Infrared Spectroscopy of Ions, Radicals and Rydberg Atoms for Ariel Astronomy

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Outline

- experimental techniques based on application of high resolution time-resolved Fourier-transform infrared spectroscopy
- Time resolved laboratory spectra of radicals and ions
- Fourier transform infrared spectroscopy together with Laser ablation technique
- High-*l* (orbital momentum) atomic Rydberg states, n-*l* levels

Different stage of the planetary evolution

Strong x-ray and UV radiation

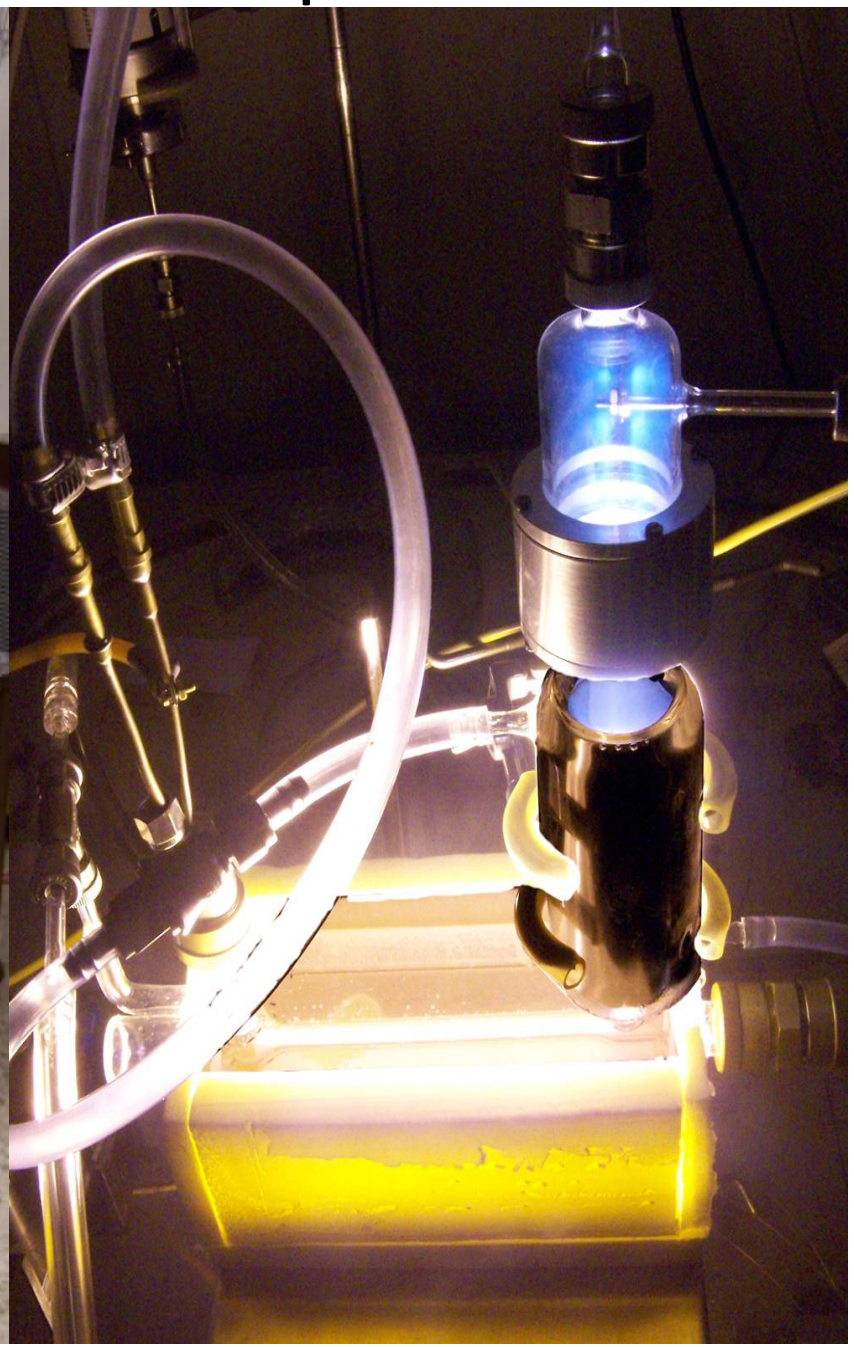
Ionization of the upper atmosphere

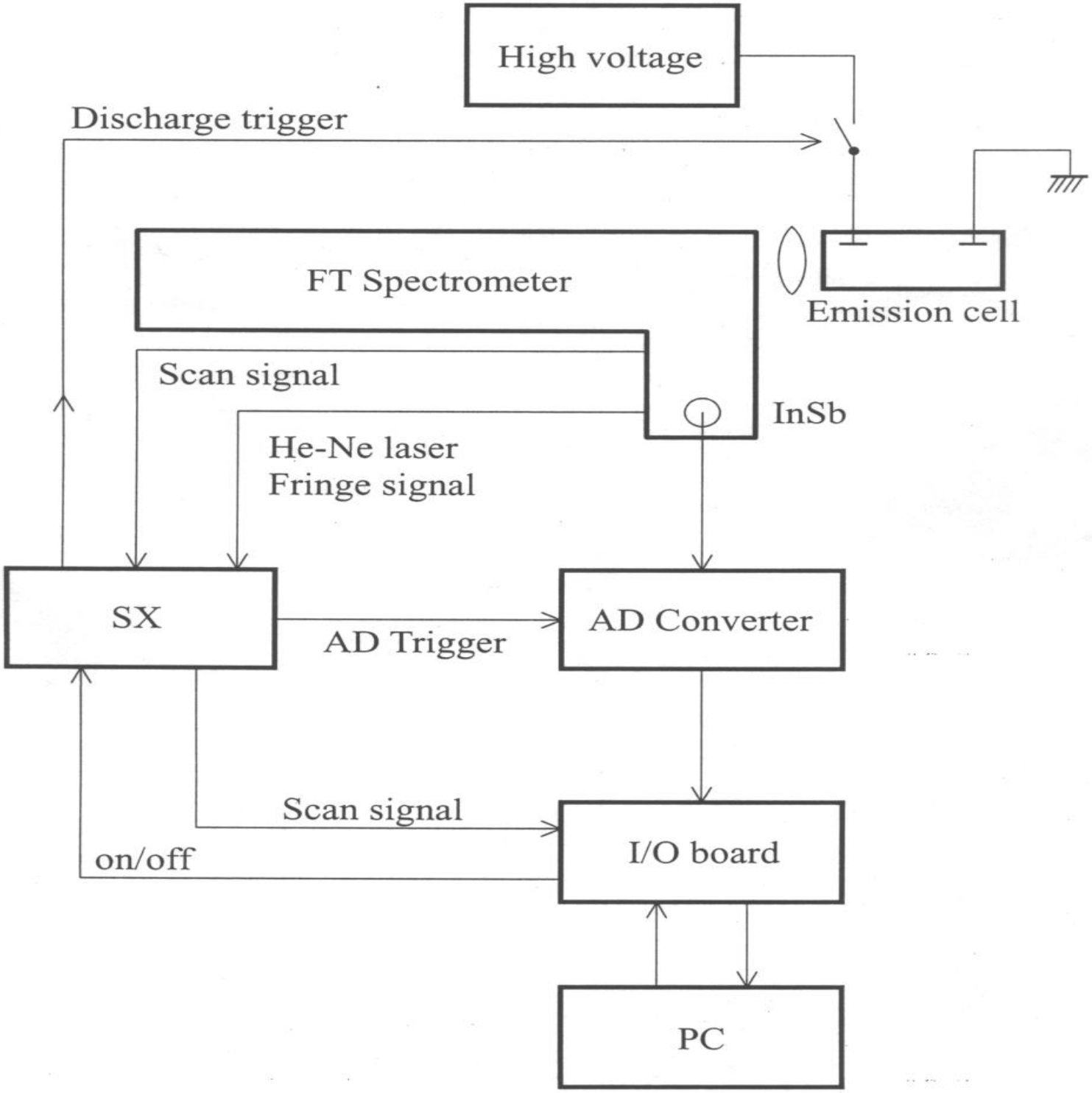
High excitation of the molecules, radicals and atoms

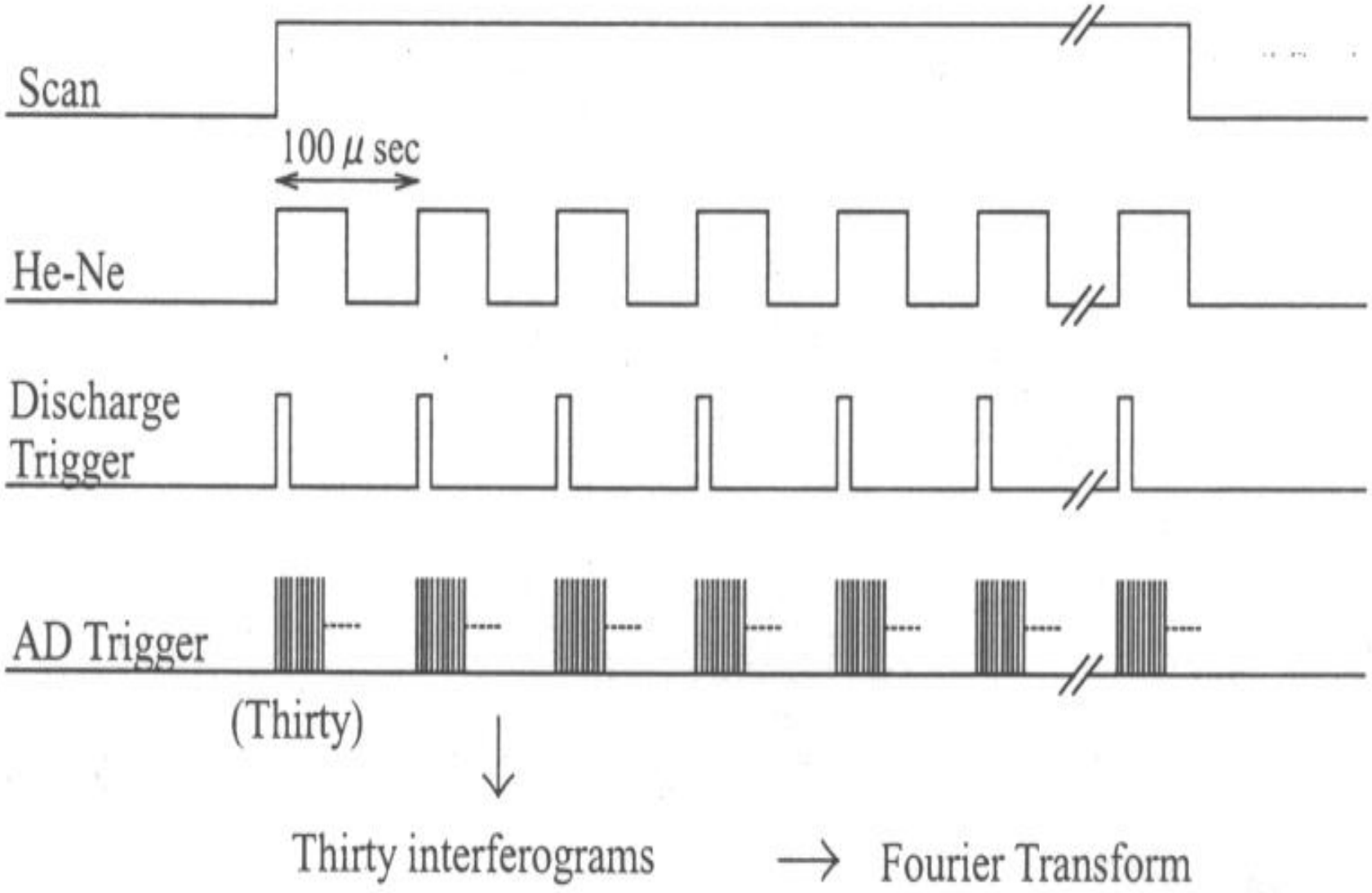
Impacts from remnants of the protoplanetary disk

