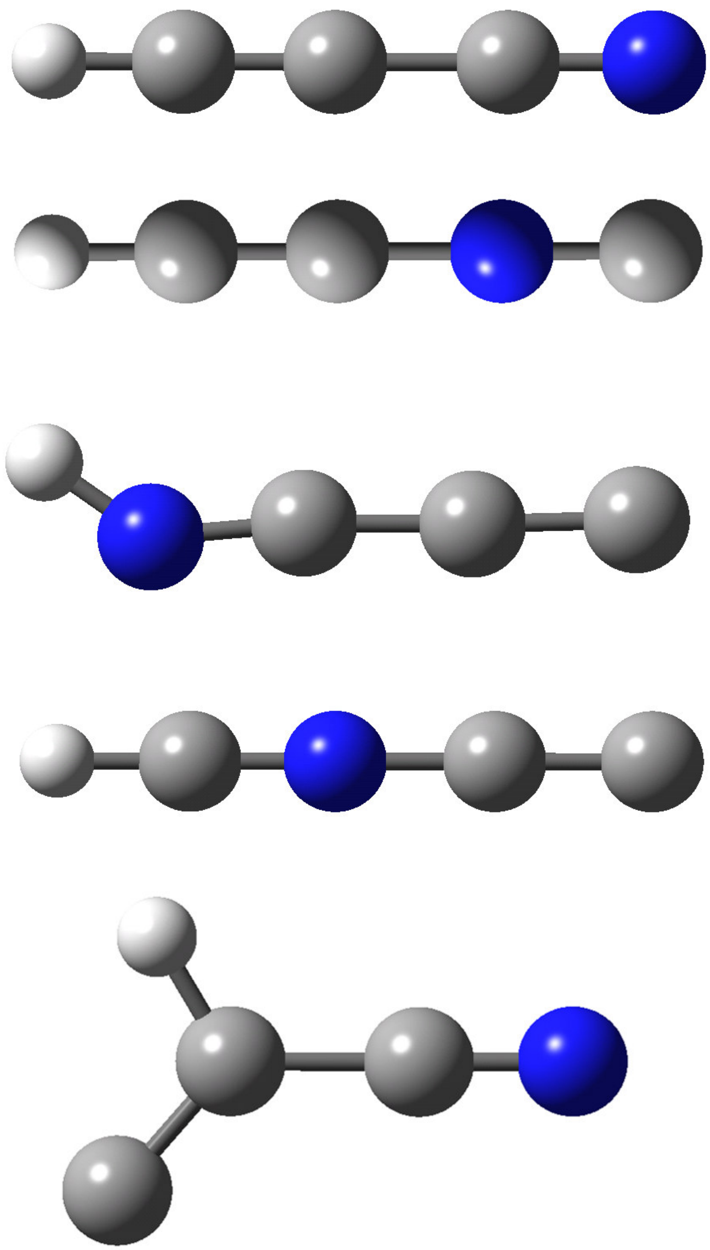
7 710
530
380
190



66 kcal/mol

GRONOWSKI & KOŁOS; *Chem. Phys. Lett.* 428 (2006) 245
GRONOWSKI & KOŁOS; *J. Molec. Structure* 834 (2007) 102

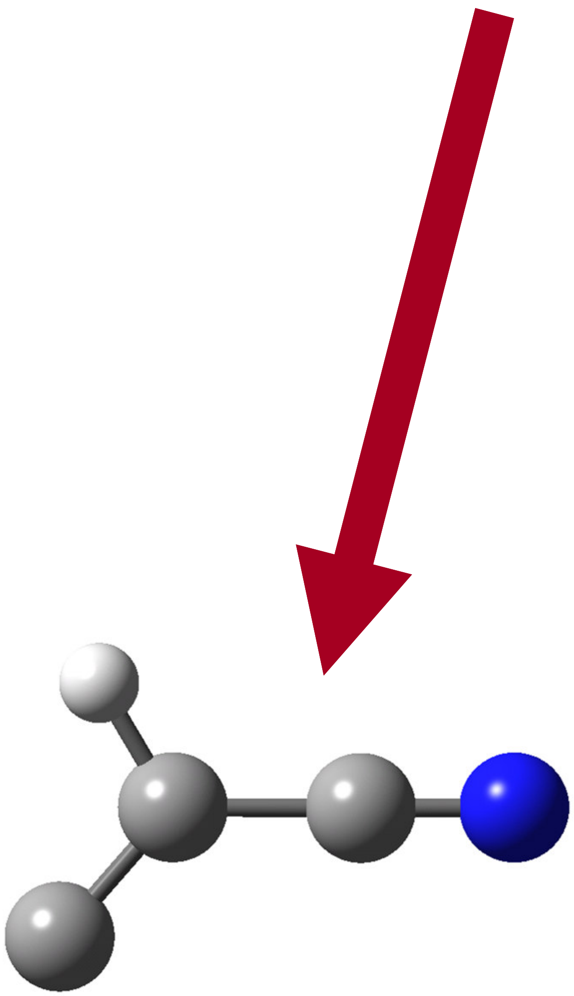
HC_3N isomers



CCSD(T)/aug-cc-pVTZ

species	Rel. energy (kcal/mol)
HCCCN	0
HCCNC	26.6
CCCNH	50.9
HCNCC	77.6
CC(H)CN	48.6

Can <u>cyanovinylidyne</u> be produced in space?



HC_3N first detected in 1971.

How is it formed?

<u>Original concept</u>:

$$HC_3NH^+ + e \rightarrow HC_3N + H^+$$
$$HC_3NH^+ + e \rightarrow H^+ + HNC_3$$

<u>Indeed</u>:

HNC_3 (along with HC_2NC) detected in 1992, but: $[HC_3N]/[HNC_3] \approx 1000$!

