

SMR: 1133/28

*WINTER COLLEGE ON
SPECTROSCOPY AND APPLICATIONS*

(8 - 26 February 1999)

*"Molecular Multiphoton Spectroscopy
Atmospheric and Astrophysical Applications"*

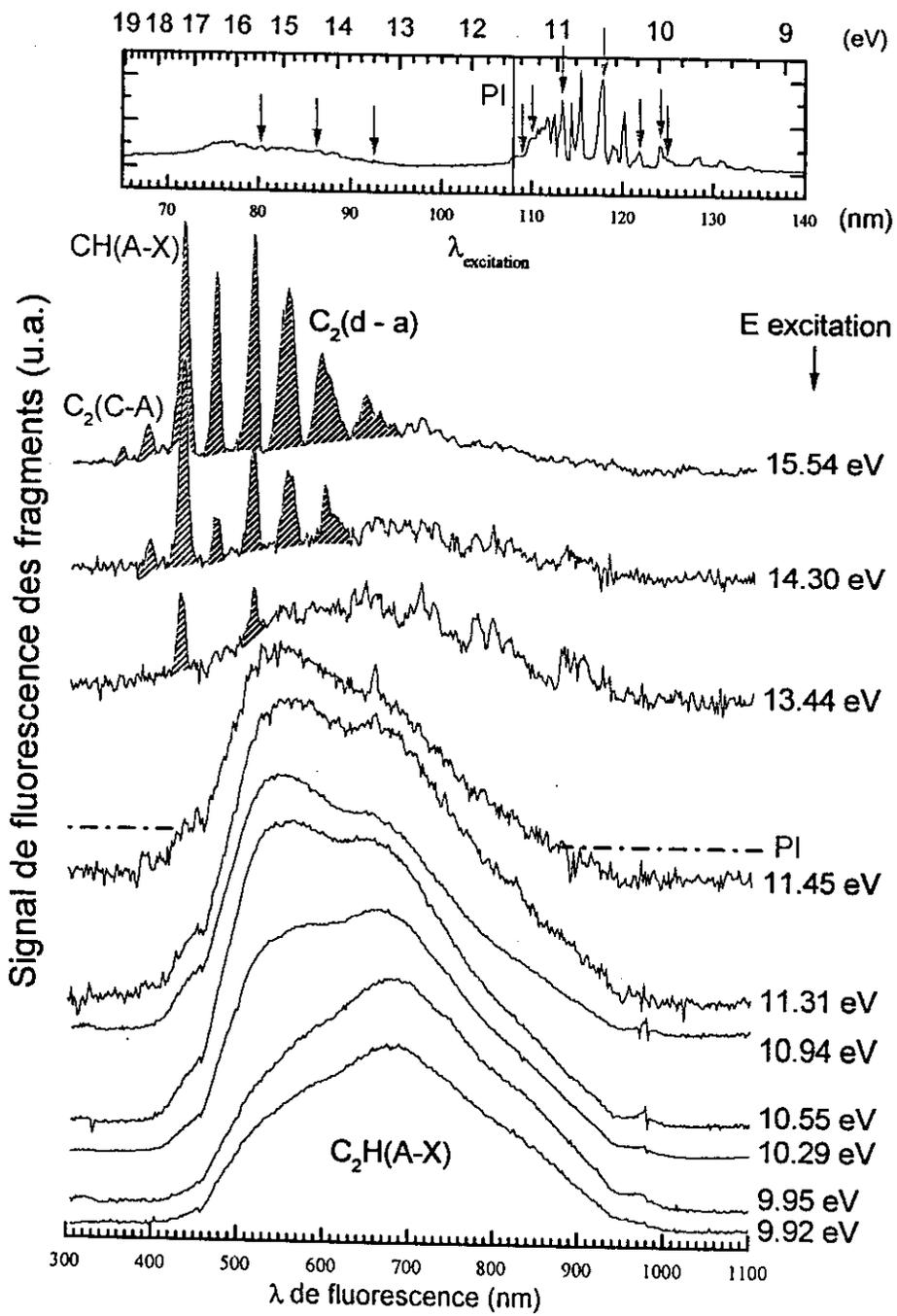
presented by:

Dolores GAUYACQ
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Université de Paris-Sud
Orsay
France

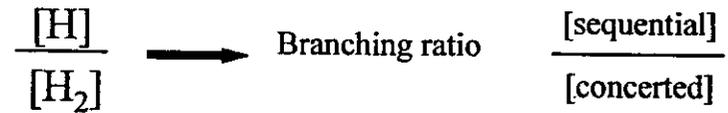
These are preliminary lecture notes, intended only for distribution to participants.

Conclusion

- **Resonant multiphoton excitation** provides a flexible alternative to VUV sources (lasers, synchrotron radiation)
- **Selectivity and sensitivity**
 ➔ atmospheric monitoring
- For **dissociation dynamics** studies, appropriate detection devices have to be implemented :
 - LIF of neutral fragments
 - Dispersed fluorescence
 - H, H₂ ionization detection
(H-fragment spectroscopy)



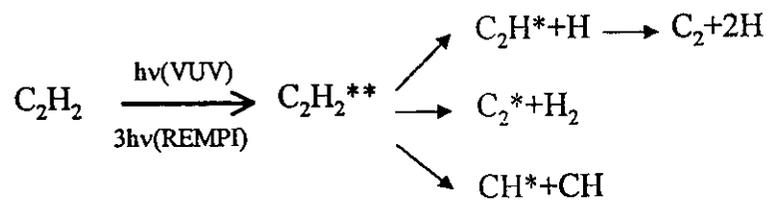
Projects



detection of heavy fragments C_2H , C_2 , CH :

- REMPI
 - LIF
- } population distribution

Experimental Approaches

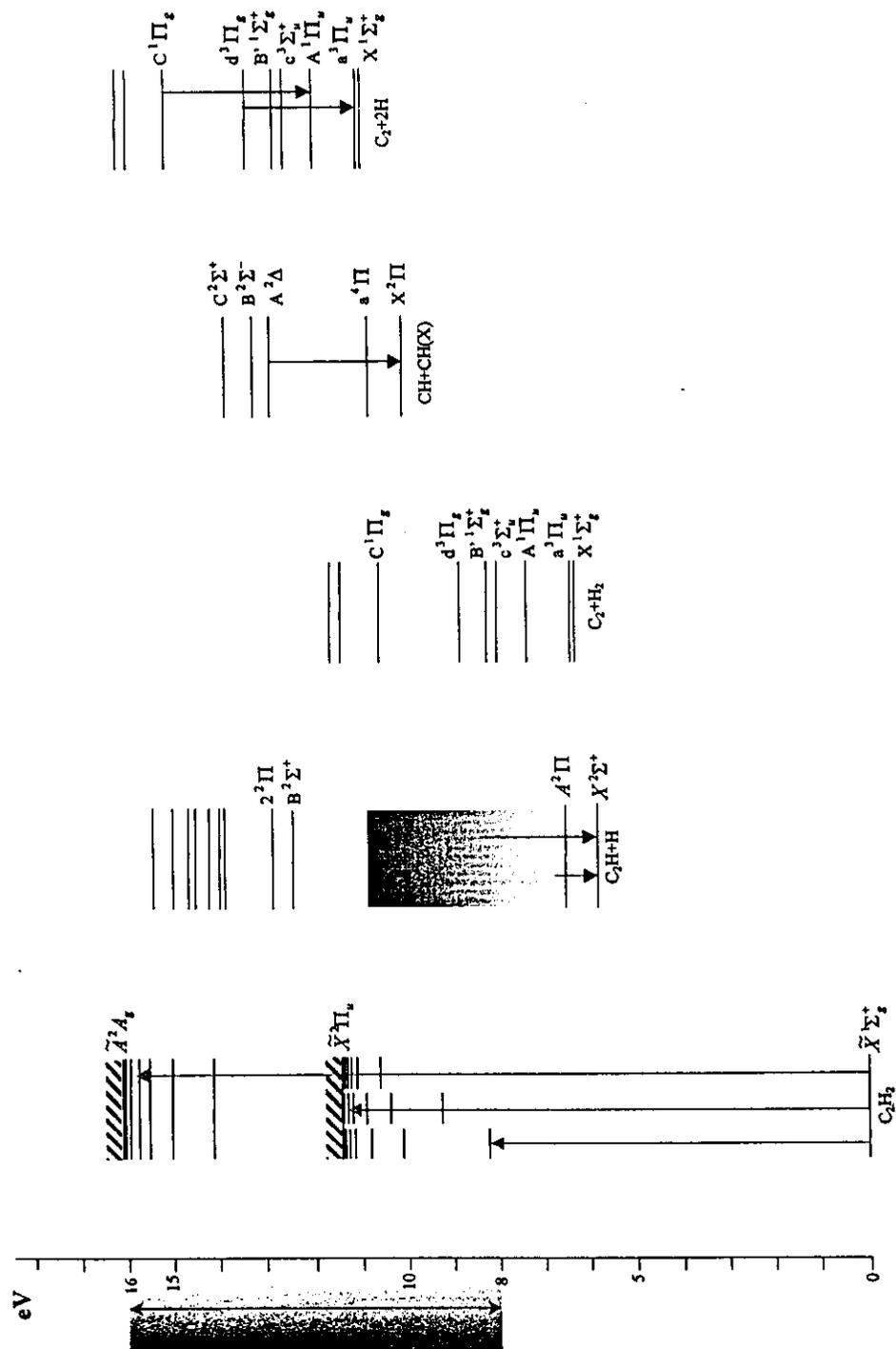


• detection of heavy fragments C_2H^* , C_2^* , CH^* :

- fluorescence analysis (SR) ←
- REMPI
- LIF

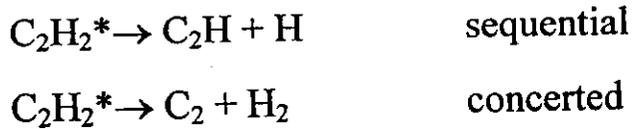
• detection of light fragments : H and H_2

- REMPI
- H-translational spectroscopy (internal state distribution)

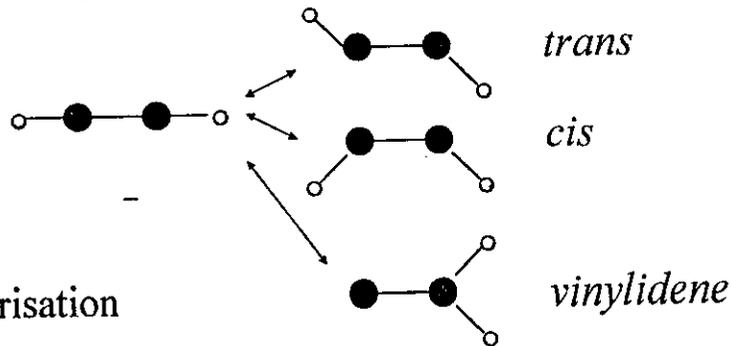


Rydberg State Dynamics

- linear geometry
⇒ strong absorption spectrum (8-11.4 eV)
- diffuse bands dominate the absorption spectrum
⇒ predissociation ?
- Dissociation mechanisms :



→ Rydberg-valence interactions



□ Isomerisation

□ Singlet-Triplet interaction

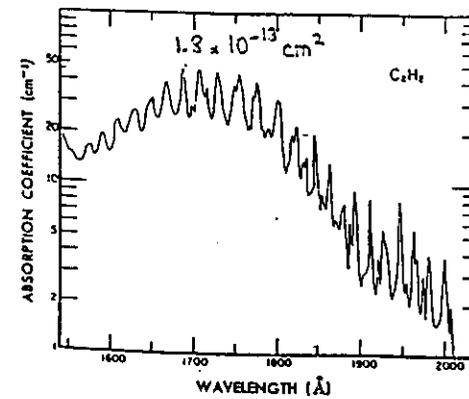


FIG. 2. Absorption coefficient of acetylene in the region 1550-2000 Å.