Lightnings

Time resolved FTIR measurement in the discharge plasma or inside of the laser spark

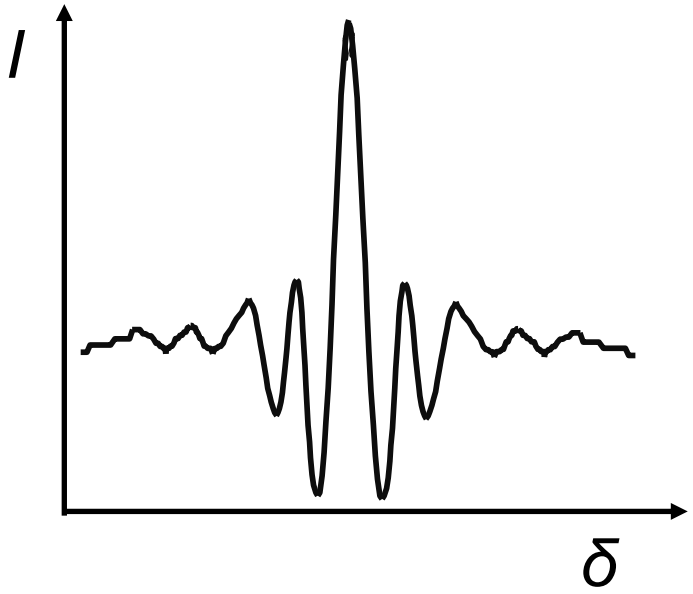



High voltage
Discharge trigger
FT Spectrometer
Emission cell
Scan signal
InSb
He-Ne laser
Fringe signal
SX
AD Converter
AD Trigger
Scan signal
on/off
I/O board
PC

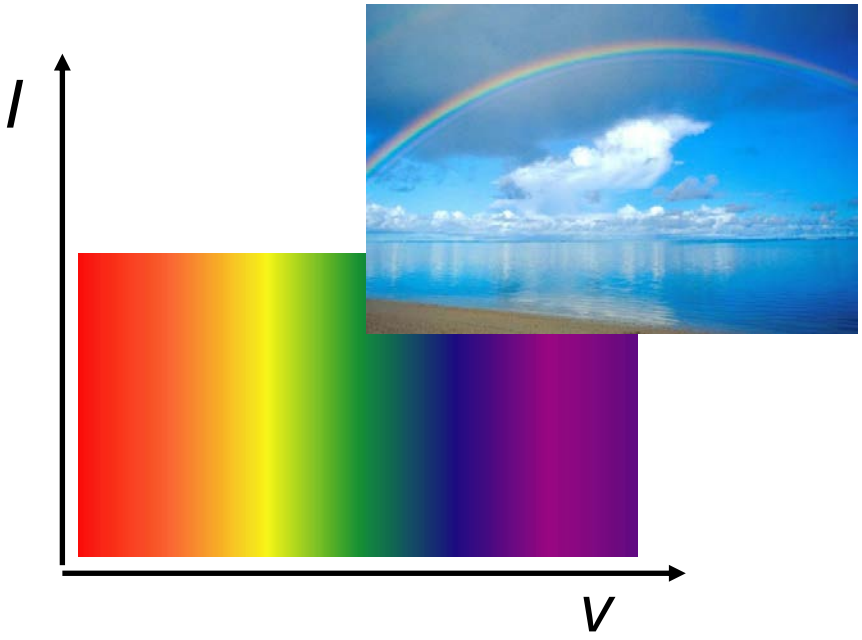

Scan
100 μ sec
He-Ne
Discharge
Trigger
AD Trigger
(Thirty)
Thirty interferograms
Fourier Transform