<u>Newer concept</u>: $$H_2C_2 + CN \rightarrow HC_3N + H$$

(with the dissociative recombination of HC_3NH^+ still being recognized as the main source of cyanoacetylene <u>isomers</u>)

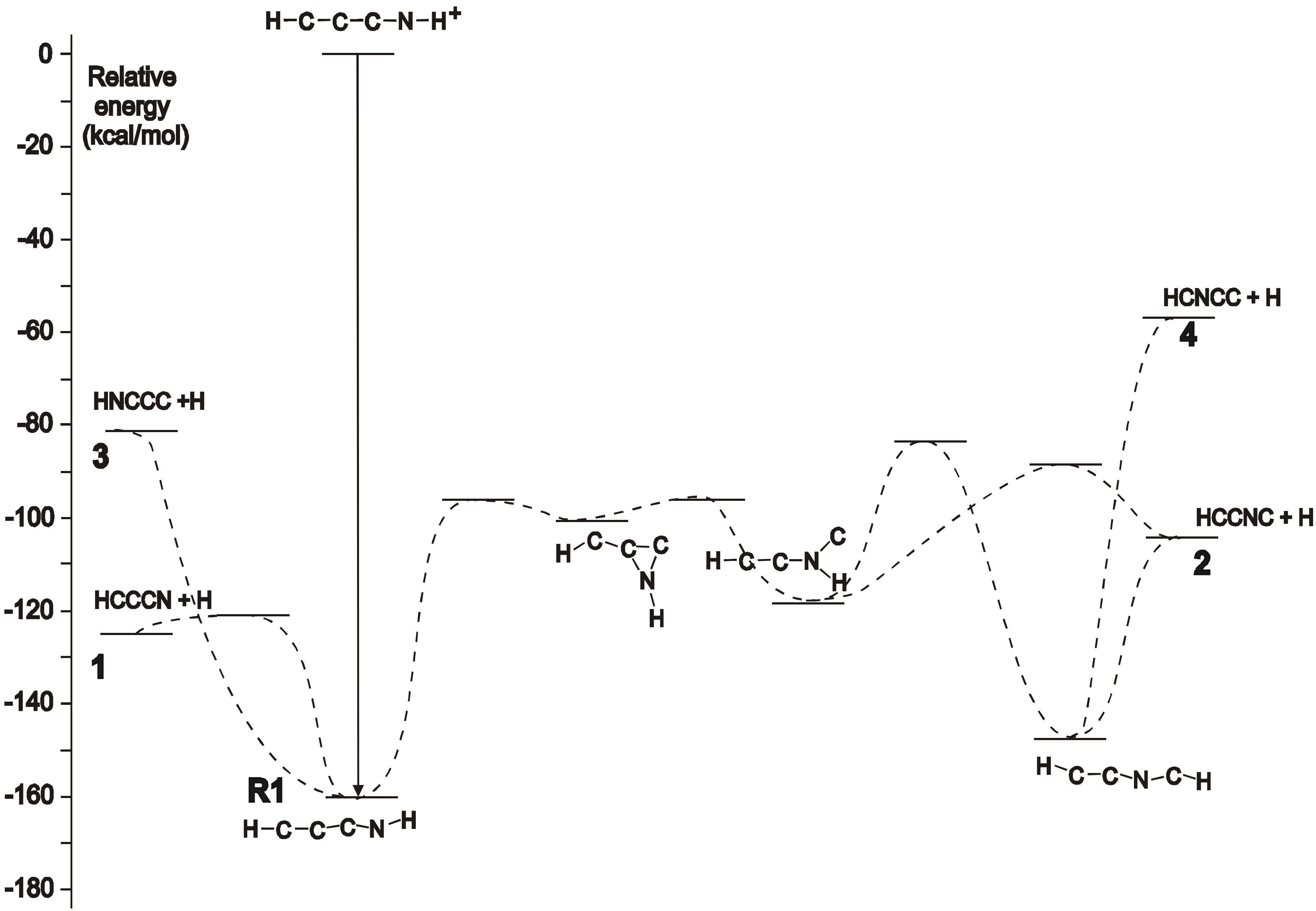
The dissociative recombination of HC_3NH^+