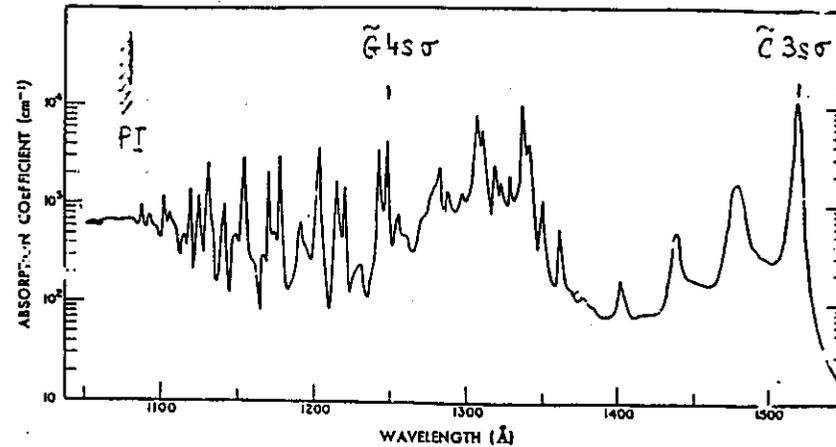


FIG. 1. Absorption coefficient of acetylene in the region 1050-1550 Å. Lower curve at left gives the photoionization coefficient. R and R' are Rydberg series. B, C, and D are non-Rydberg bands.

Nakayama J. Chem. Phys. 40 558 (1964)

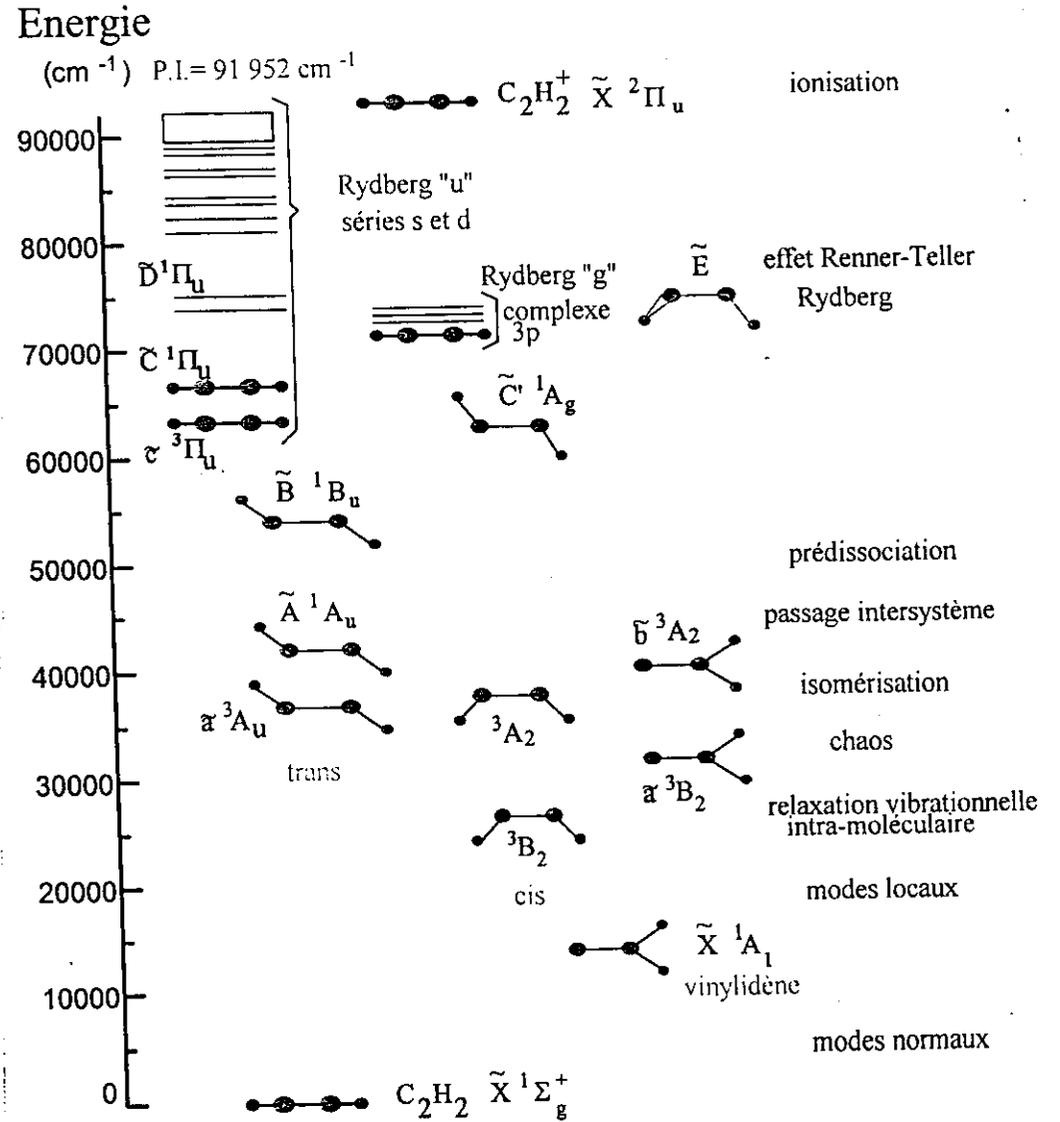
ACETYLENE

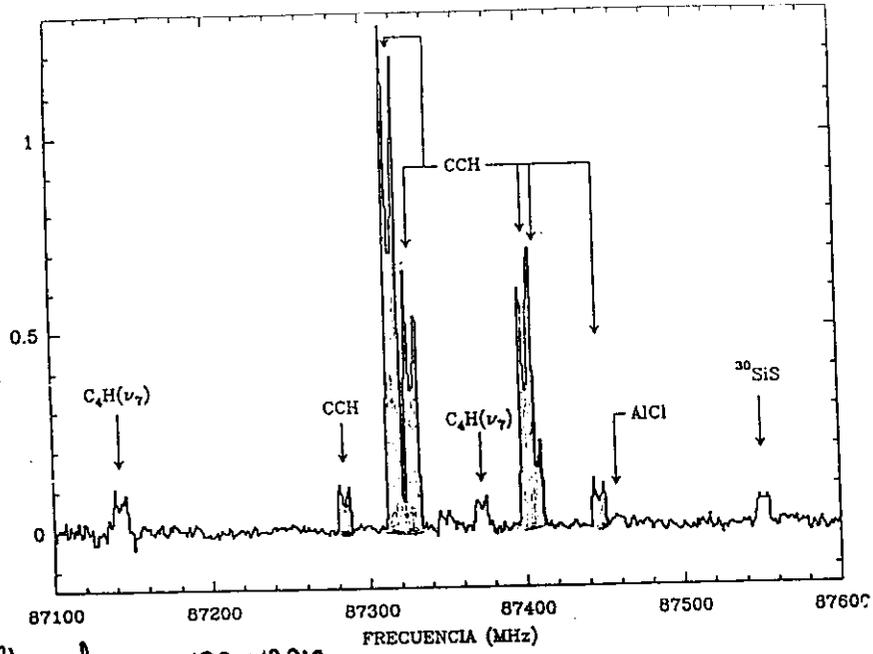
*C₂H₂ is a constituent of stellar atmospheres and interstellar clouds.

*C₂H₂ and its photodissociation product, C₂H, form carbon reservoir in the interstellar space.

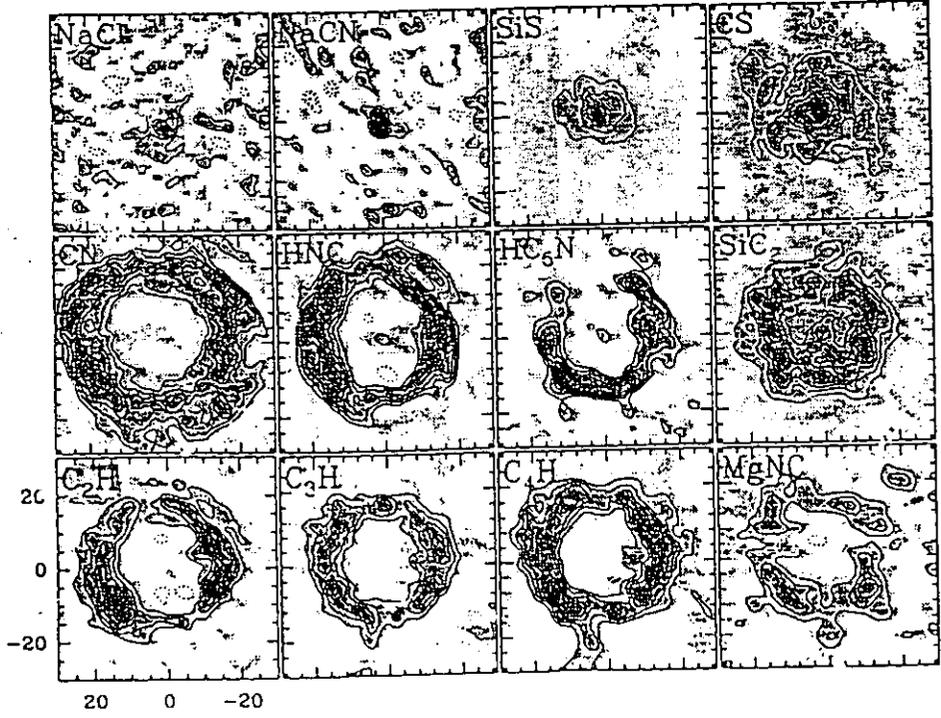
*The photodissociation cross section of C₂H₂ depends on the photon wavelength (resonant states):

ROLE OF THE RYDBERG STATES ?