Fourier transformation

Interferogram



Spectrum

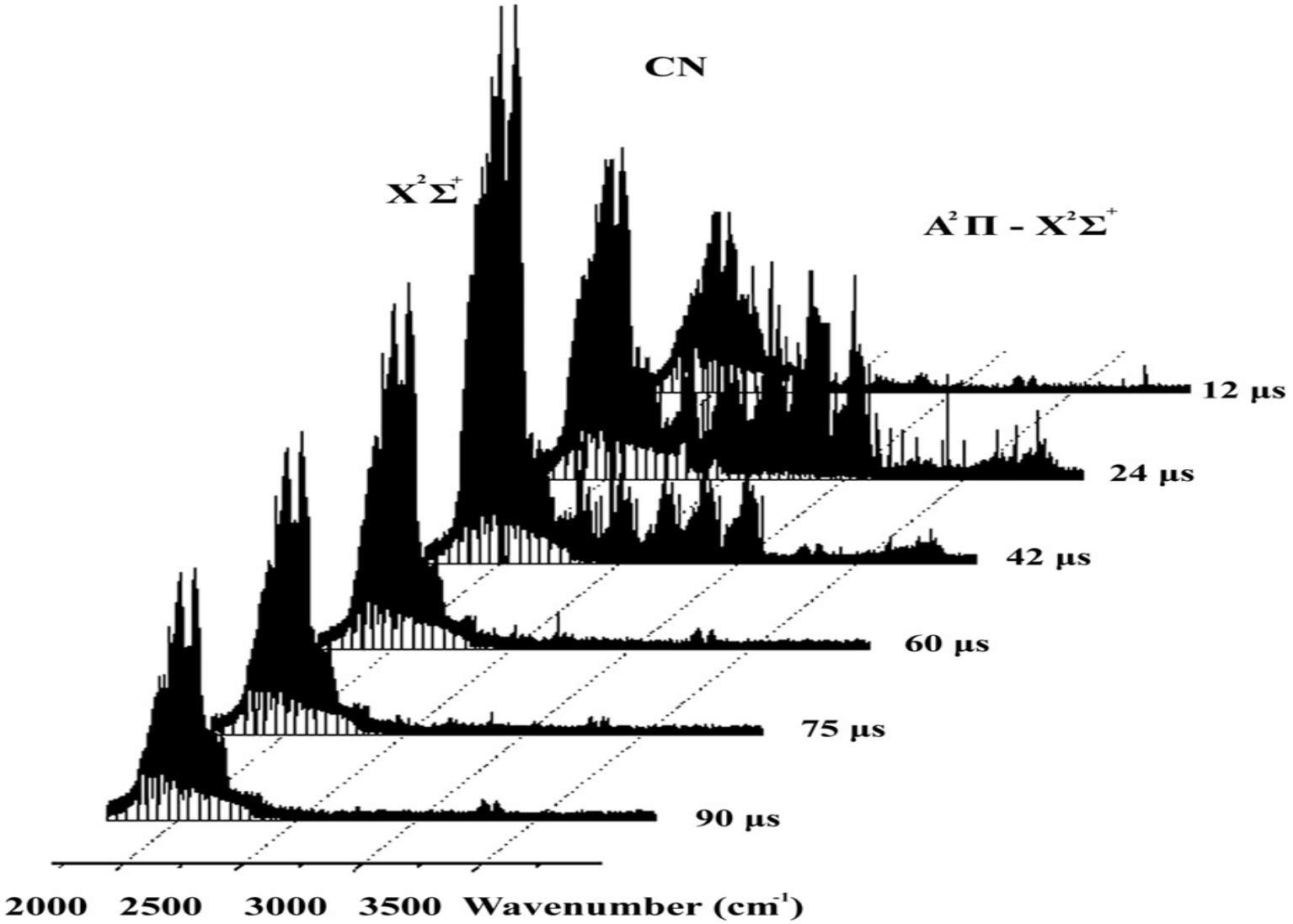


$$I(\delta) = \int_{-\infty}^{\infty} B(\nu)\cos(2\pi\nu\delta)d\nu$$

FT

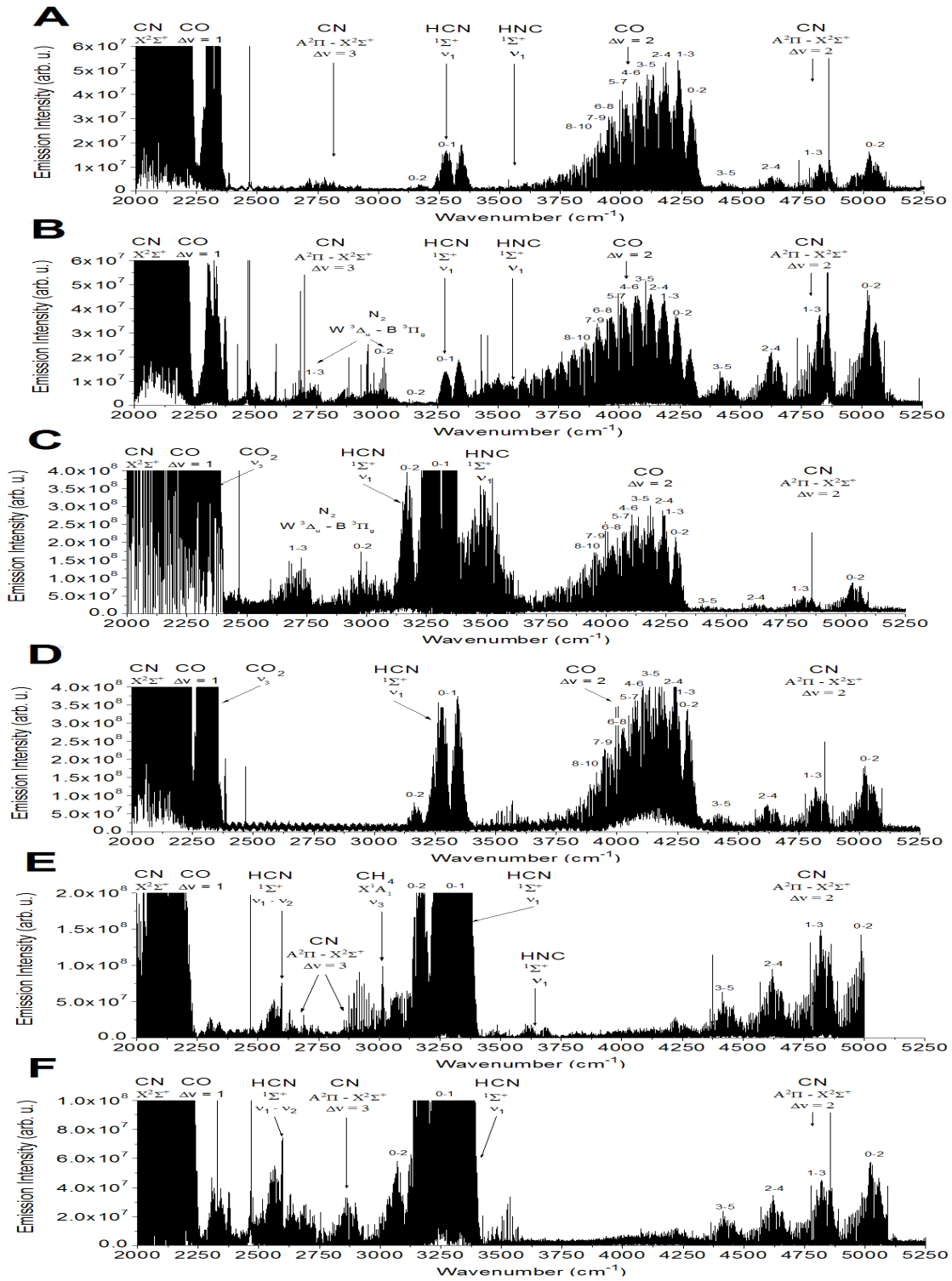
$$B(\nu) = \int_{-\infty}^{\infty} I(\delta)\cos(2\pi\nu\delta)d\delta$$

Ar + $(CN)_2$ discharge



The time-resolved emission FT spectrum from a pulsed discharge in a $(CN)_2$ and He mixture. The discharge pulse duration was 20μs. The 30 time-resolved spectra were collected from t = 0–90 μs with a step of 3 μs. The spectra of C_2H_2 and C_2 were observed at 3300 and 3600 cm^{-1}.