$$HC_3NH^+ + e \rightarrow HC_3NH$$

$$\downarrow$$

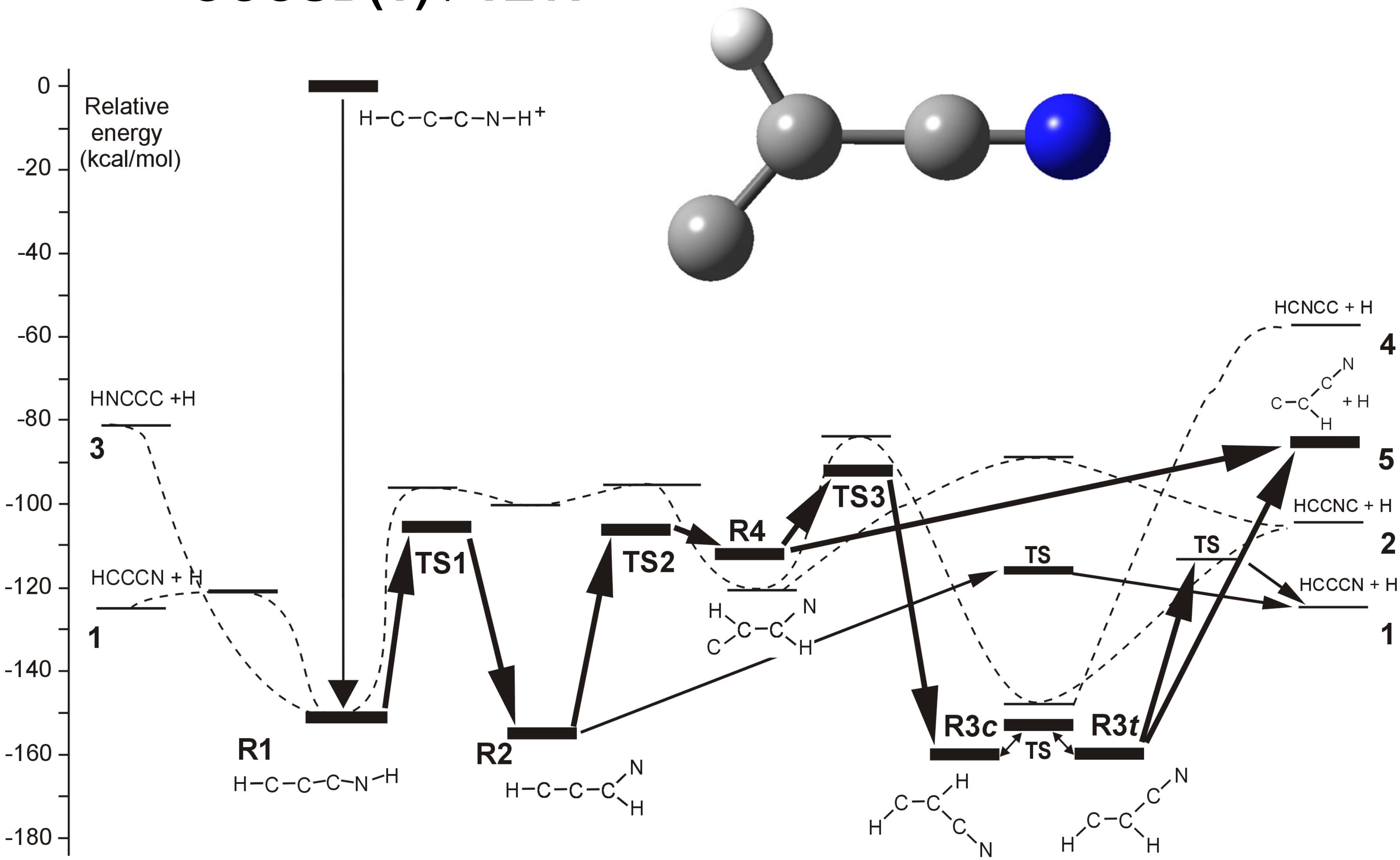
$$H + \text{an } HC_3N \text{ isomer}$$

HC_3NH^+ creation : $HCCH^+ + HNC \rightarrow HC_3NH^+ + H$
or the protonation of HC_3N