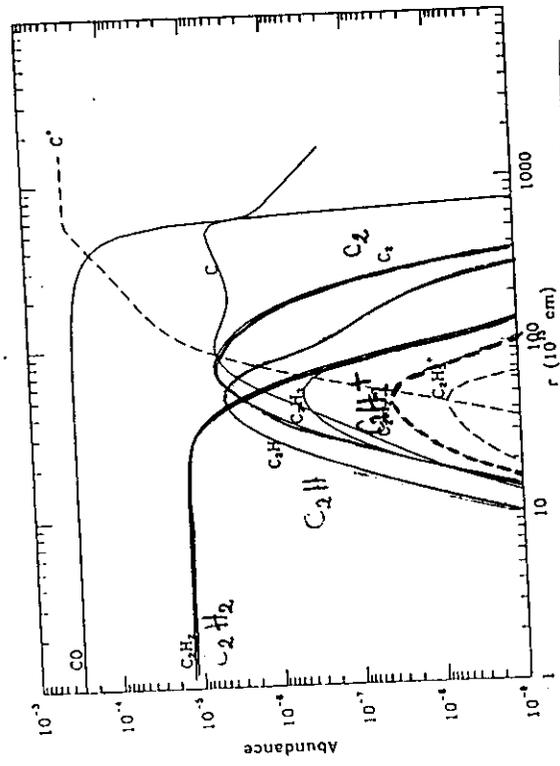
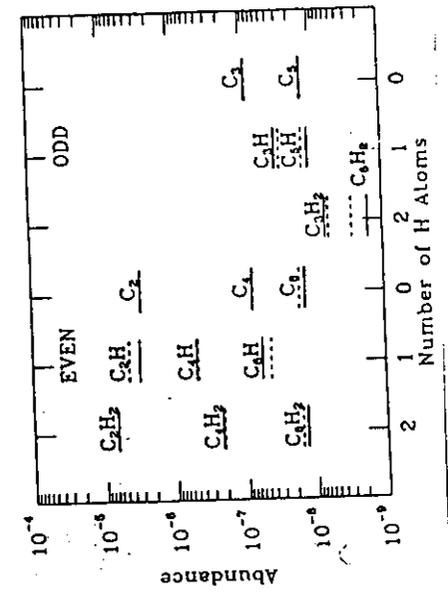
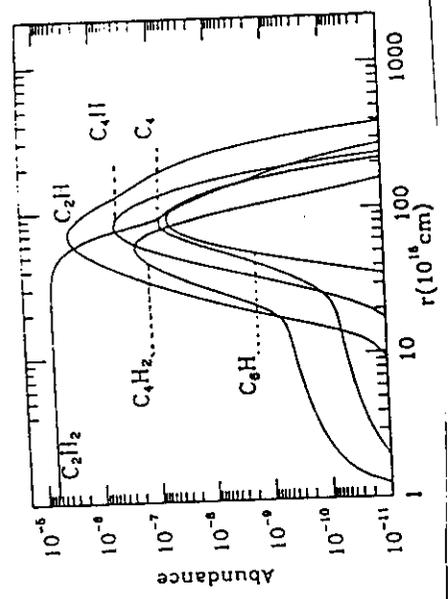




l' envelope IRC +10216



Guélin et al., 1995



Jorgensen et al. Ap.J. 396, 115 (1992)
 Cherchneff et Glasgow Ap.J. 419, L41 (1993) →
 "The formation of Carbon Chain Molecules in IRC +10216"

a red giant...
envelope of a C-star (e.g. IRC +10216)

Astrophysical Application Photodissociation of Acetylene in Circumstellar Envelopes

- C_2H_2 is one of the most abundant molecules in the astrophysical media
- Photodissociation of acetylene in the outer envelope of a carbonated star, IRC +10-216 ; observations and models
- Dissociation mechanisms of the Rydberg states of C_2H_2 ; laboratory studies
- Projects

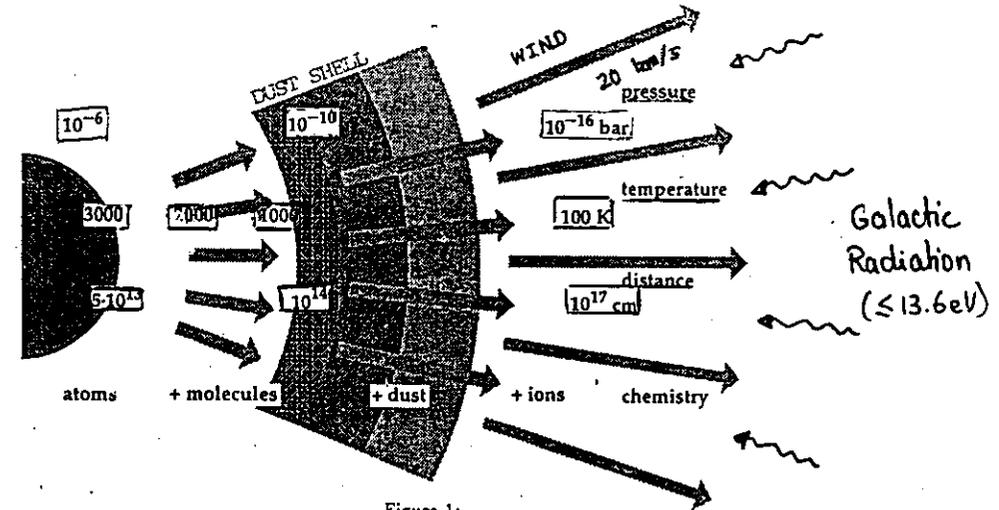
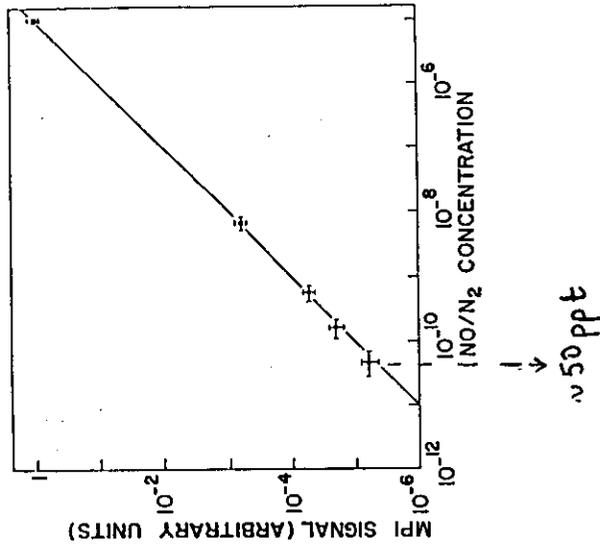
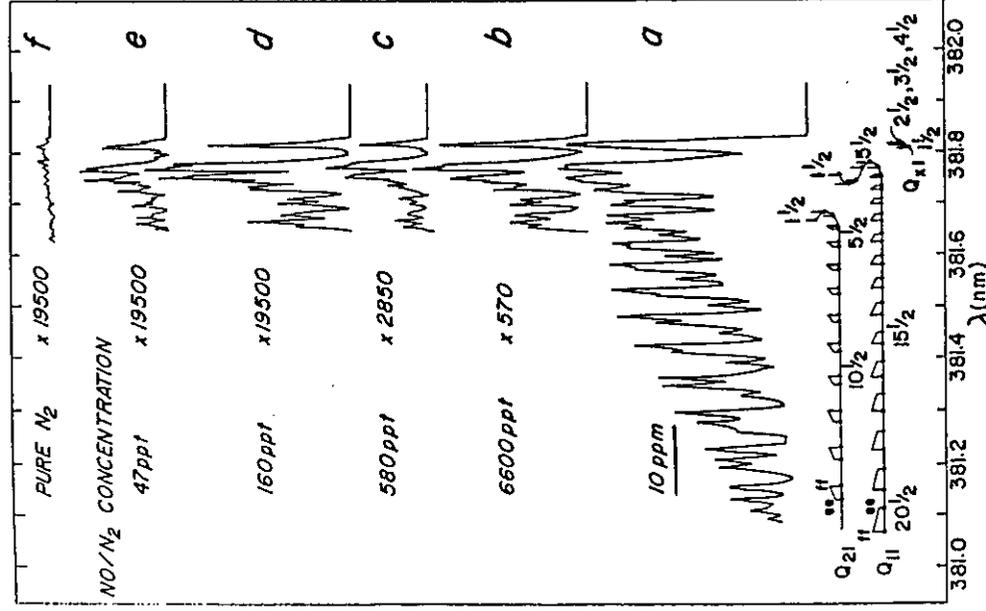
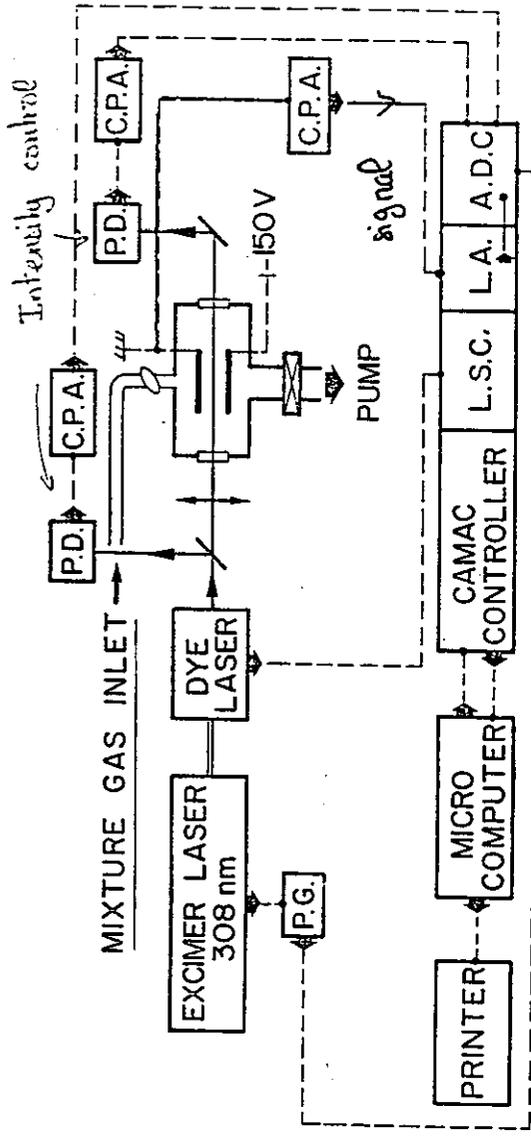


Figure 1:
General schematic structure of a dust forming envelope of a C-star. Like in a flow tube, with increasing distance from the star the temperature drops until condensation occurs. Simultaneously the pressure decreases as well until the chemistry becomes completely frozen. Finally, the chemical composition of the outflow material includes a gas of atoms, complex molecules, and ions with an admixture of dust grains of different sizes.