Planetary atmospheres



NH_3, CO, H_2O

$HCONH_2$, N_2, H_2O

HCHO, N_2, H_2O

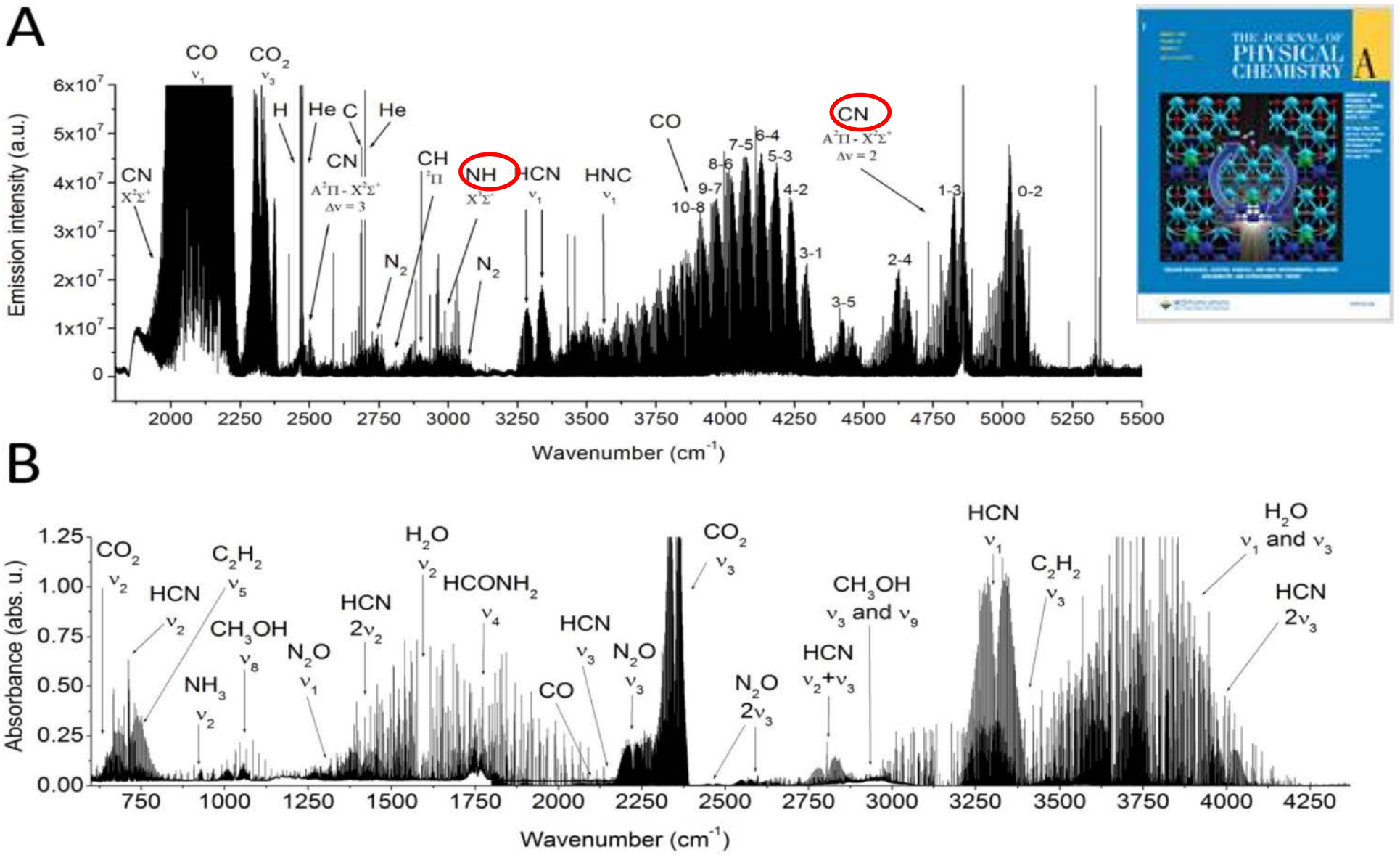
CH_3OH, N_2, H_2O

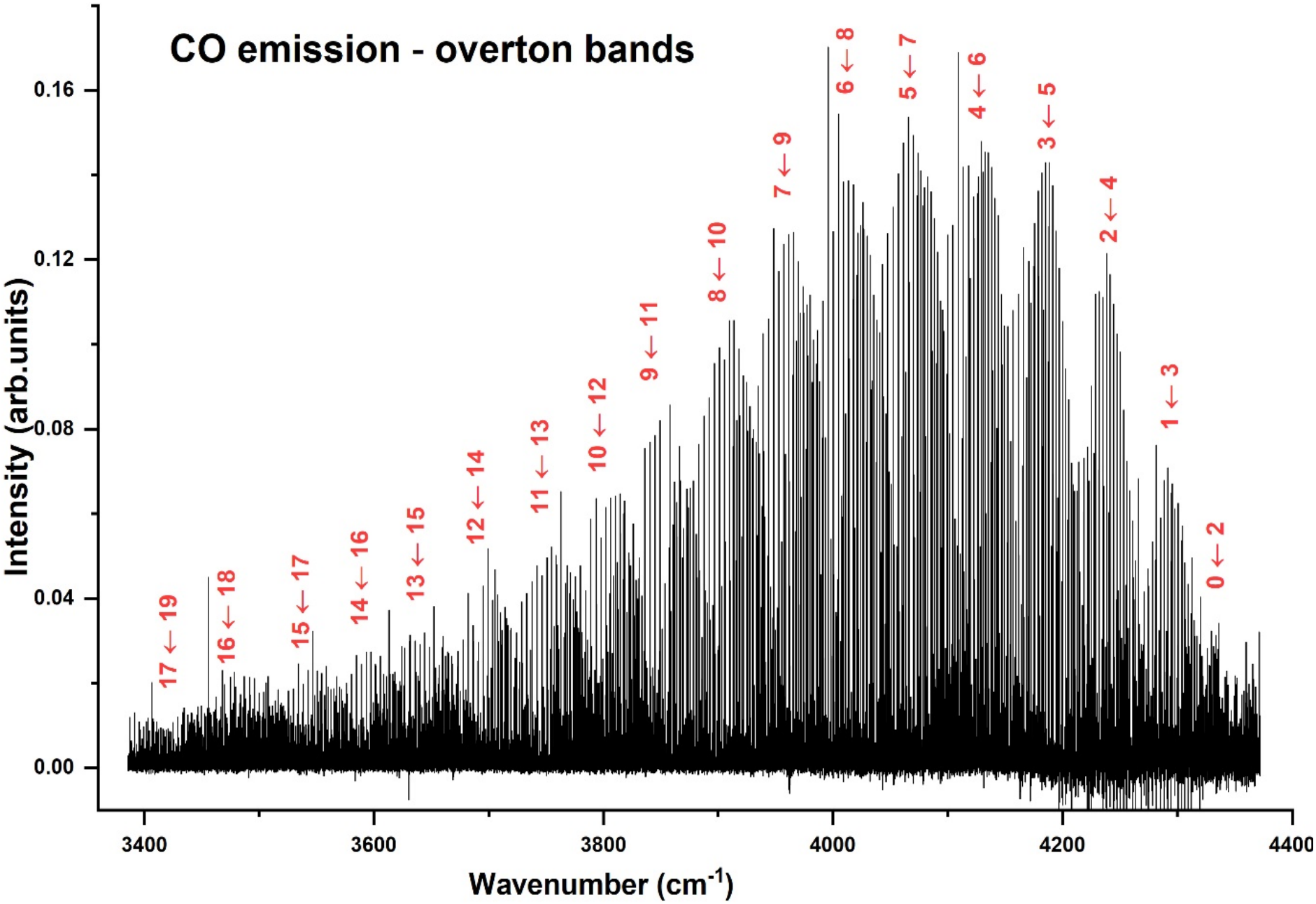
CH_4, N_2, H_2O

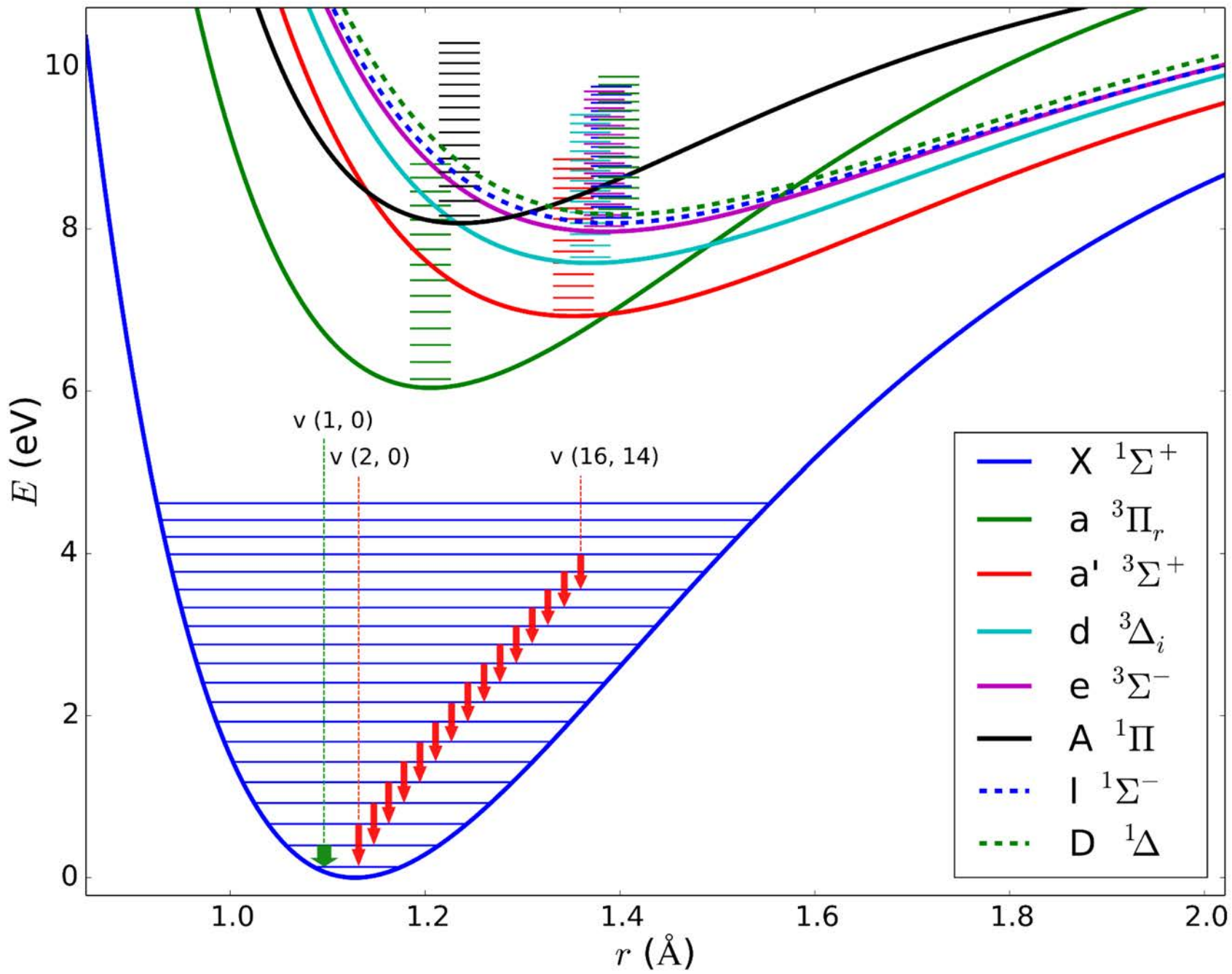
CH_3CN, N_2, H_2O

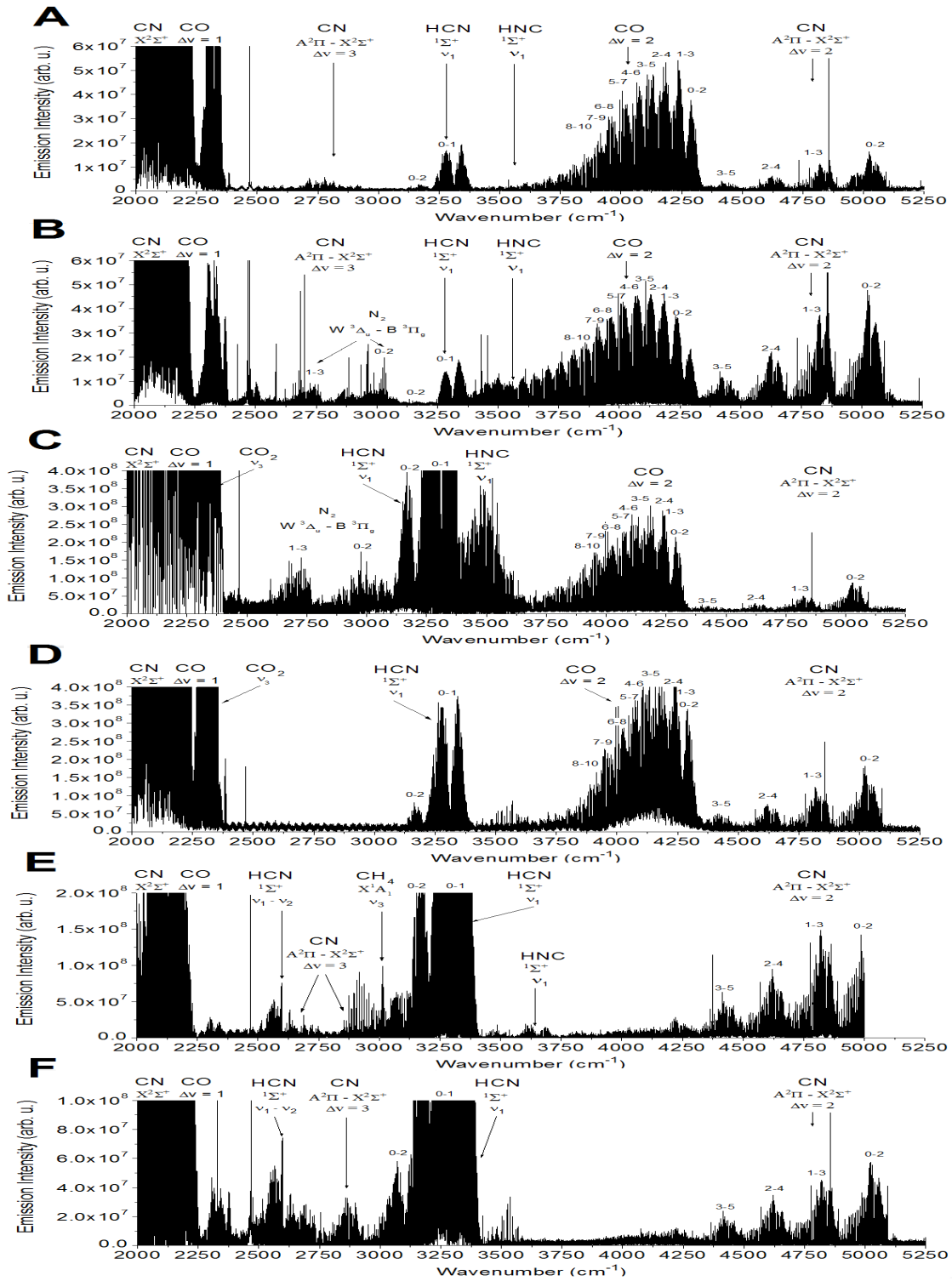
Discharge Chemistry of formamide

Ferus M , Civis S et al. (2014) , *J. Phys. Chem. A* 118:719–736.




CO emission - overton bands
Intensity (arb.units)
0.16
0.12
0.08
0.04
0.00
3400
3600
3800
4000
4200
4400
Wavenumber (cm-1)
17 ← 19
16 ← 18
15 ← 17
14 ← 16
13 ← 15
12 ← 14
11 ← 13
10 ← 12
9 ← 11
8 ← 10
7 ← 9
6 ← 8
5 ← 7
4 ← 6
3 ← 5
2 ← 4
1 ← 3
0 ← 2


10
8
6
4
2
0
E (eV)
1.0
1.2
1.4
1.6
1.8
2.0
r (Å)
v (1, 0)
v (2, 0)
v (16, 14)
X $^1\Sigma^+$
a $^3\Pi_r$
a' $^3\Sigma^+$
d $^3\Delta_i$
e $^3\Sigma^-$
A $^1\Pi$
I $^1\Sigma^-$
D $^1\Delta$