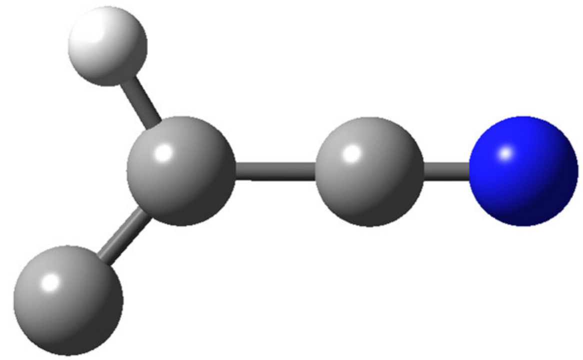


OSAMURA et al. *Ap. J.* 519 (1999) 697

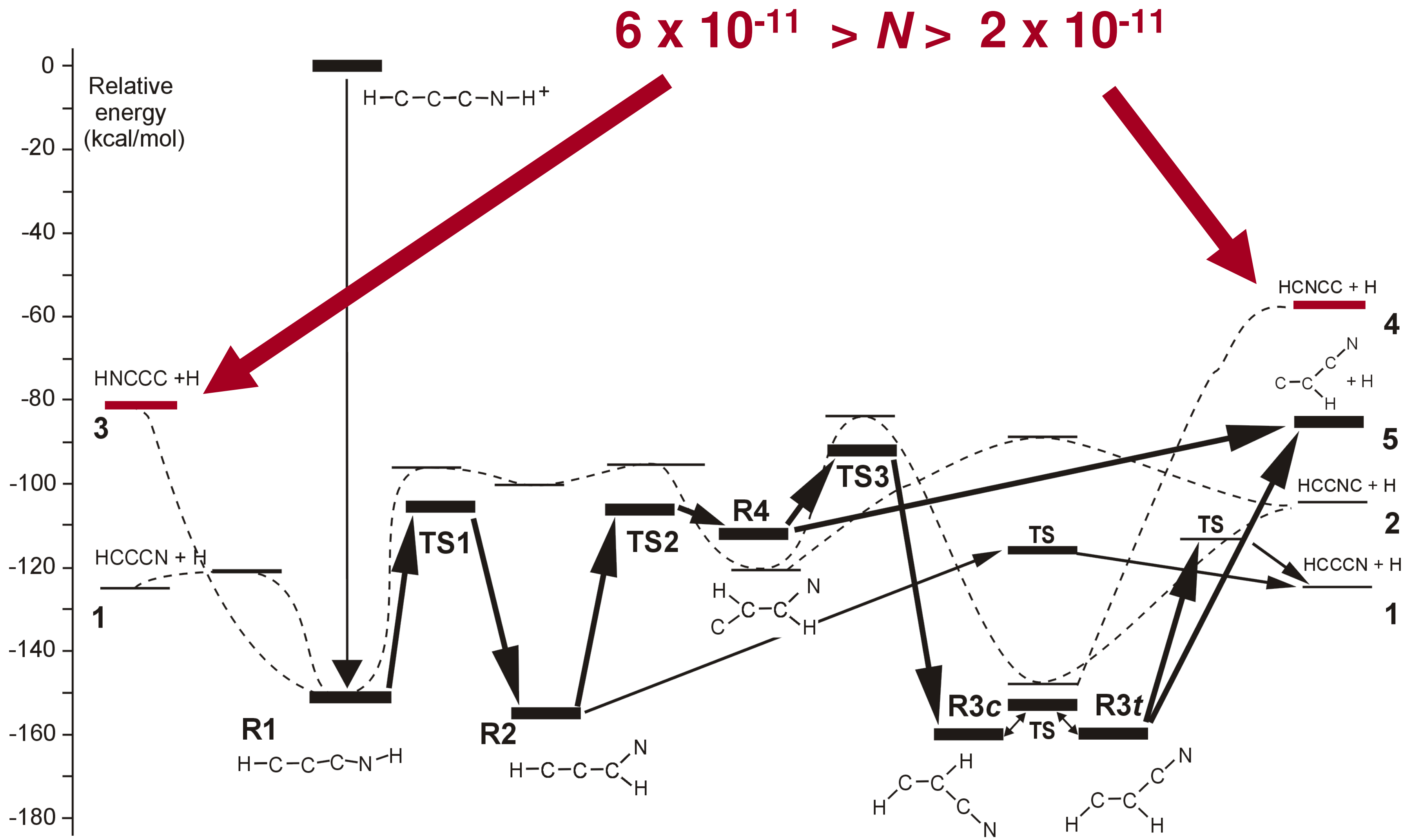
UCCSD(T) / TZVP



KOŁOS, GRONOWSKI, & DOBROWOLSKI, *A. & Ap.*, in preparation



Can cyanovinylidyne be detected?



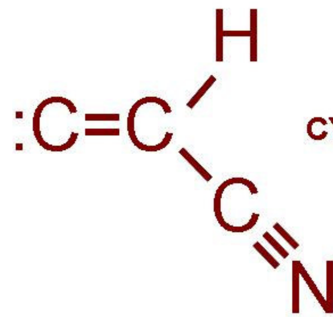
6 x 10-11 > N > 2 x 10-11
Relative energy (kcal/mol)
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
H–C–C–C–N–H+
HNCCC +H
3
HCCCN + H
1
R1
H–C–C–C–N–H
TS1
R2
H–C–C–C–N–H
TS2
R4
TS3
R3c
TS
R3t
HCNCC + H
4
+ H
5
HCCNC + H
2
HCCCN + H
1

Cyanovinylidene, rotational spectroscopy

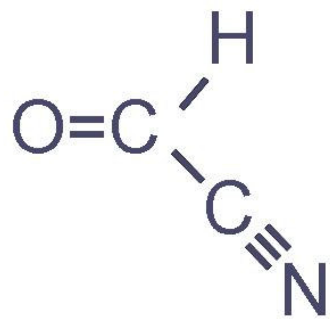
CCSD(T) prediction:

A_o= 72 773 MHz
B_o= 5 431 MHz
C_o= 5 054 MHz

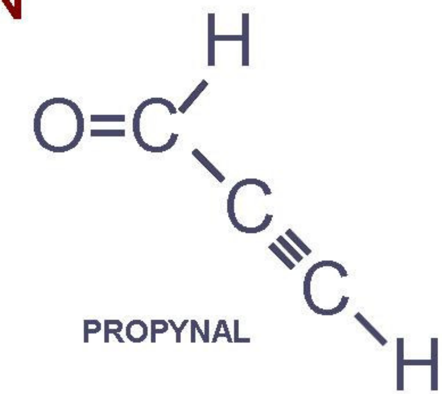
(scaling factor 1.010)



CYANOVINYLIDYNE



CYANOFORMALDEHYDE



PROPYNAL

CCSD/cc-pVTZ
electric dipole moment
prediction: 2.77 D

Cyanovinylidene, vibrational spectroscopy
CCBD(T) anharmonic predictions

Mode / symmetry	Wavenumber cm^{-1}	Intensity km/mol
1 / *A'*	2916.7	53
2 / *A'*	2257.2	22
3 / *A'*	1661.4	79
4 / *A'*	973.6	2
5 / *A'*	896.6	2
6 / *A'*	388.8	2
7 / *A'*	141.0	23
8 / *A''*	614.2	20
9 / *A''*	352.9	0

INTERSTELLAR ANIONS

$(CC)_nCCH^-$ series:

***n* = 2:** C_6H^-

McCarthy et al., *Ap. J.* 652, L141 (**2006**)

***n* = 1, 3:** C_4H^- and C_8H^-

Cernicharo et al., *A.& Ap.* 467, L37 (**2007**)
Brünken et al., *Ap. J.* 664, L43 (**2007**)
Gupta et al., *Ap. J.* 655, L57 (**2007**)

$(CC)_nCN^-$ series:

***n* = 1:** C_3N^-

P. Thaddeus et al., Astrophys. J. **677**, 1132 (2008).

Experimental studies on $(CC)_nCN^-$

► **mass spectrometry, soot/graphite arcing in N_2 atmosphere**

Wang et al. *Chem. Phys. Lett.* 237, 463 (1995)

CN^-, C_3N^- , ... $C_{13}N^-$ (n = 0 – 6)

► **matrix isolation of mass-selected ions**

Grutter et al. *J. Chem. Phys.* 110, 1492 (1999)