Detection of NO Traces Using Resonantly Enhanced Multiphoton Ionization



Detection of NO Traces Using Resonantly Enhanced Multiphoton Ionization: A Method for Monitoring Atmospheric Pollutants

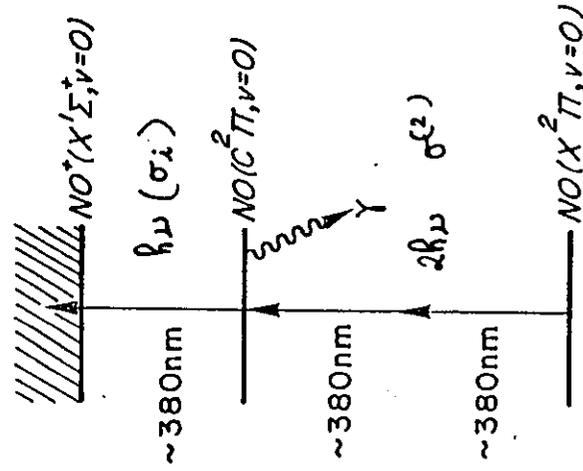
S. Guizard, D. Chapoulard, M. Horani, and D. Gauyacq

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Received 28 November 1988/Accepted 18 January 1989

Abstract. Resonantly enhanced multiphoton ionization (REMPI) is proposed as an ultrasensitive detection method for *real-time* monitoring of atmospheric pollutants in situ. The technique is demonstrated in the laboratory for NO diluted in pure nitrogen at 560 mbar. The MPI current resulting from $(2+1)$ photon ionization of NO via the resonant $C^2\Pi$ ($v=0$) state has been measured for several NO concentrations. Detection levels as low as 50 ppt have been obtained.

PACS: 33.80.Rv, 42.68



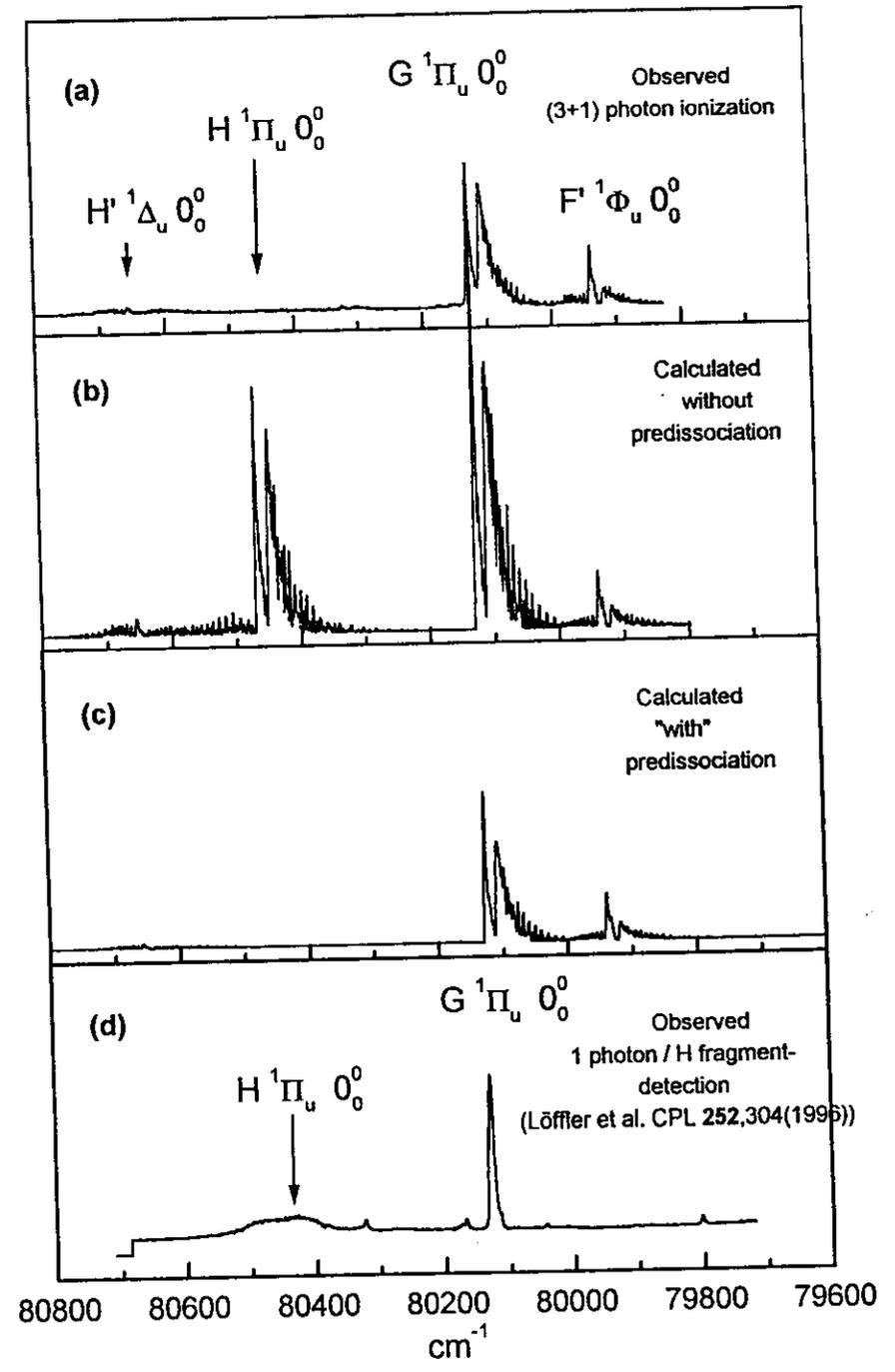
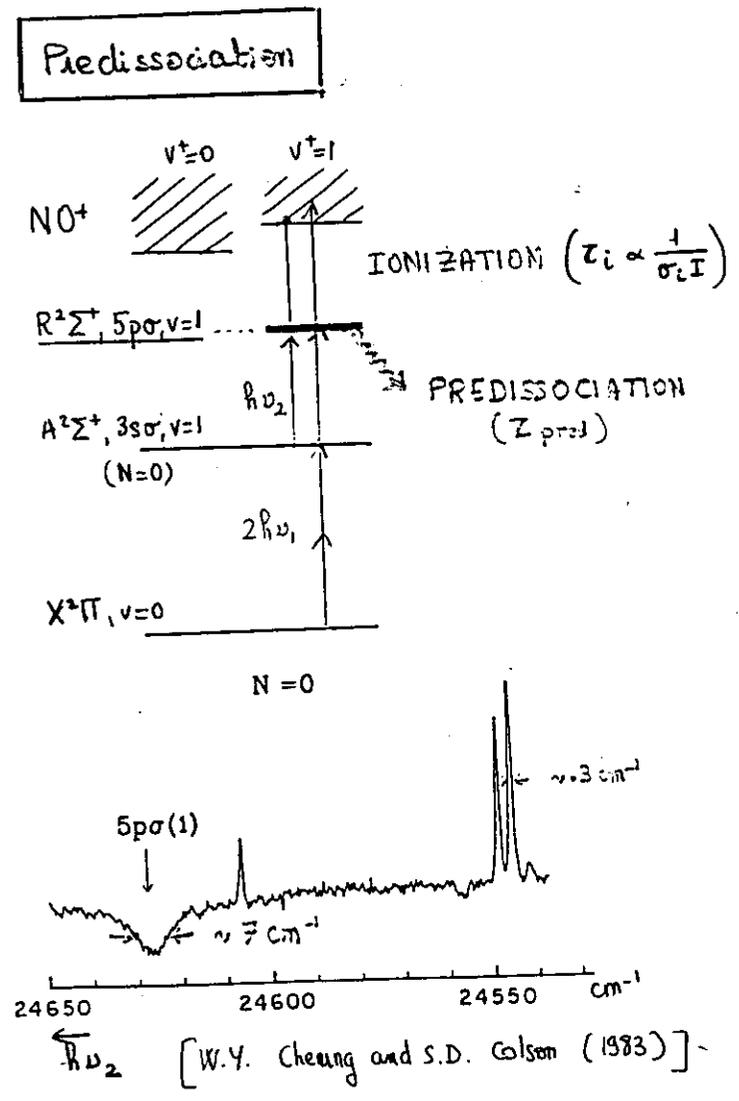
$$\sigma_i^{(2)} I^2 \ll \sigma_i I + \delta$$

$$\Rightarrow n_i \approx \sigma_i^{(2)} I^2 N_0 \tau \frac{\sigma_i I}{\sigma_i I + \delta}$$

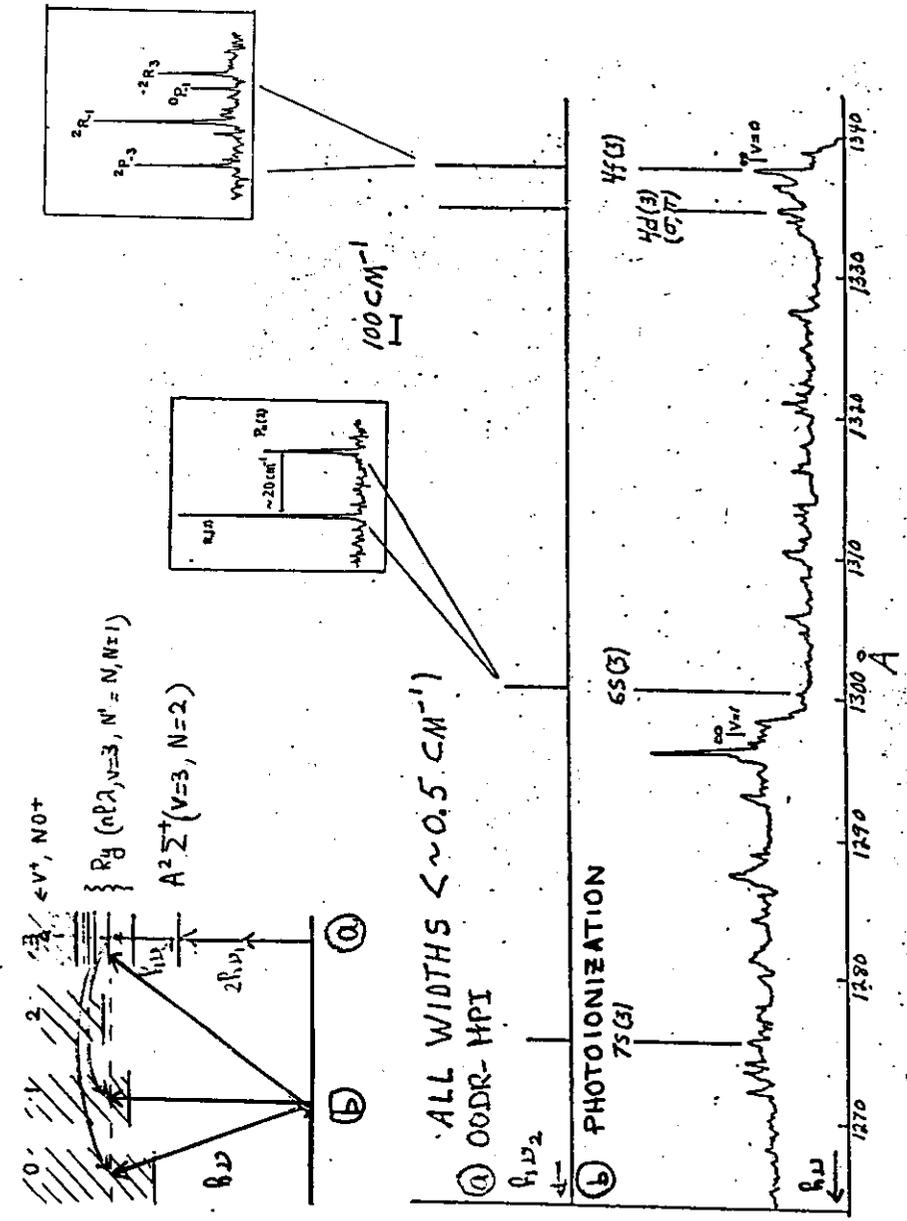
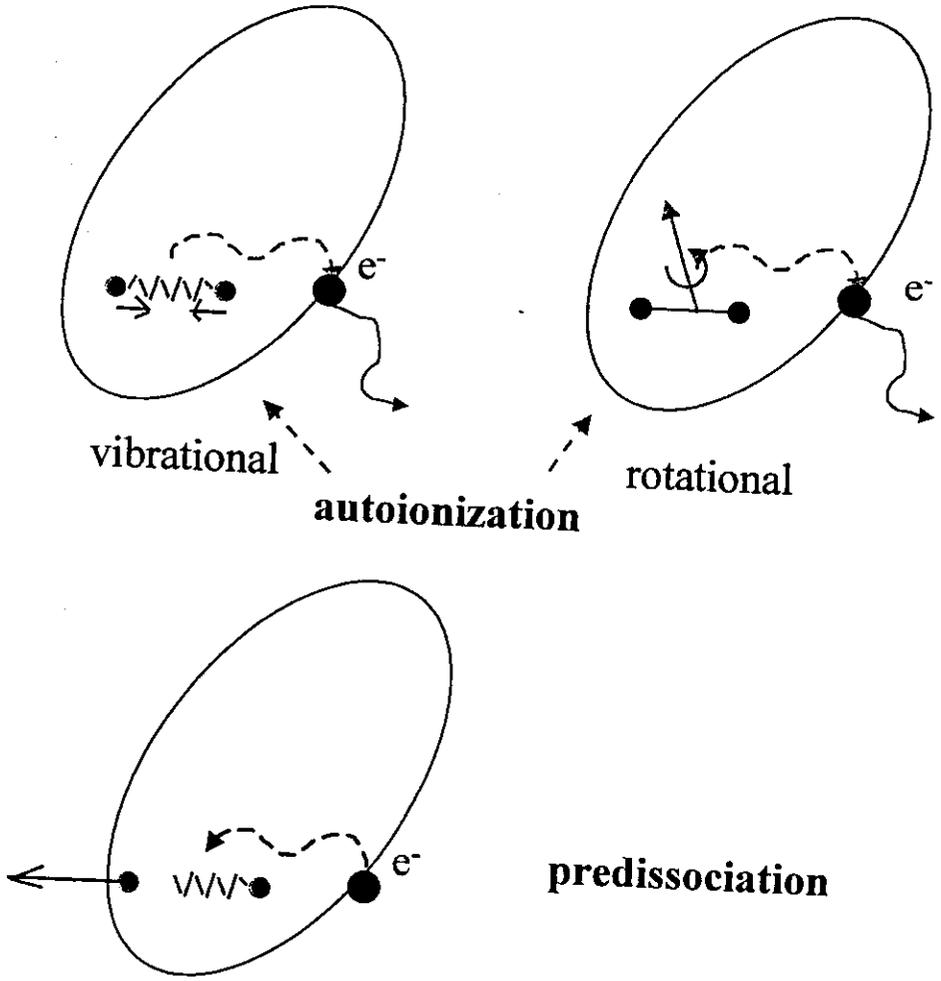
$$\sigma_i I \gg \delta$$