NH_3, CO, H_2O

$HCONH_2$, N_2, H_2O

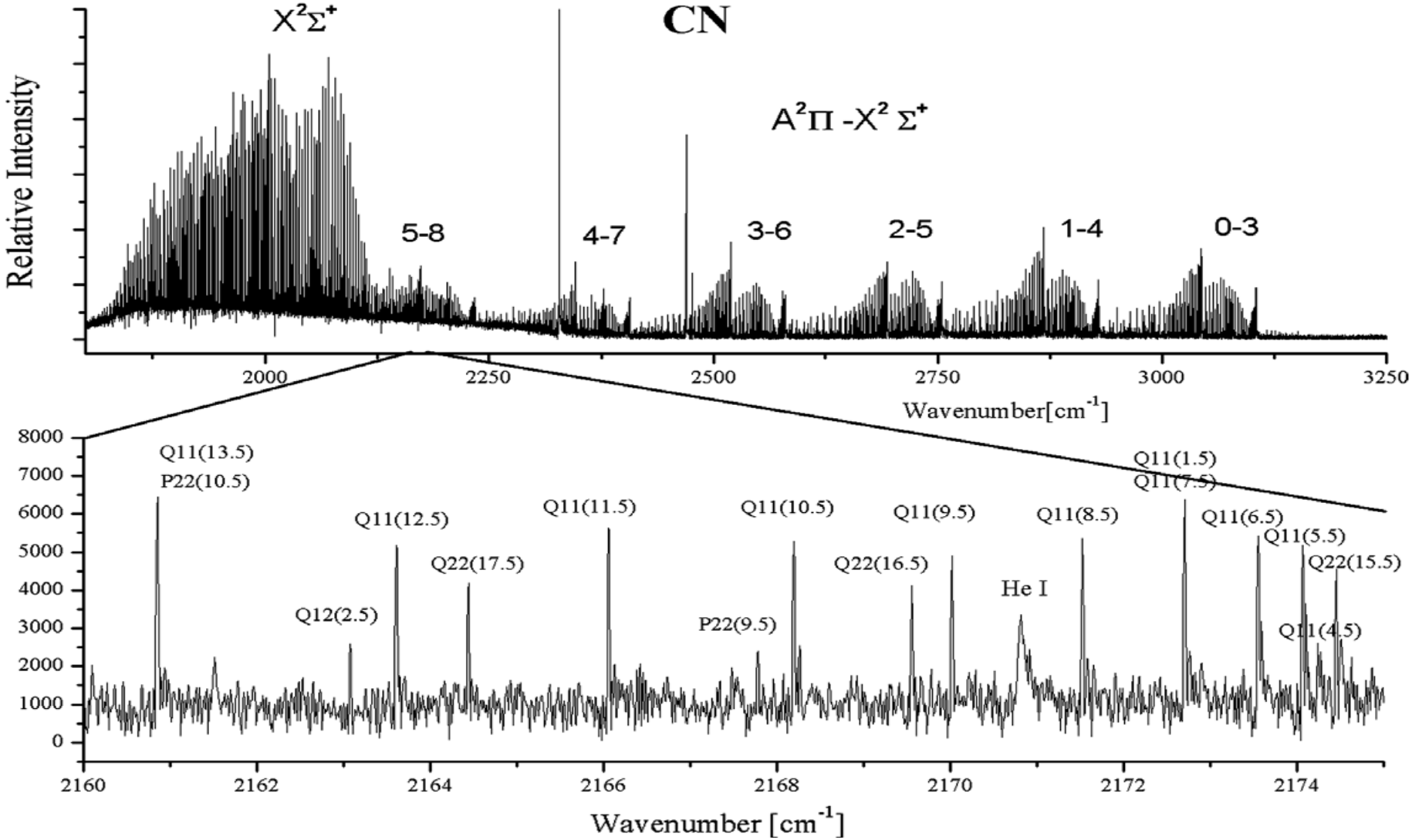
HCHO, N_2, H_2O

CH_3OH, N_2, H_2O

CH_4, N_2, H_2O

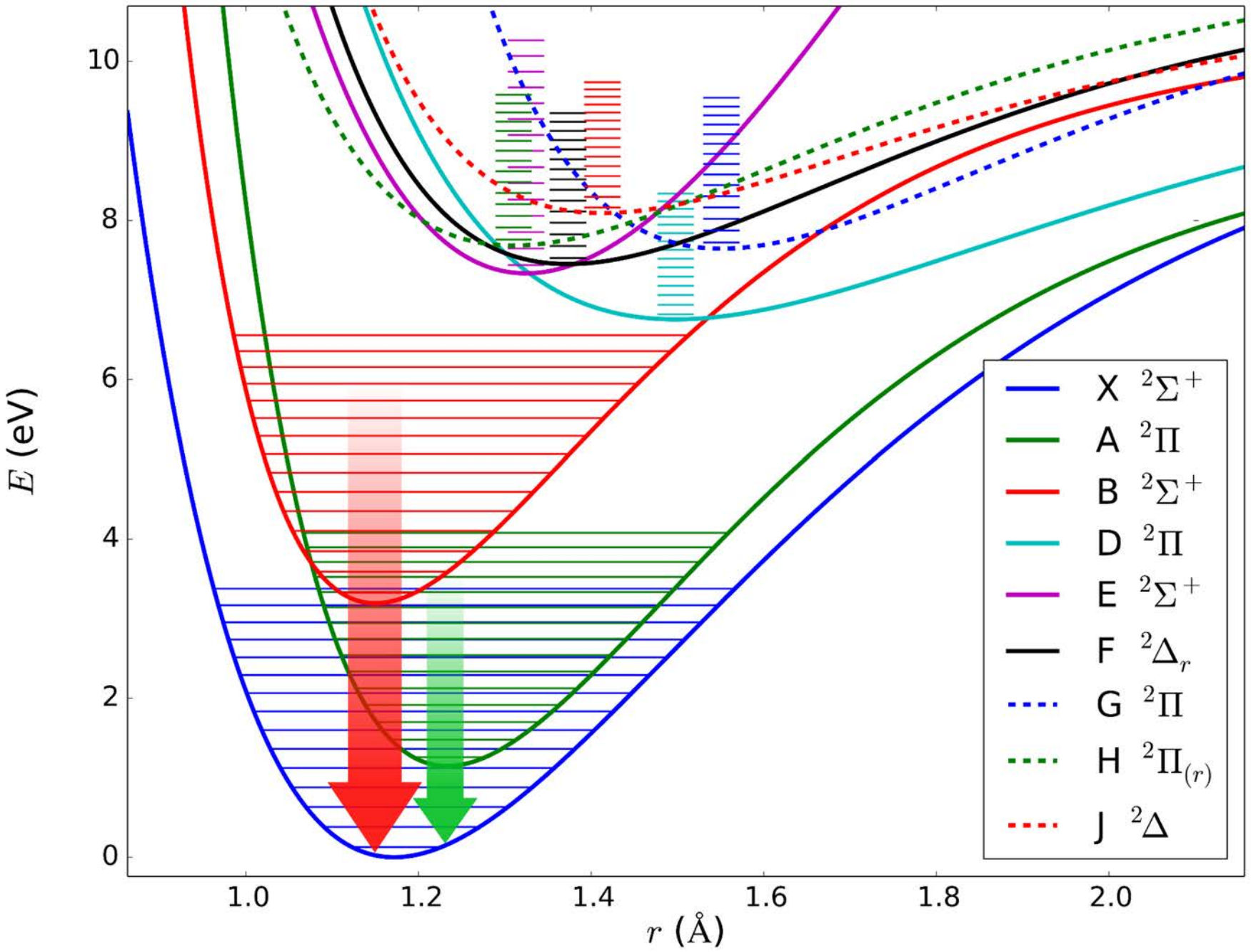
CH_3CN, N_2, H_2O

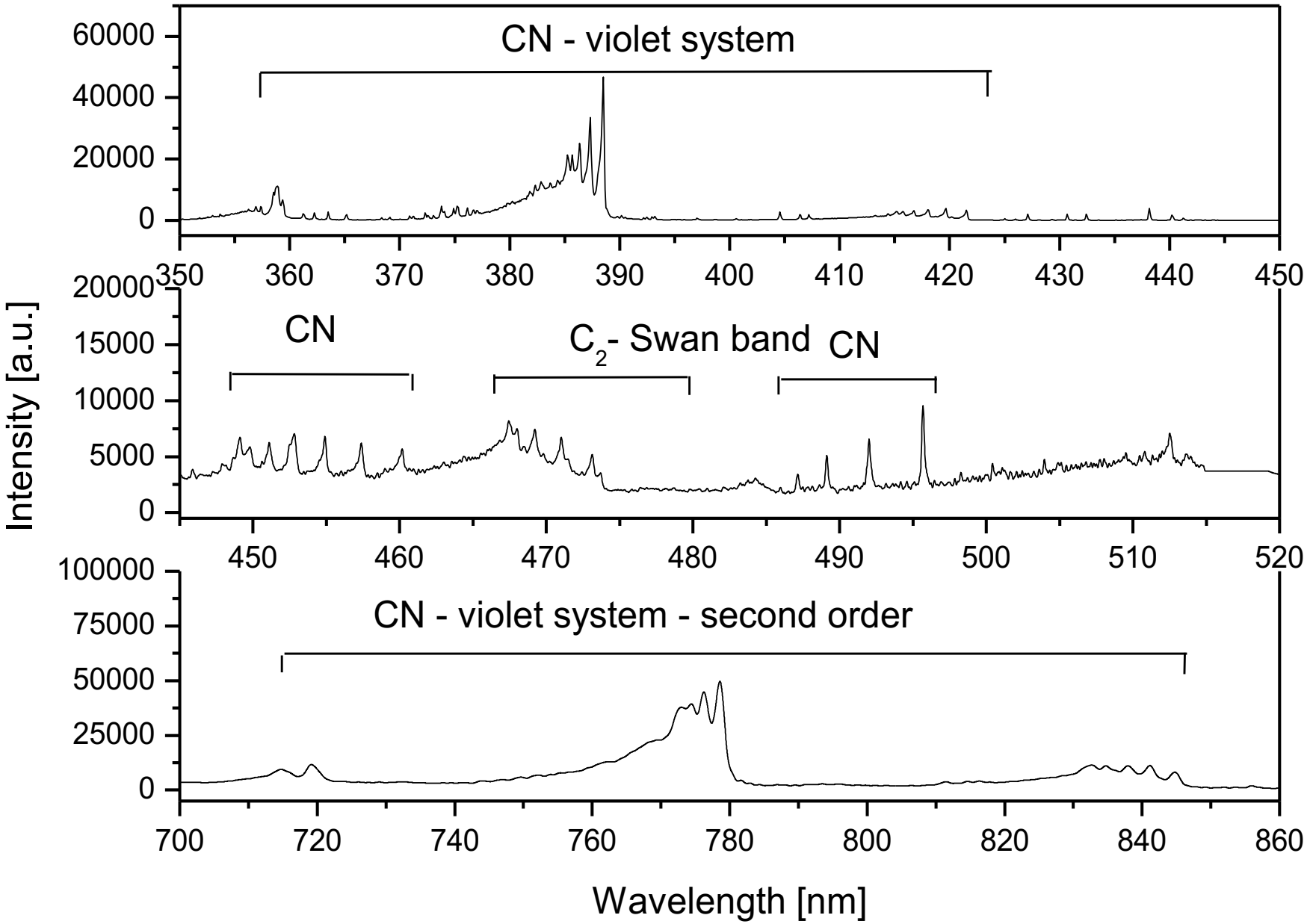
$(CN)_2$ discharge



V. Horká, S. Civiš, V. Špirko, K. Kawaguchi:onic state“, ***Coll. Czech. Chem. Commun.***, 2004, **69**, 73-89

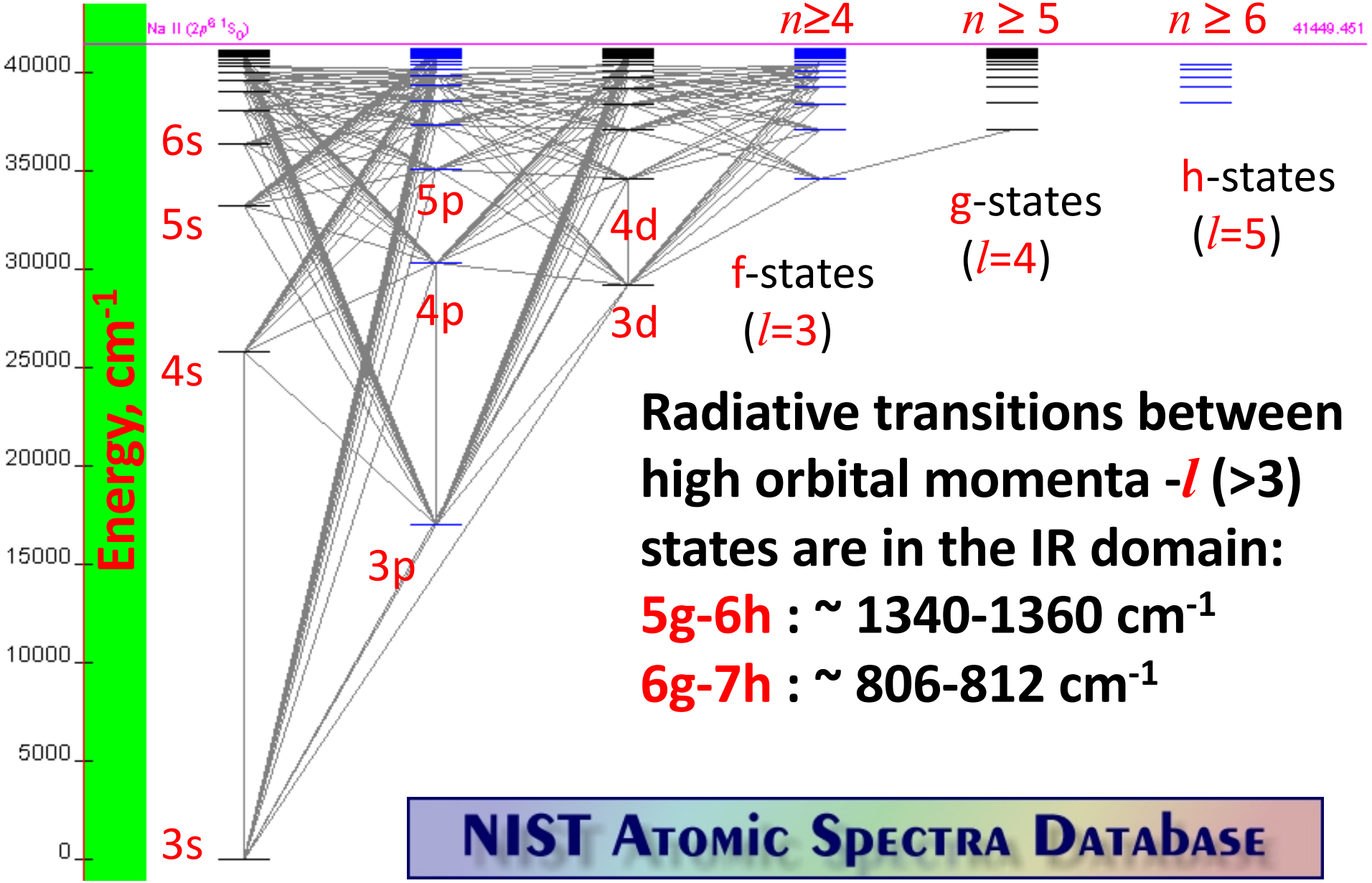
Civiš, S; Šedivcová-Uhliková, T; Kubelik, P. et al.: ***J. Mol. Spectrosc***, 2008, **250,** 20-26


E (eV)
r (Å)
0
2
4
6
8
10
1.0
1.2
1.4
1.6
1.8
2.0
X $^2\Sigma^+$