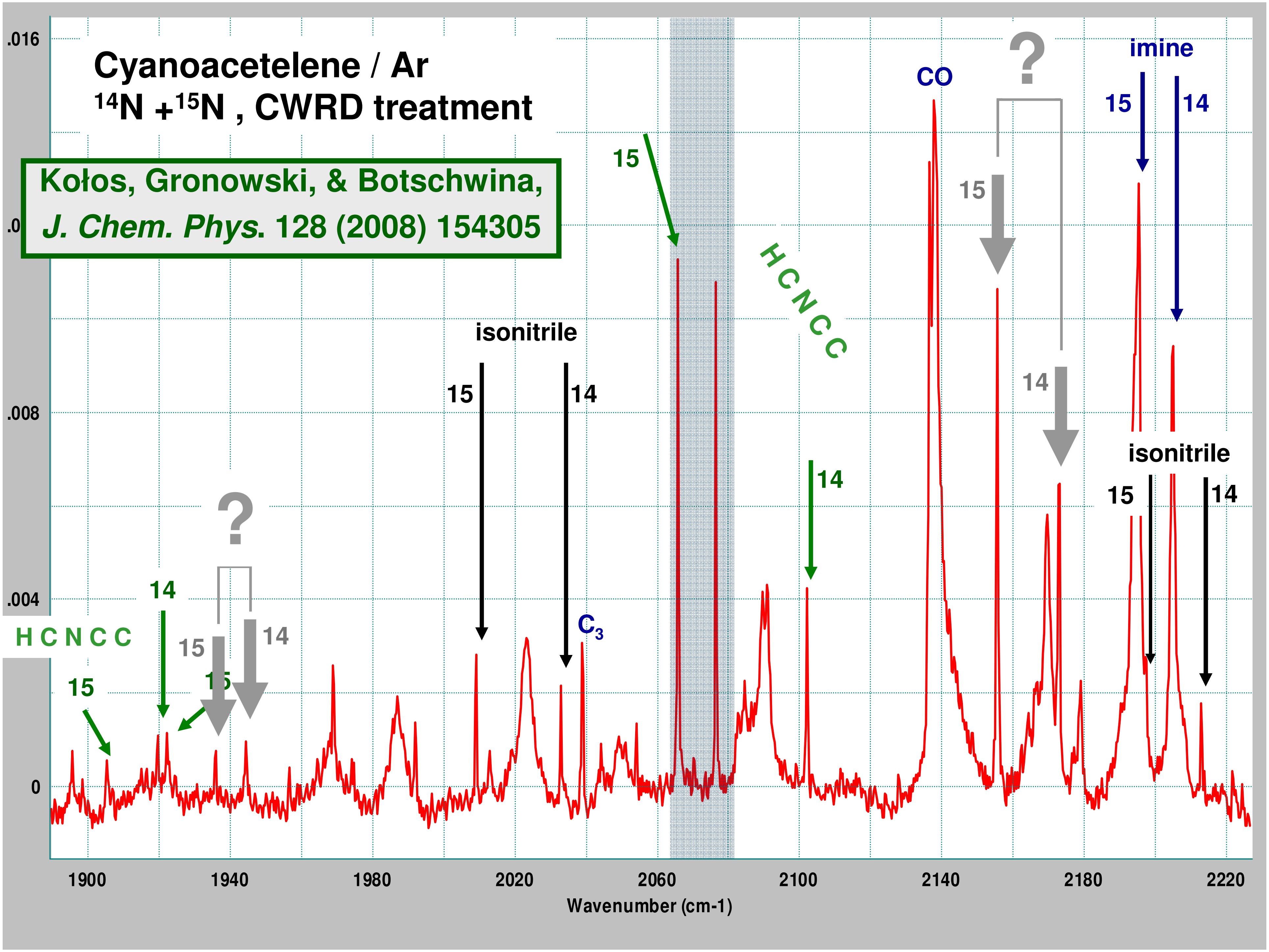
electronic spectra n = 3 – 6

IR spectra n = 2 – 4

n = 1 ?

The Cold-Window-Radial-Discharge

(*CWRD*)