$$\Rightarrow n_i \approx \sigma_i^{(2)} I^2 N_0 \tau$$

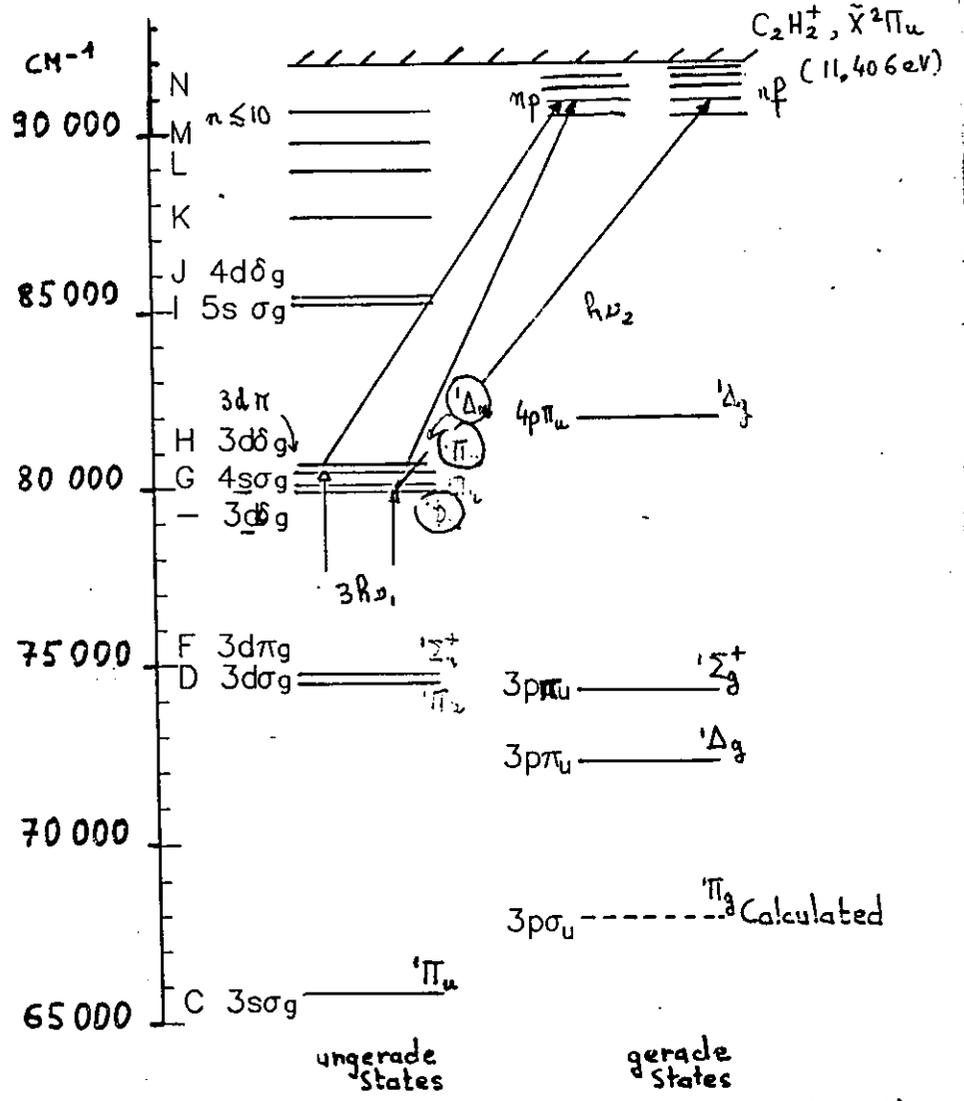
For I, τ constant
 $n_i \propto N_0$



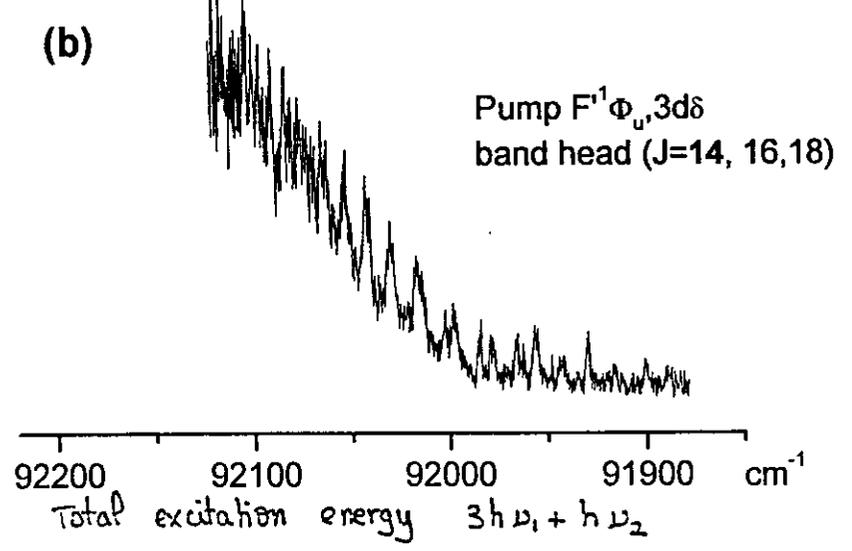
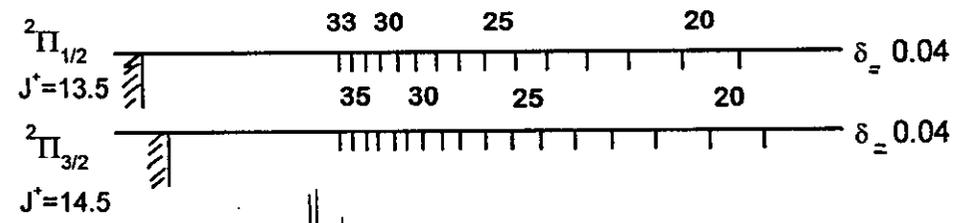
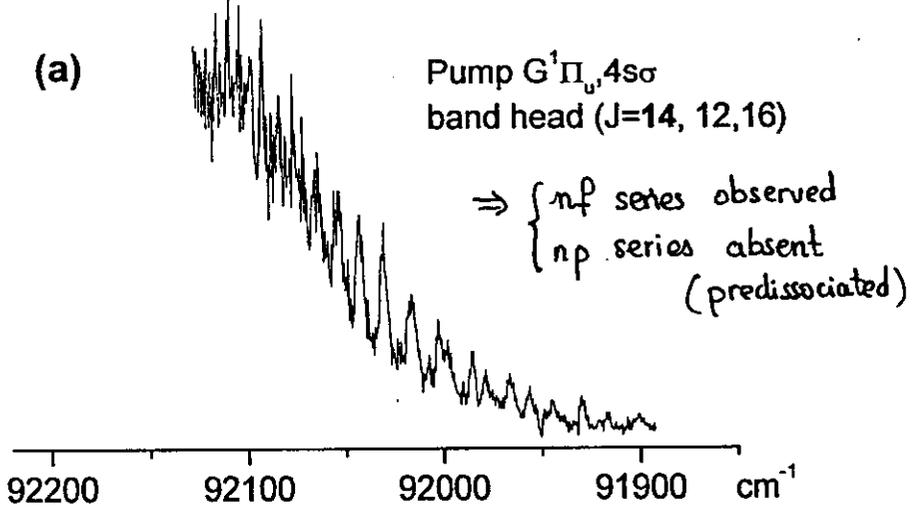
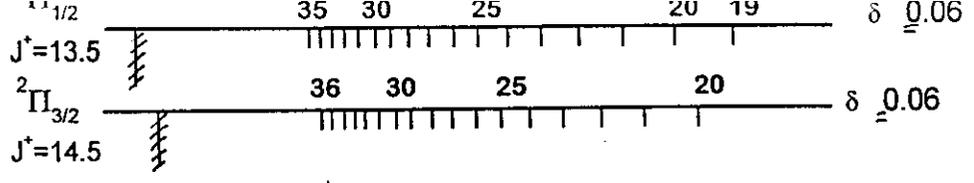
Dynamics of Molecular Rydberg states