A $^2\Pi$
B $^2\Sigma^+$
D $^2\Pi$
E $^2\Sigma^+$
F $^2\Delta_r$
G $^2\Pi$
H $^2\Pi_{(r)}$
J $^2\Delta$


CN - violet system
60000
40000
20000
0
350
360
370
380
390
400
410
420
430
440
450
CN
C2- Swan band
CN
20000
15000
10000
5000
0
450
460
470
480
490
500
510
520
CN - violet system - second order
100000
75000
50000
25000
0
700
720
740
760
780
800
820
840
860
Intensity [a.u.]
Wavelength [nm]

Atomic spectra

Atomic *nl* levels: an example (Na)



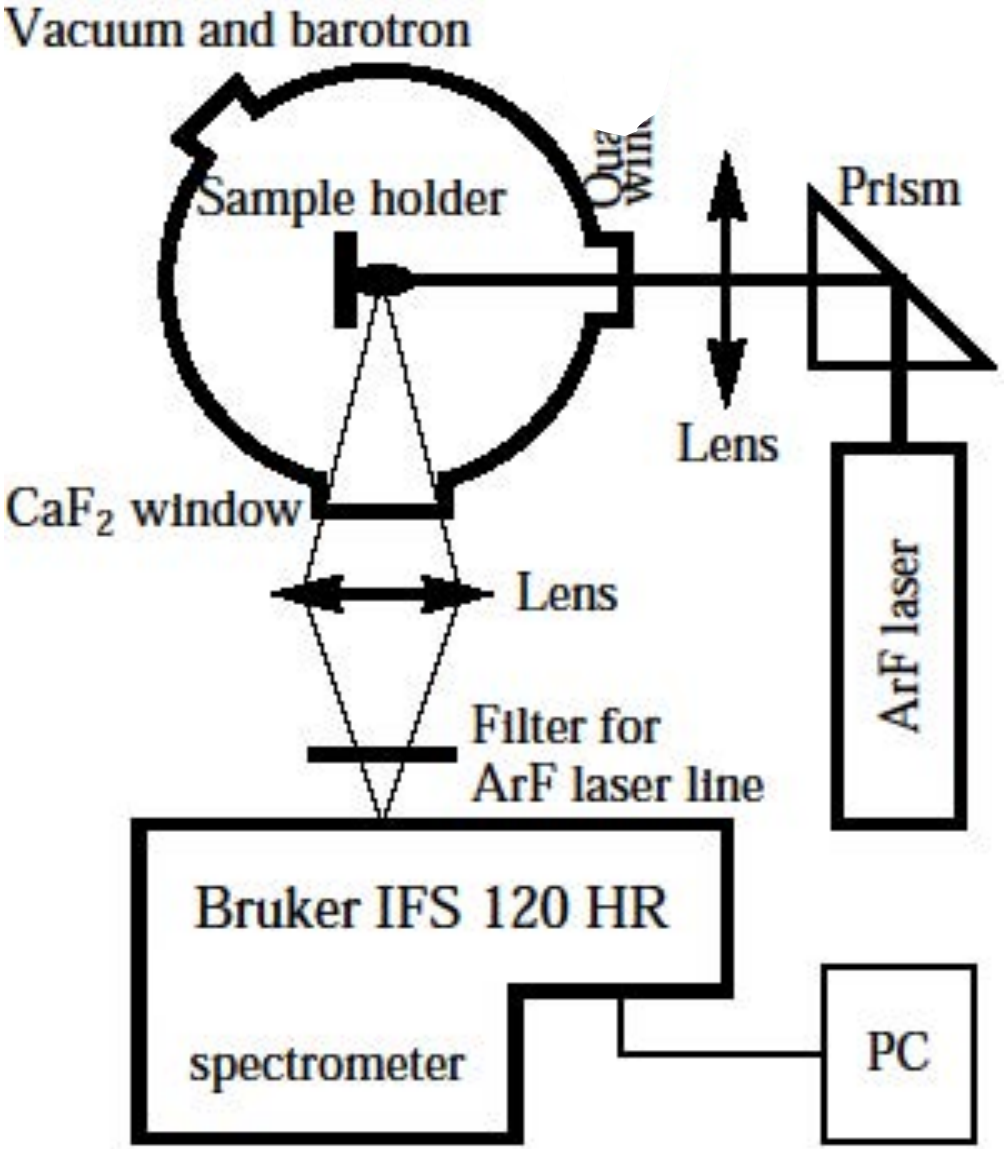
Radiative transitions between high orbital momenta -*l* (>3) states are in the IR domain:

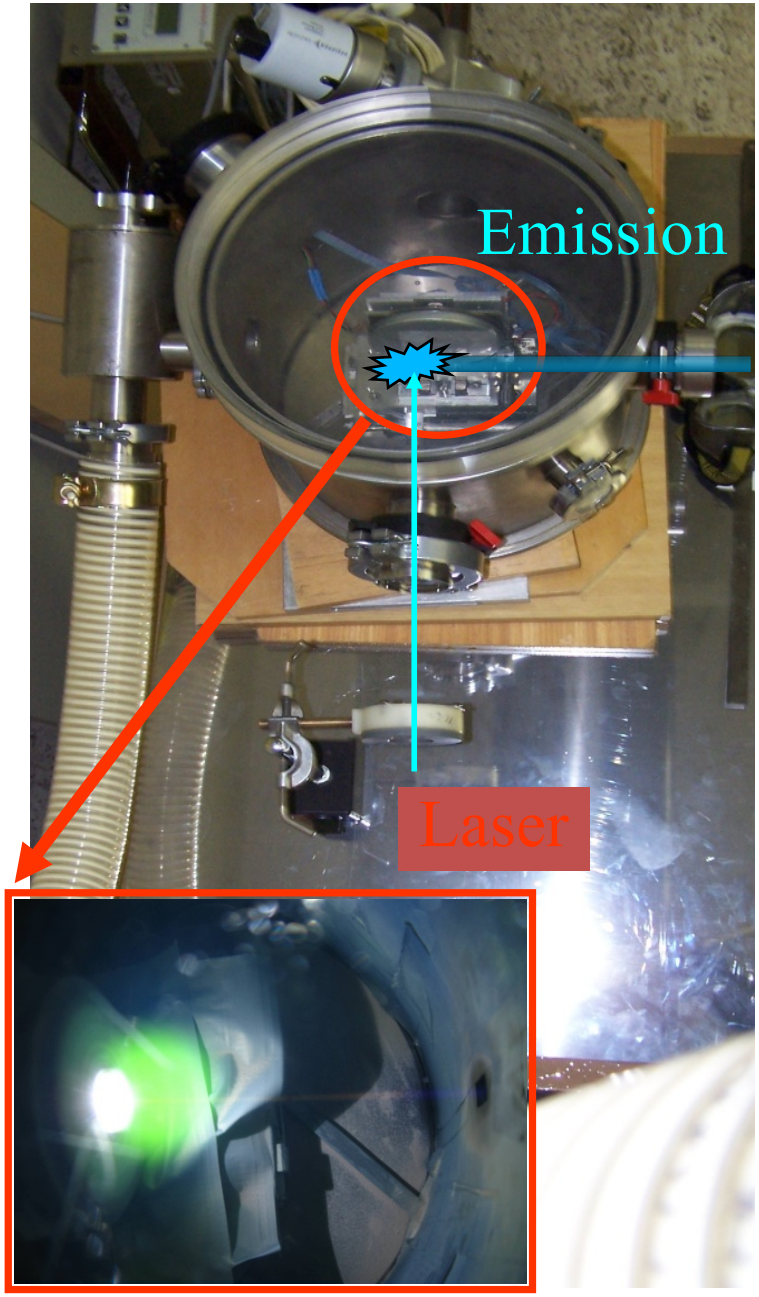
5g-6h : ~ 1340-1360 cm^{-1}

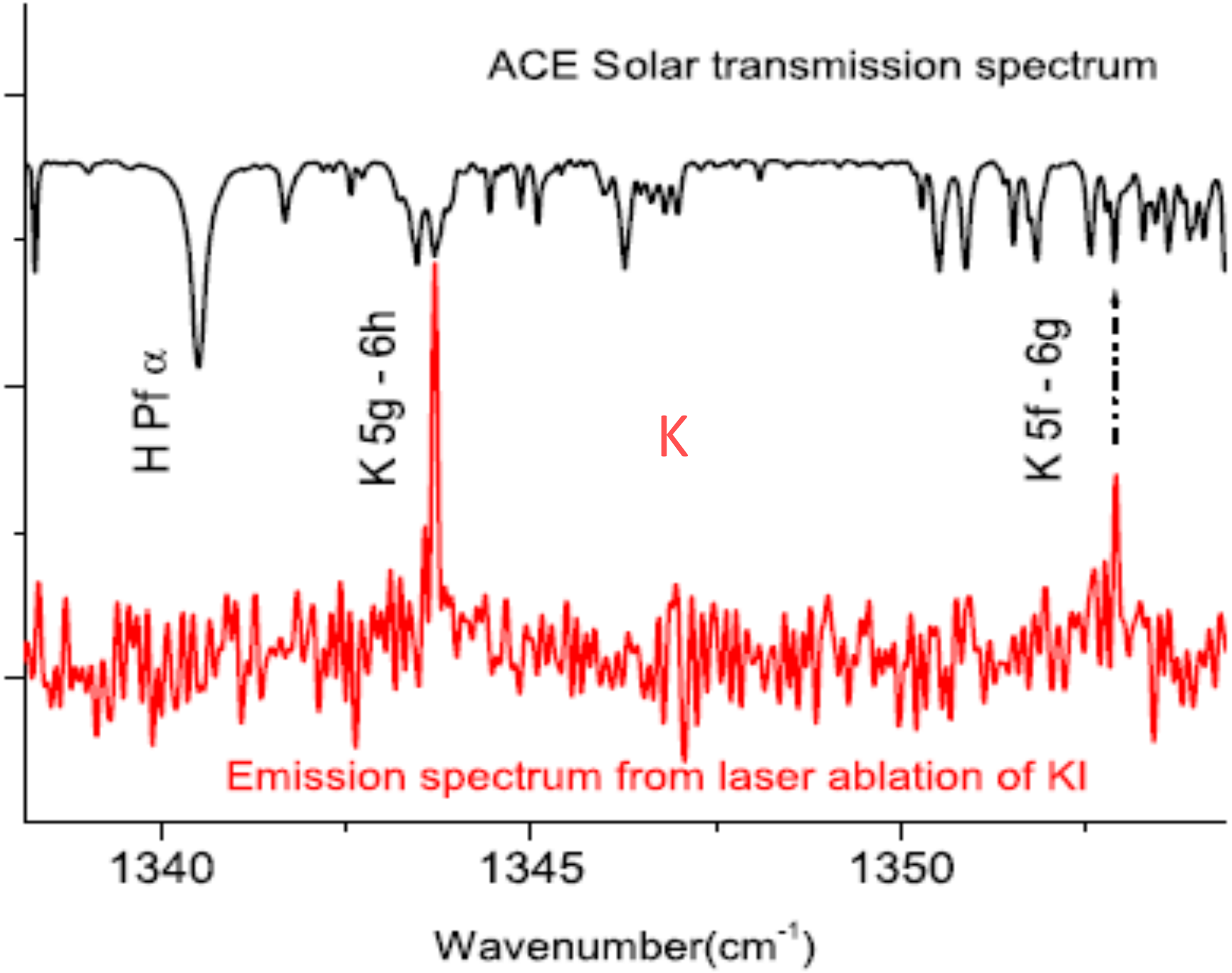
6g-7h : ~ 806-812 cm^{-1}

NIST Atomic Spectra Database

Time resolved FTIR measurement in the laser spark (laser ablation)

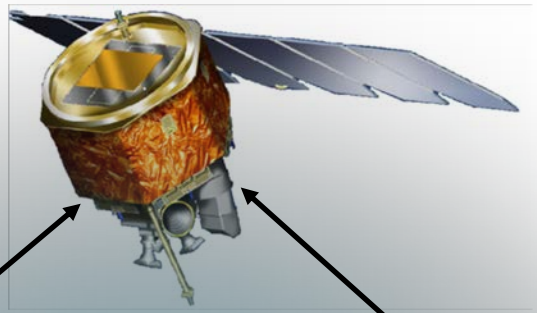


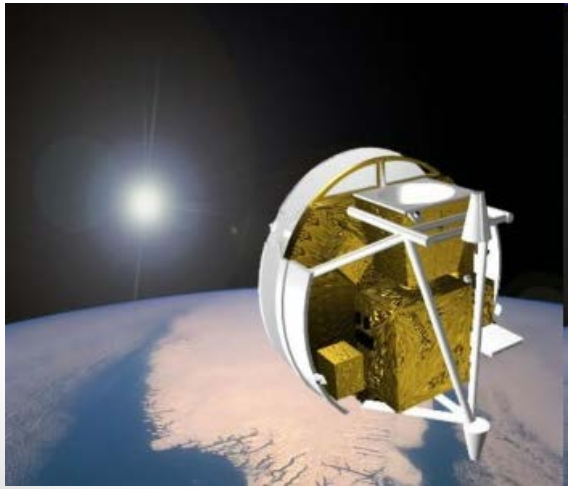


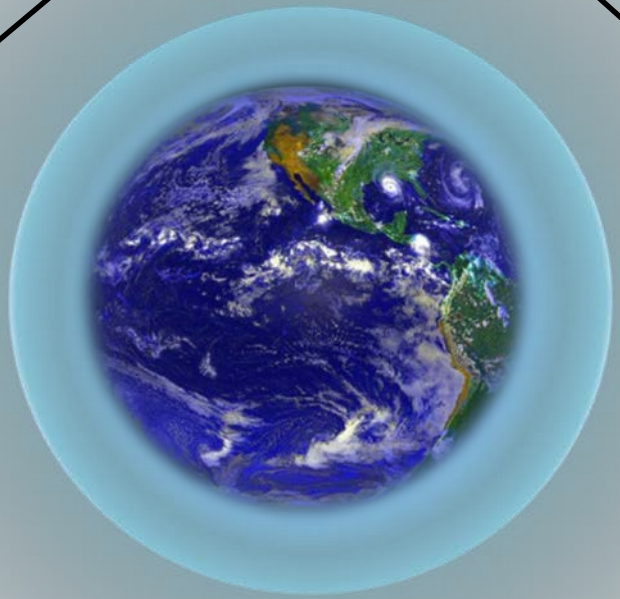

ACE Solar transmission spectrum
H Pf α
K 5g - 6h
K
K 5f - 6g
Emission spectrum from laser ablation of KI
1340
1345
1350
Wavenumber(cm-1)

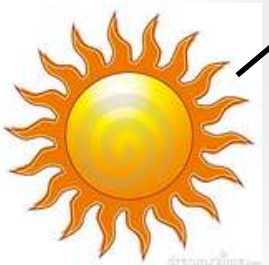
Satelite: Atmospheric Chemistry Experiment