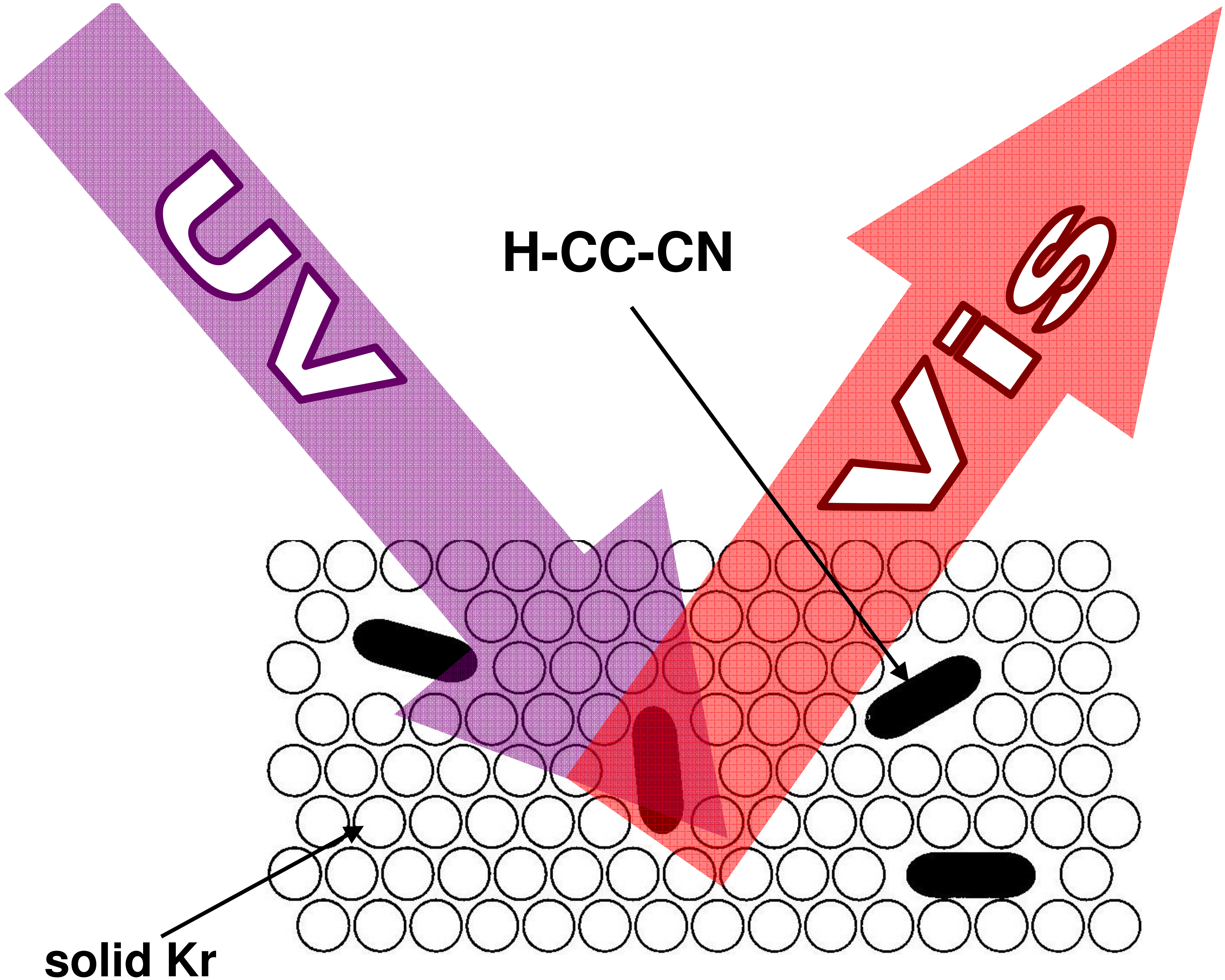
Cyanoacetelene / Ar
14N +15N , CWRD treatment
Kołos, Gronowski, & Botschwina,
J. Chem. Phys. 128 (2008) 154305
.016
.008
.004
0
H C N C C
15
14
?
15
14
isonitrile
15
14
C3
15
H C N C C
14
CO
?
15
14
imine
15
14
isonitrile
15
14
1900
1940
1980
2020
2060
2100
2140
2180
2220
Wavenumber (cm-1)

A single-nitrogen-containing non-hydride produced out of HC_3N

— $C_3N\cdot$ **no agreement with calculations**
P. Botschwina, M. Horn, J. Flügge & S. Seeger, J. Chem. Soc. Faraday Trans. 89, 2219 (1993)

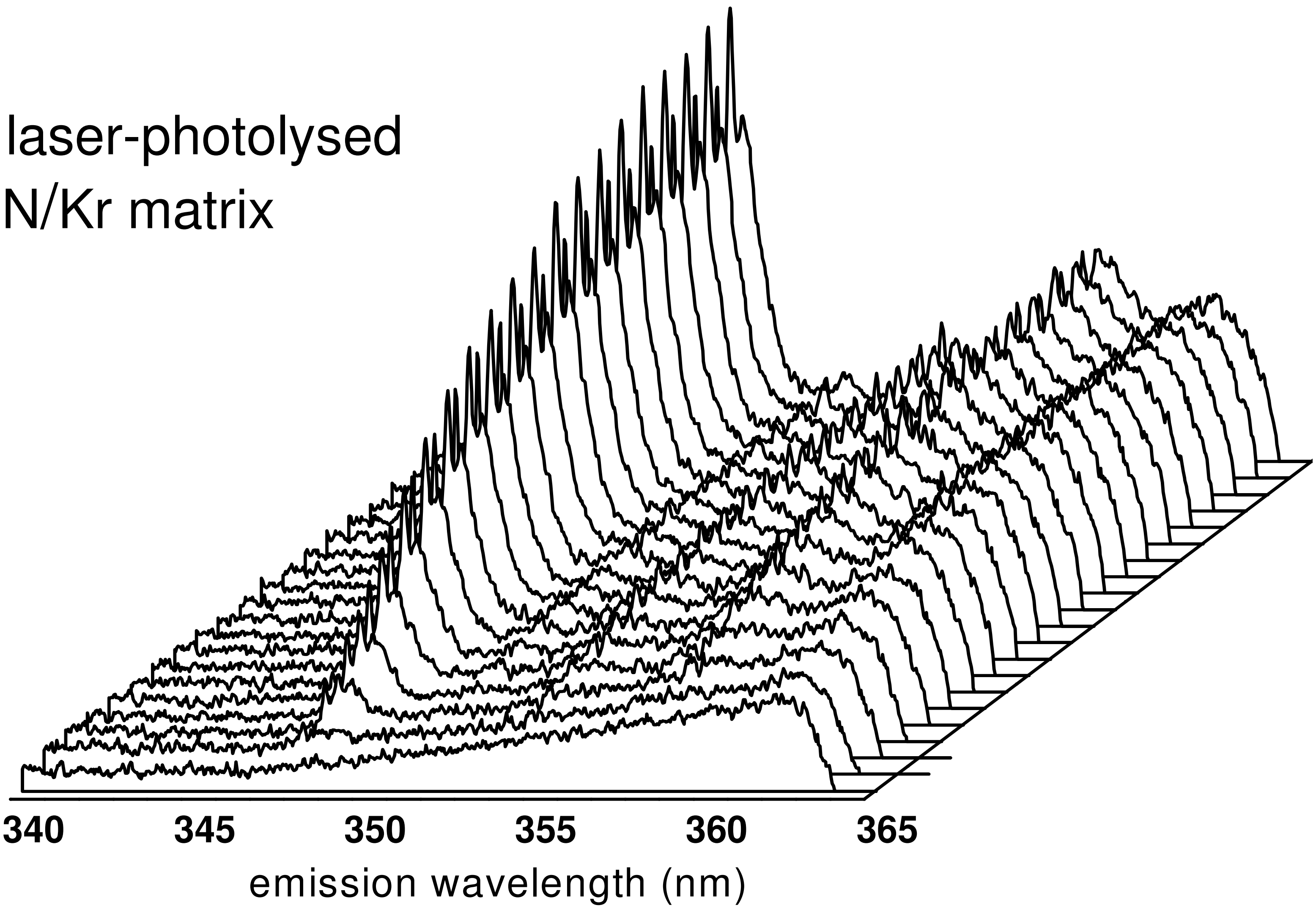
— C_3N^+ **as above; tentative identification of a band at 2202 cm^{-1} (Ne)** by
A. M. Smith-Gicklhorn, M. Lorenz, R. Kołos & V. E. Bondybey, J. Chem. Phys. 115, 7534 (2001)