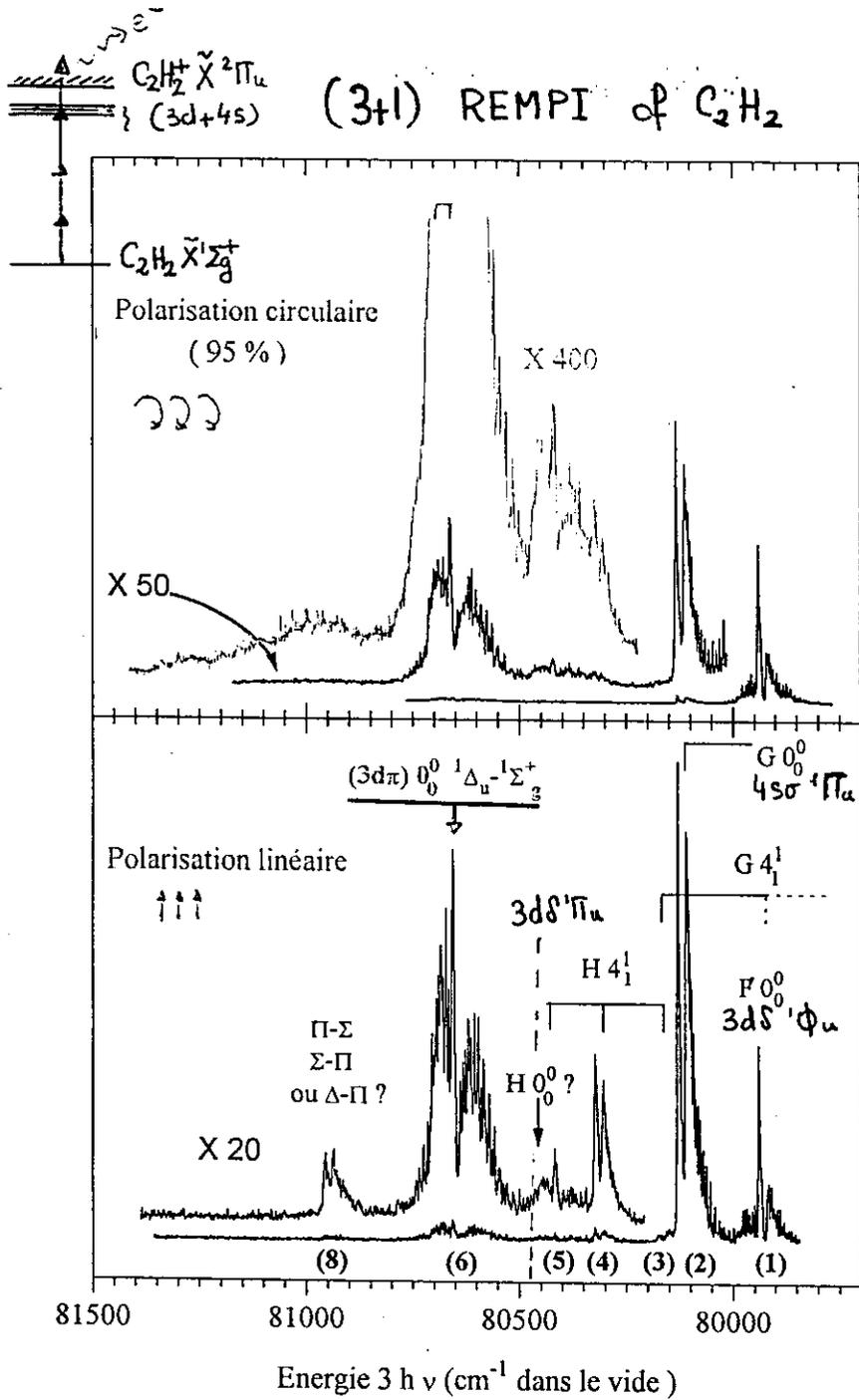


OBSERVED RYDBERG STATES OF ACETYLENE



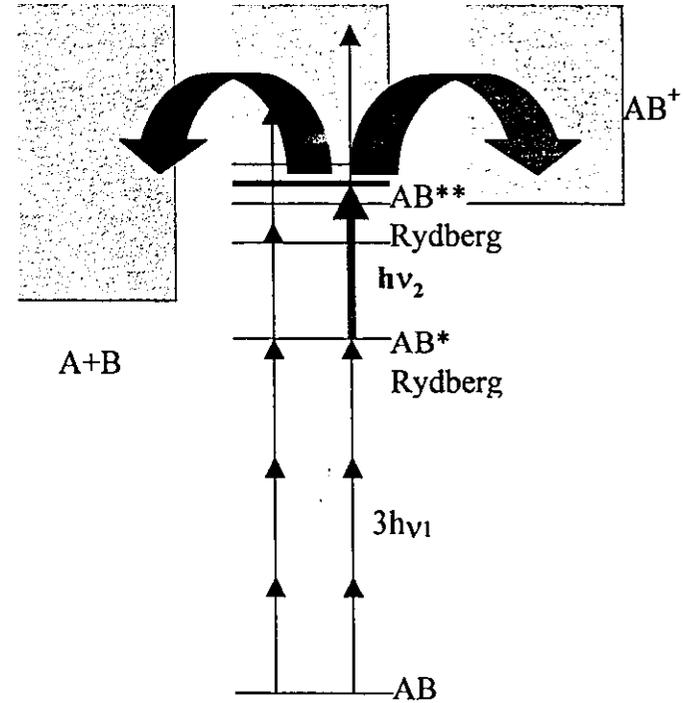
Absorption spectra	Herman and Collin	Physica Scripta	25, (1982) 275
Multiphoton Ionisation	Colvada et. al	J. Chem. Phys.	87, (1987) 851
Multiphoton Ionisation	Stohfeld et. al	J. Chem. Phys.	87 (1987) 5105
	Fujii et. al	J. Chem. Phys.	96 (1992) 117



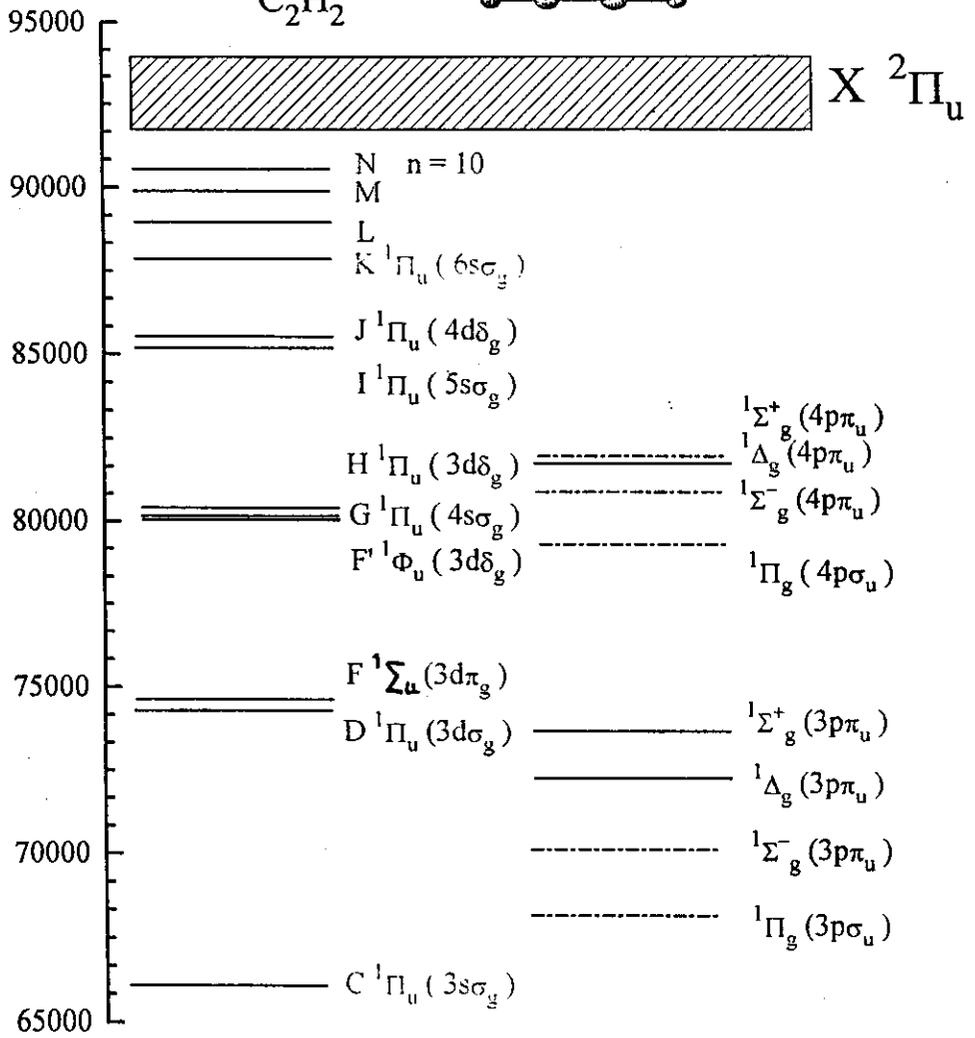
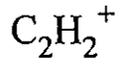


Two-color REMPI

predissociation photoionization autoionization



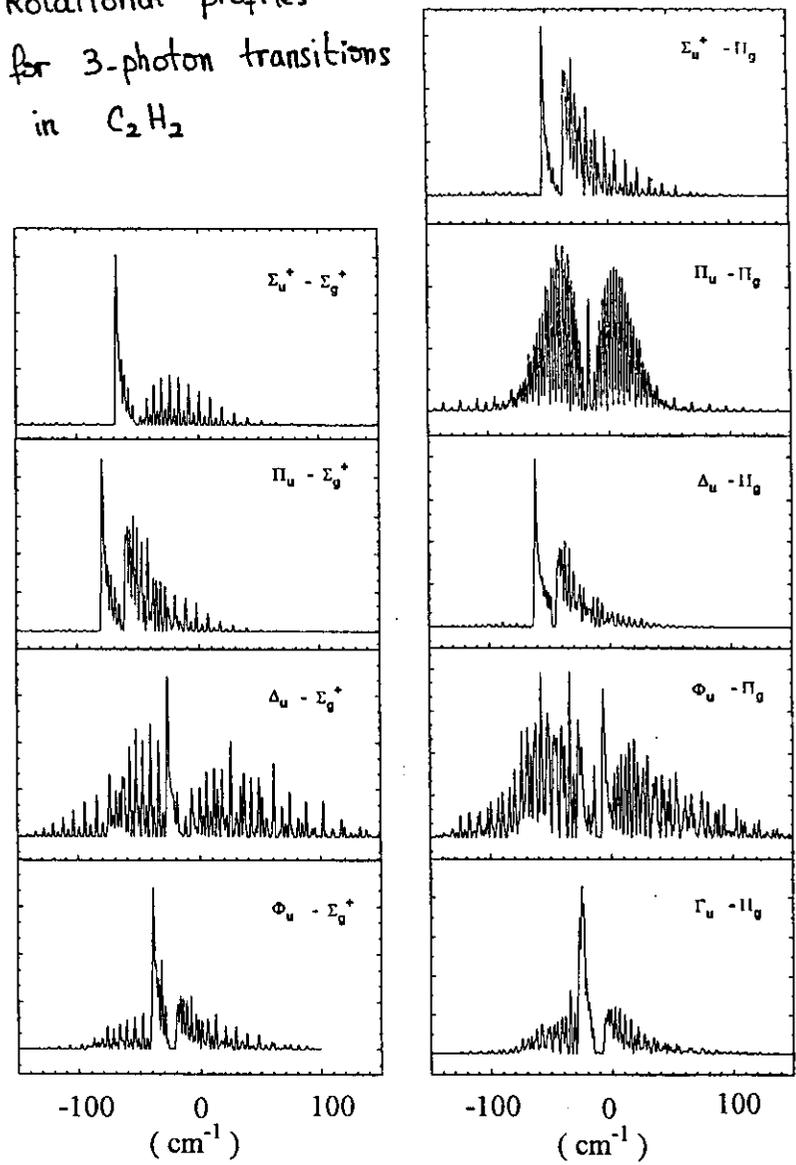
- Selection rules for Rydberg-Rydberg transitions ($h\nu_2$)
 - $\Delta v=0$
 - $\Delta J=0, \pm 1$