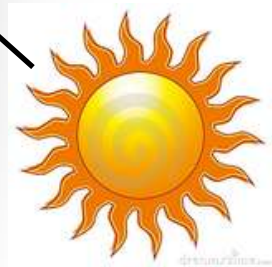
2003
Orbital high 650 km



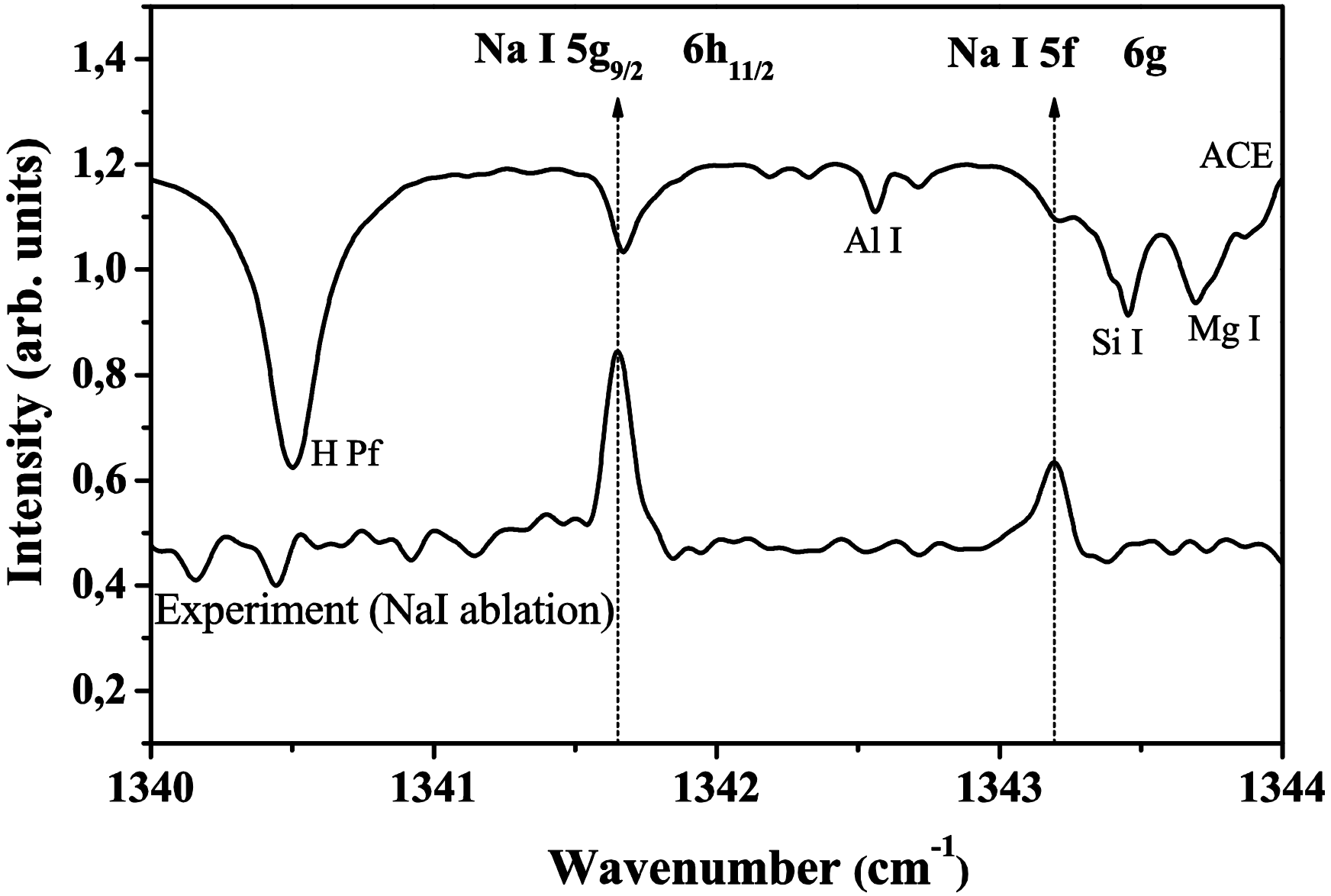






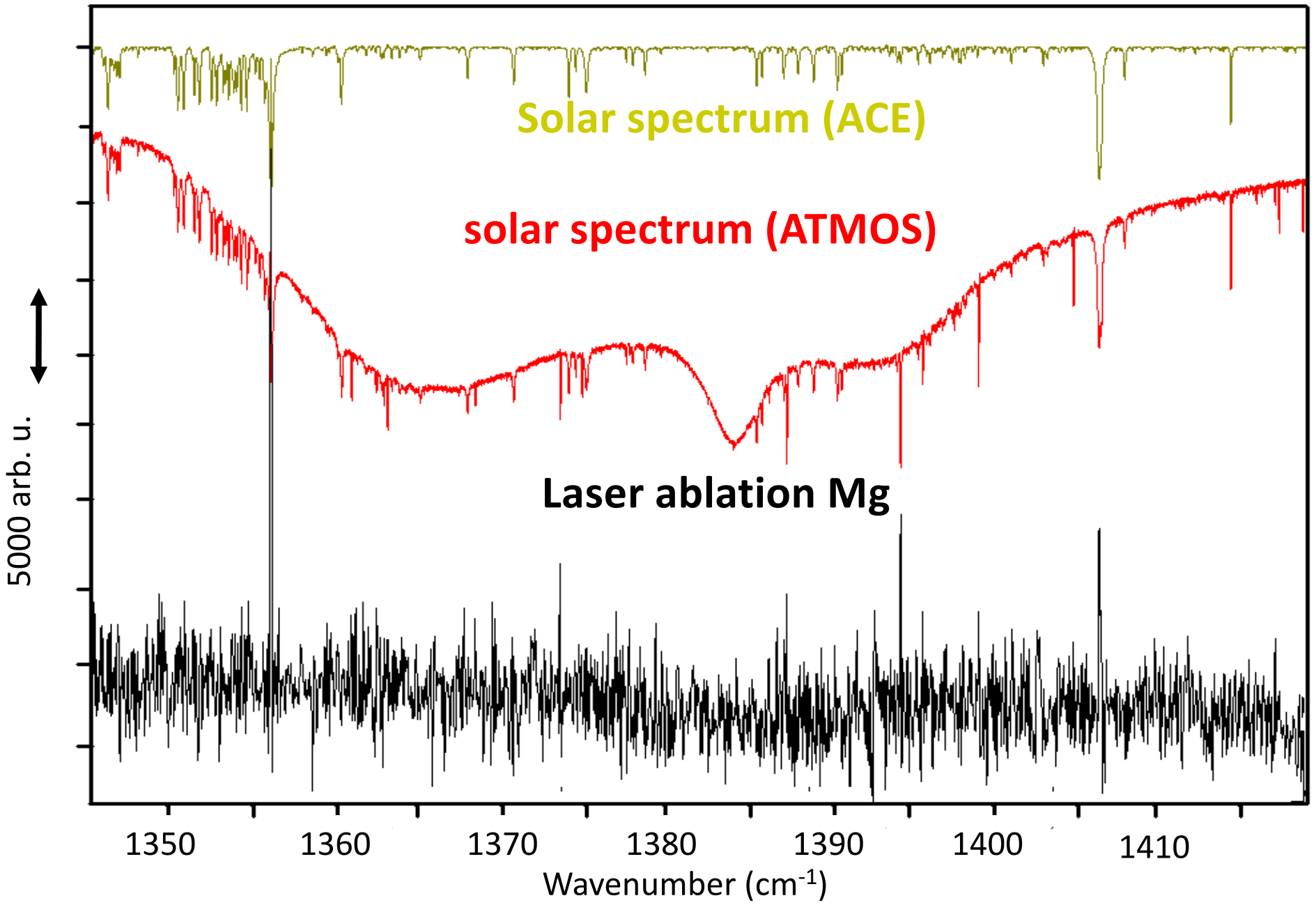


Na

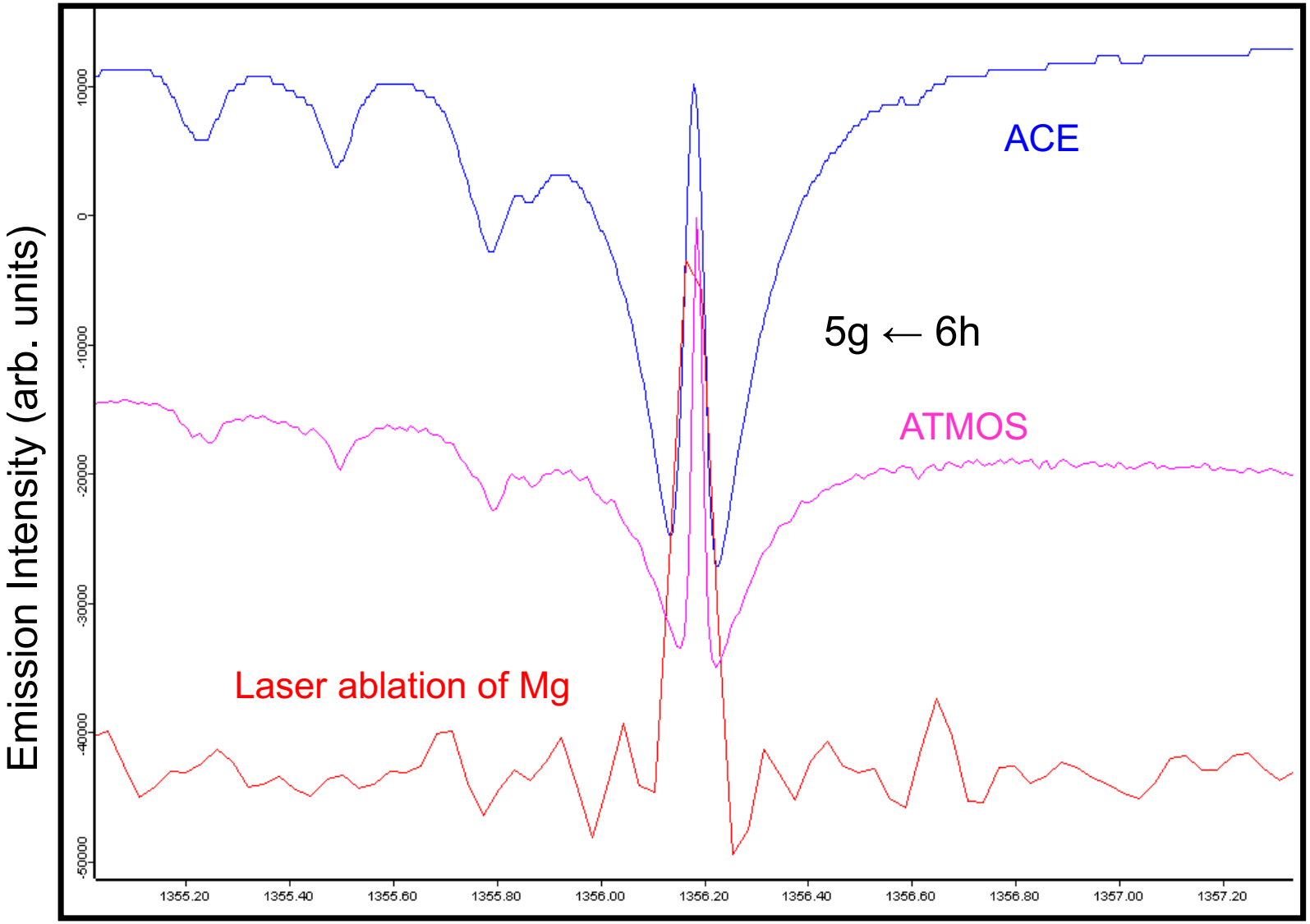


Civiš S., Chernov V.E. *et al.*, Astronomy and Astrophysics 2012

Mg


Solar spectrum (ACE)
solar spectrum (ATMOS)
Laser ablation Mg
5000 arb. u.
1350
1360
1370
1380
1390
1400
1410
Wavenumber (cm-1)

Mg



Mg – line 7.37 μm,
1356,18 cm^{-1}

Civis *et.al* A&A 554, A24 (2013)

Our results – Rydberg states

Atom	Lines (total)	New lines	New levels	References
Au	43	32	8	Phys. Rev. A **81**, 012510 (2010)
Ag	18	12	3	Phys. Rev. A **82**, 022502 (2010)
Cu	25	20	4	J. Phys. B **44**, 105002 (2011)
Li	4	4		Astron. & Astrophys. **545**, A61 (2012)
Na	25	17	3	Astron. & Astrophys. **542**, A35 (2012)
K	38	25	3	Astron. & Astrophys. **541**, A125 (2012)
Rb	33	21	6	J. Phys. B **44**, 175002 (2012)
Cs	40	21	2	J.Opt. Soc. Am. B**29**, 112 (2012)
Mg	36	3	2	Astron. & Astrophys. **554**, A24 (2013)
Ca	31	26	12	
Sr	23	19	10	J. Quant. Spectrosc. Radiat. Transf. **129**, 324 (2013)
Zn	54	47	15	J. Quant. Spectrosc. Radiat. Transf. **134**, 64 (2014)
In	34	18	5	J. Anal. At. Spectrom. **29**, 2275 (2014)
Ne	287	26	14	Astron. & Astrophys. **582**, A12 (2015)
Ar	105	77	2	J. Quant. Spectrosc. Radiat. Transf. **182** (2016) 337–345
He	100	5	-	The Journal of Chemical Physics **139**, 104314 (2013)

Summary

Fourier Transmission Emission Spectroscopy

is directly used in our laboratory for:

- Detection of short lived radicals
- Detection of Rydberg states of atoms
- Application in astronomy, chemical composition of the exoplanet atmospheres
- Exploration of the Origin of Life