— C_3N^- **a band at 2194 cm^{-1} (Ar) already atributed to C_3N^-** by
Z. Guennoun, I. Couturier-Tamburelli, N. Piétri & J.P. Aycard, Chem. Phys. Lett. 368, 574 (2003).

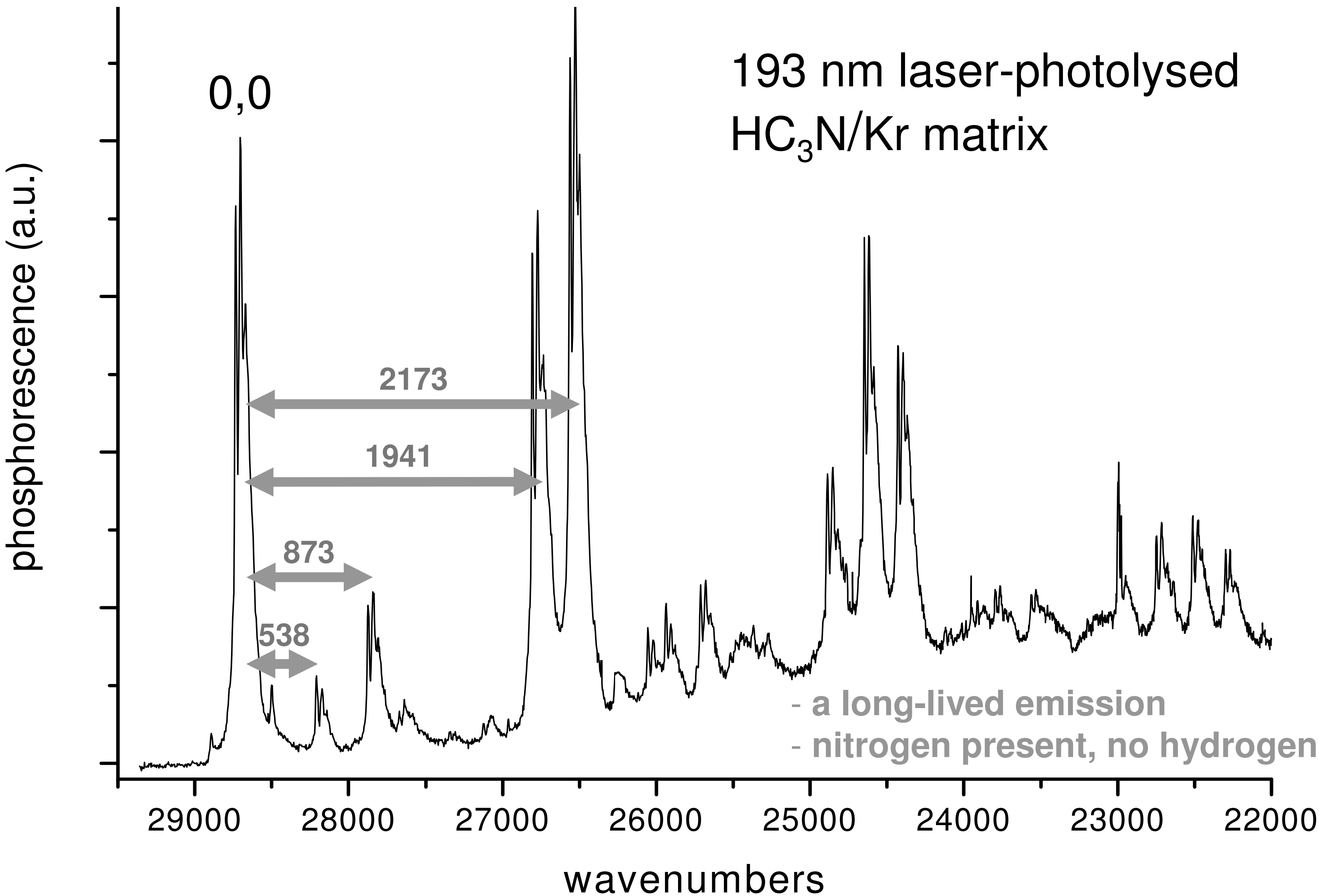

UV
VIS
H-CC-CN
solid Kr

ArF laser-photolysed

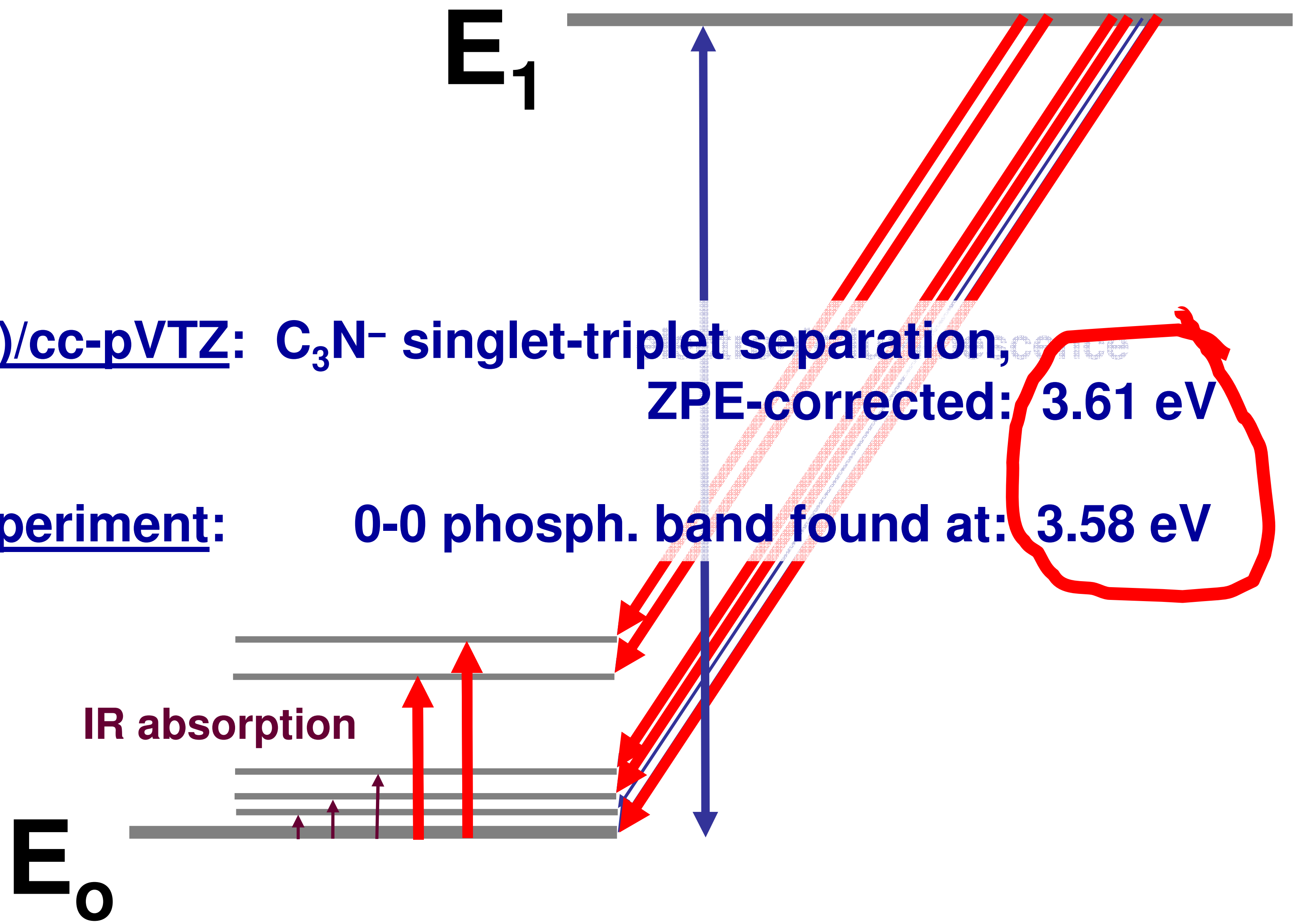
HC_3N/Kr matrix



- long-lived
- nitrogen present, no hydrogen



M. Turowski, M. Gronowski, C. Crépin, S. Douin, S. Boyé-Péronne, L. Monéron ,
R. Kołos, *J. Chem. Phys*. 128 (2008) 164304



BD(T)/cc-pVTZ: C_3N^- singlet-triplet separation,
ZPE-corrected: 3.61 eV

Experiment: 0-0 phosph. band found at: 3.58 eV

Vibrational spectroscopy of $CCCN^{-}$

	CCSD(T)		IR absorption in Ar		Phosphoresc. in Ar	
	cm^{-1} (*km/mol*)	14N-to-15N freq. shift	cm^{-1} (*% intensity*)	14N-to-15N freq. shift	cm^{-1}	14N-to-15N freq. shift
ν_1	2182.3 (*474.3*)	-18.2	2178.7 (*52*)	-22.6	2173	-20
			2173.0 (*100*)	-17.2		