Etats ungerade

Etats gerade

Rotational profiles
for 3-photon transitions
in C_2H_2



MULTIPHOTON SELECTION RULES

n photons

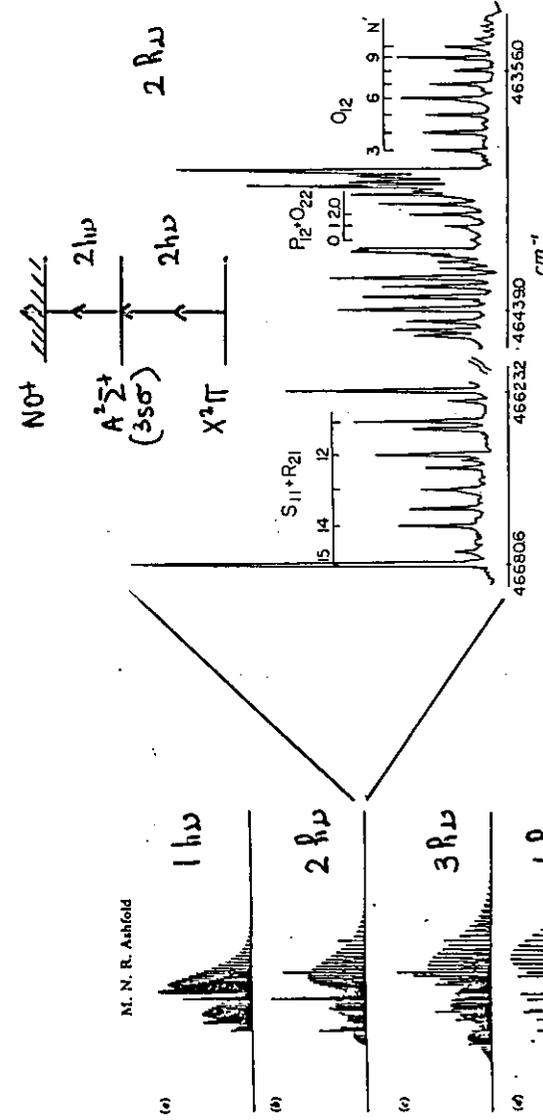
1) Electronic $\Delta \Lambda = 0, \pm 1, \pm 2, \pm 3, \dots \pm n$

2) Rotational $\Delta J = 0, \pm 1, \pm 2, \pm 3, \dots \pm n$

Branches Q R S T ...
P O N ...

3) Parity $\left\{ \begin{array}{l} + \leftrightarrow + \text{ even number of photons} \\ - \leftrightarrow - \text{ odd number of photons} \end{array} \right.$

Consequence = Spectral congestion increases with the number of photon



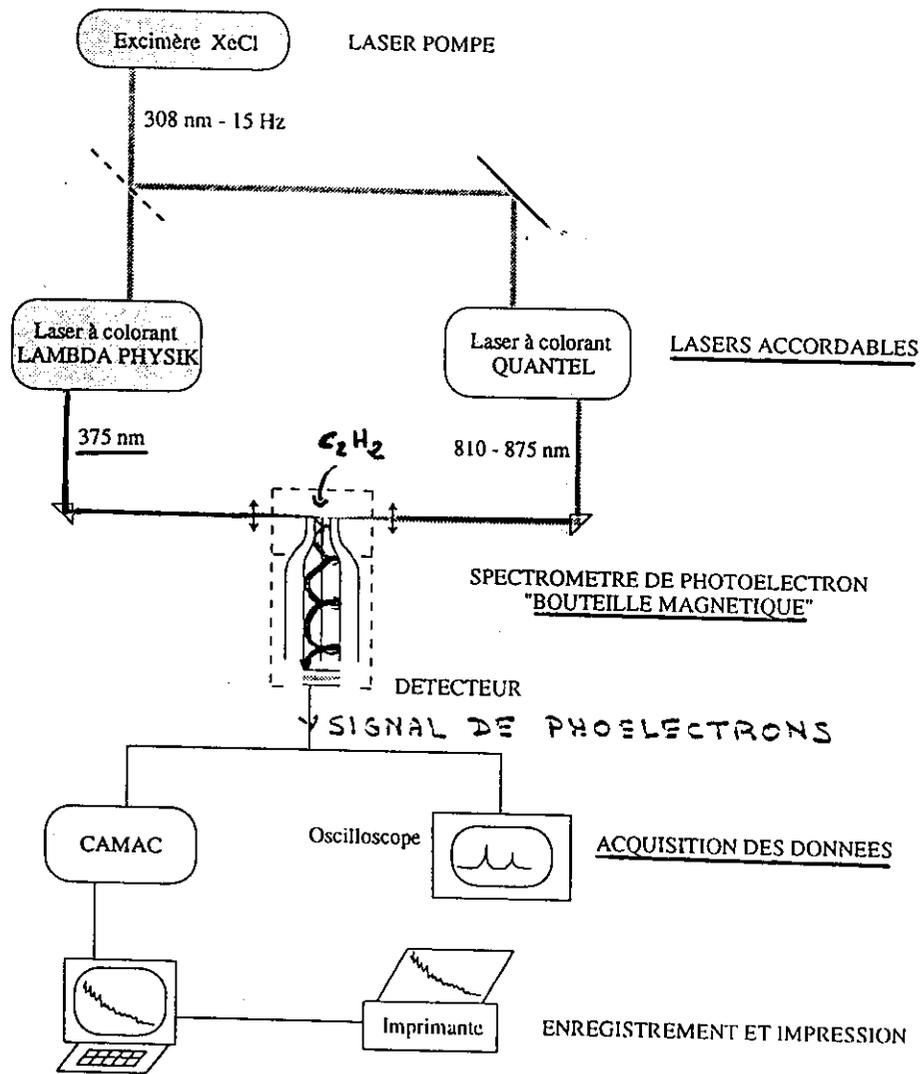
Portions of the A - X(1,0) two-photon spectrum, showing the various "jump" lines used in these experiments. The energy scale corresponds to twice the laser frequency in vacuum wavenumbers. Note that the lines are labeled by their N' quantum numbers in the spectrum instead of the conventional J'' values, since we are interested in the rotational levels of the $A^2\Sigma^+$ state being populated. Elsewhere in the text, the J'' convention is used.

calculated rotational structure for NO $A^2\Sigma^+ - X^2\Pi$ (n h\nu)
H.N.R.Ashfold Mol. Phys., 58, 1, (1986)

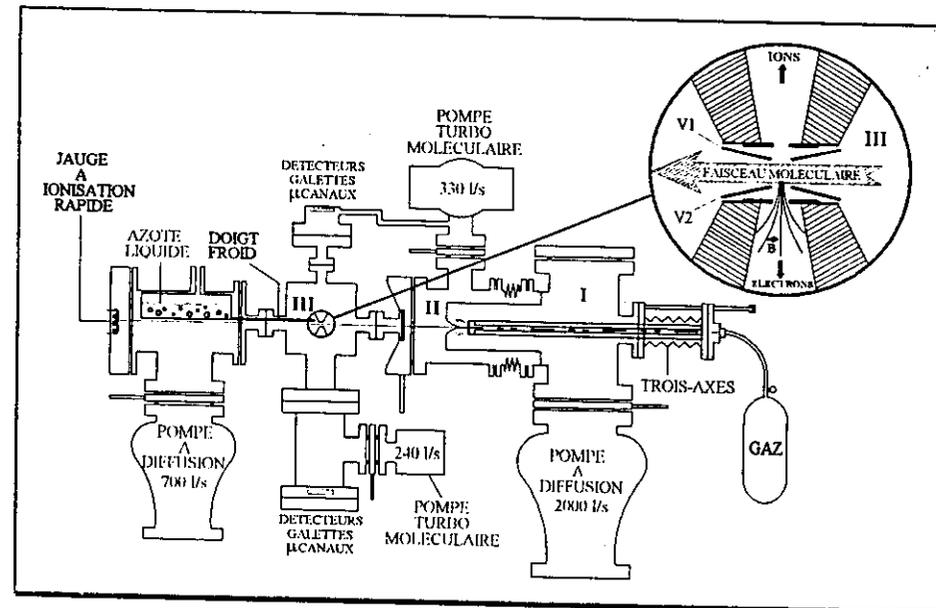
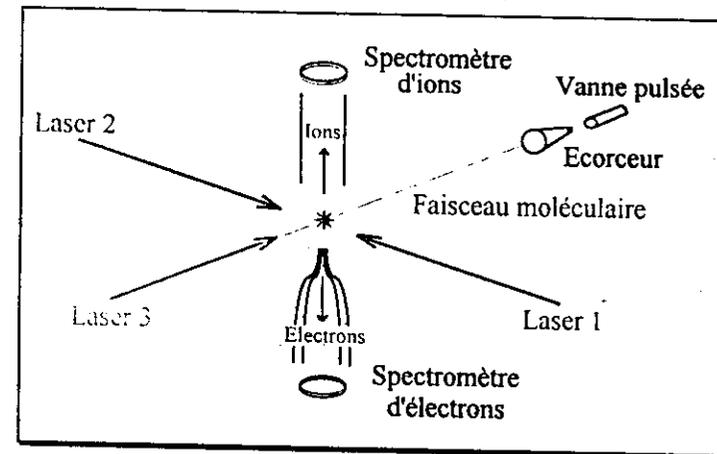
observed (2+2) MPI spectrum

Multiphoton Spectroscopy

- Selections rules
- One-color REMPI
- Two-color REMPI

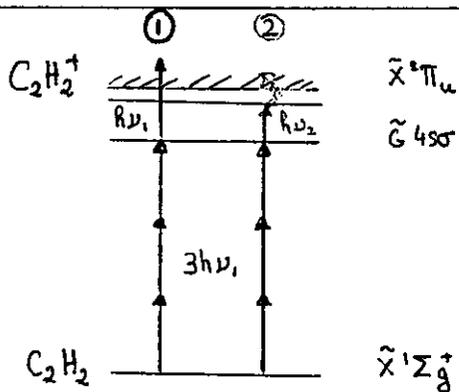
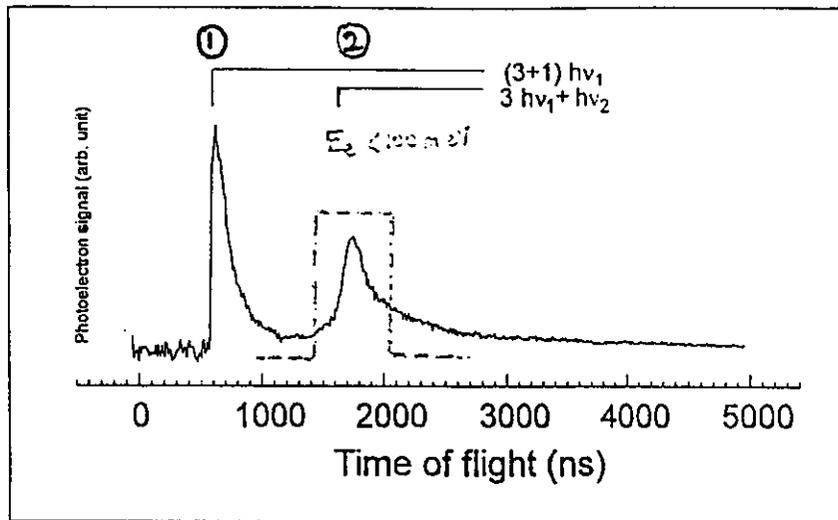


Dispositif expérimental



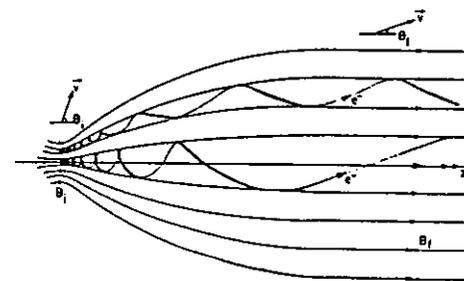
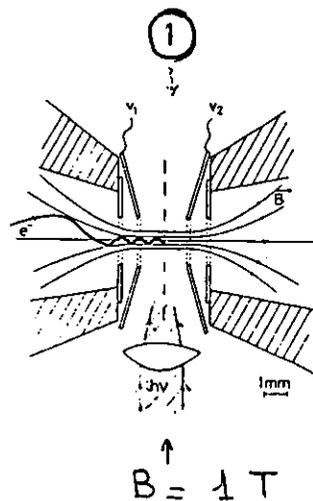
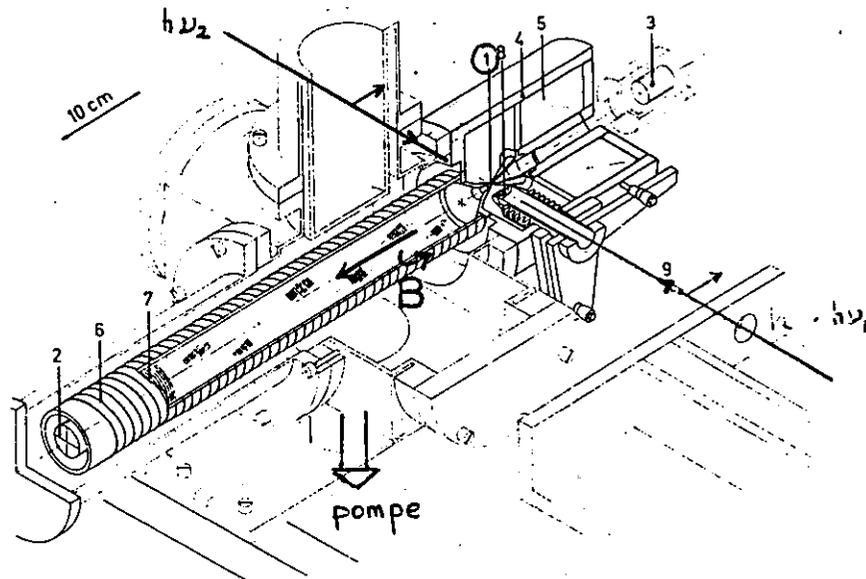
Photoelectron detection: REMPI-PES

⇒ "zero-background" spectroscopy



"Magnetic Bottle" Photoelectron Spectrometer

Spectromètre de photoélectrons par temps de vol



{ collection efficiency = 50%
Resolution ~ 20 meV

P. KRUIT Ph.D Thesis, Amsterdam (1981)

Experiment

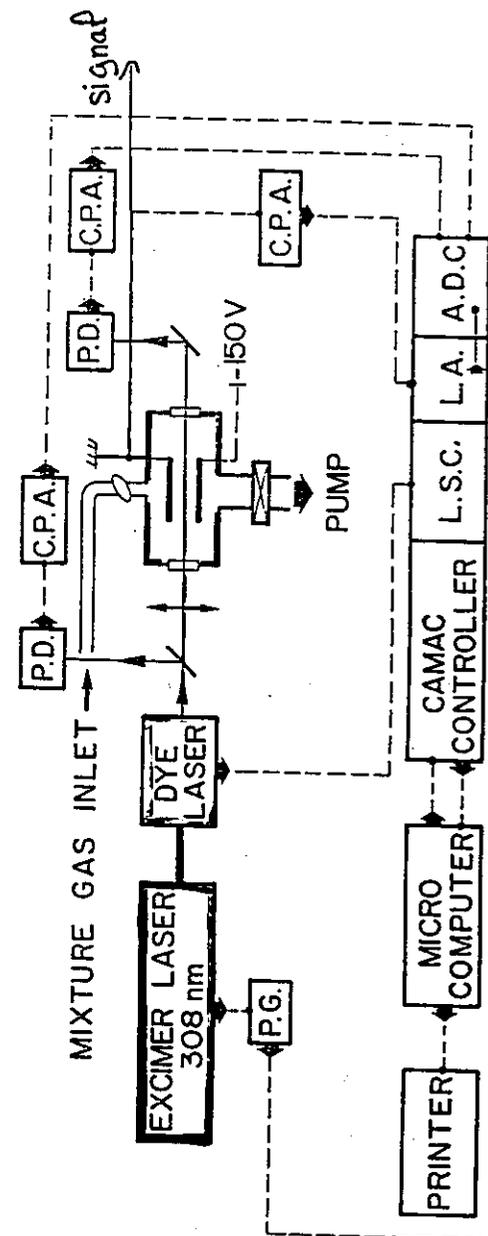
excitation sources :

- 1,2 or 3 tunable pulsed lasers (ns pulses) in the IR-UV range

detection devices :

- ionization cell
- photoelectron spectrometer
- ion mass analysis

Ionization cell



Multiphoton processes

Historical

- 1931 theoretical predictions (M. Göppert-Mayer)
- 1959 first observation (radio-frequency)
- 1960 first observation (IR 1.06 μm)
- 1970 tunable pulsed lasers \rightarrow REMPI

n-photon excitation probability

$$W = \sigma_n I^n$$

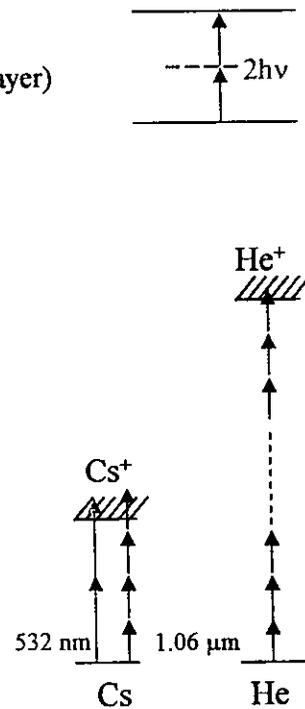
Orders of magnitude

	Cs		He
n	2	4	22
λ (nm)	532	1.06	1.06
I_{laser} ($\text{W}\cdot\text{cm}^{-2}$)	$4 \cdot 10^8$	$2 \cdot 10^{10}$	$4 \cdot 10^{14}$

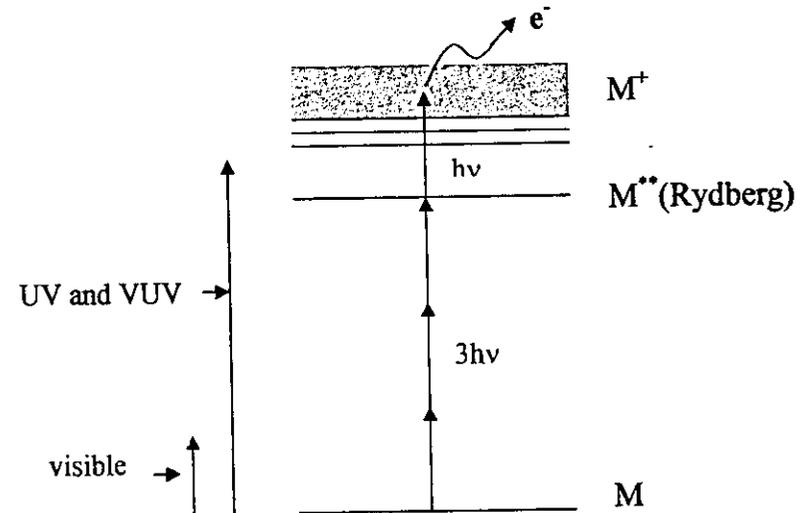
Comparison with the intra-atomic field

$$I = \epsilon_0 c / 2 |E_0|^2 \approx 10^{15} \text{ W}\cdot\text{cm}^{-2} \iff E_0 = 10^9 \text{ V}\cdot\text{cm}^{-1}$$

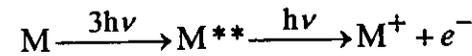
- "weak field" $I \leq 10^8 - 10^9 \text{ W}\cdot\text{cm}^{-2}$
exciting photon - resonances
- "strong field" $I \geq 10^{11} \text{ W}\cdot\text{cm}^{-2}$
perturbing photon - "dressed atom"



Resonantly Enhanced MultiPhoton Ionization (REMPI) = a tool for Rydberg state spectroscopy



One color experiment :



- one-photon ionization strongly allowed for Rydberg states
- new electronic states accessible (multiphoton selection rules)
- ion or electron signal \Rightarrow information on the structure of the resonant Rydberg state.

Molecular Multiphoton Spectroscopy
Atmospheric and astrophysical
applications

Dolores GAUYACQ

*Laboratoire de Photophysique Moléculaire
Université de Paris-Sud, ORSAY (France)*

- description of the process
- tool for molecular physics : Rydberg state spectroscopy and dynamics
- experimental setup
- atmospheric application : a method for monitoring atmospheric pollutants
- Astrophysical application : photodissociation in the circumstellar envelopes