ν_2	1940.9 (*46*)	-8.2	1944.3 (*14*)	-8.3	1942	-9
ν_3	866.7 (*10.0*)	-10.1			873	-10
ω_4	532.8 (*11*)	-1.1			538	0
ω_5	203.0 (*14*)	-13.3				

Most intense IR absorptions of C_5N^- (freq. in cm^{-1})

	Theory		Experiment	
mode	CCSD(T)[a]	BD(T)[b]	Ar[b]	Ne[c]
ν_1	**2204** *(1245 km/mol)*	2207	2183.8	
ν_2	**2129** *(580 km/mol)*	2126	2111.3	2115.9[c]
ν_3	**1928** *(253 km/mol)*	1925	1923.2	

[a] Botschwina *et al.* (2008)

[b] Coupeaud, Turowski, Gronowski, Piétri, Kołos, Aycard; *J. Chem. Phys*. 128 (2008) 154303

[c] Grutter, Wyss, Maier, *J. Chem. Phys*. 110 (1999) 1492

OUTLOOK

1. The search for cyanovinylidene, in particular at UV/visible wavelengths.

2. Electronic spectroscopy of allowed (singlet-singlet) transitions for C_3N^- and C_5N^- anions.

3. Gas-phase spectroscopy of what has already been identified in frozen solids.

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