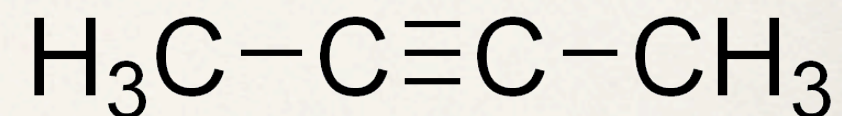
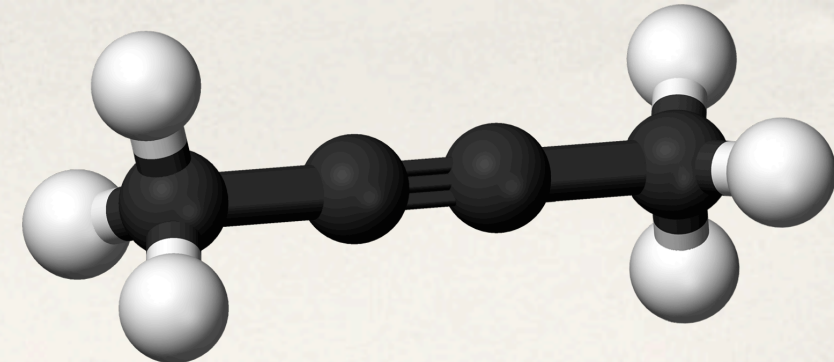
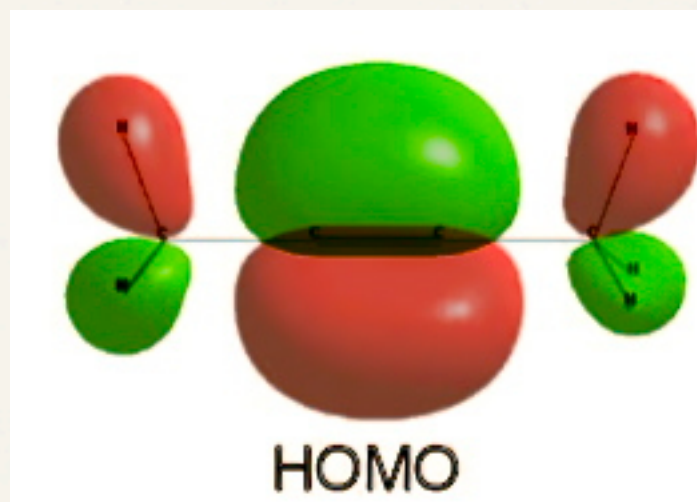
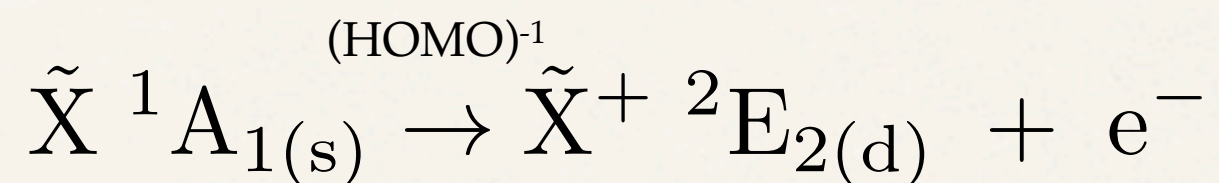




ETH
Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich



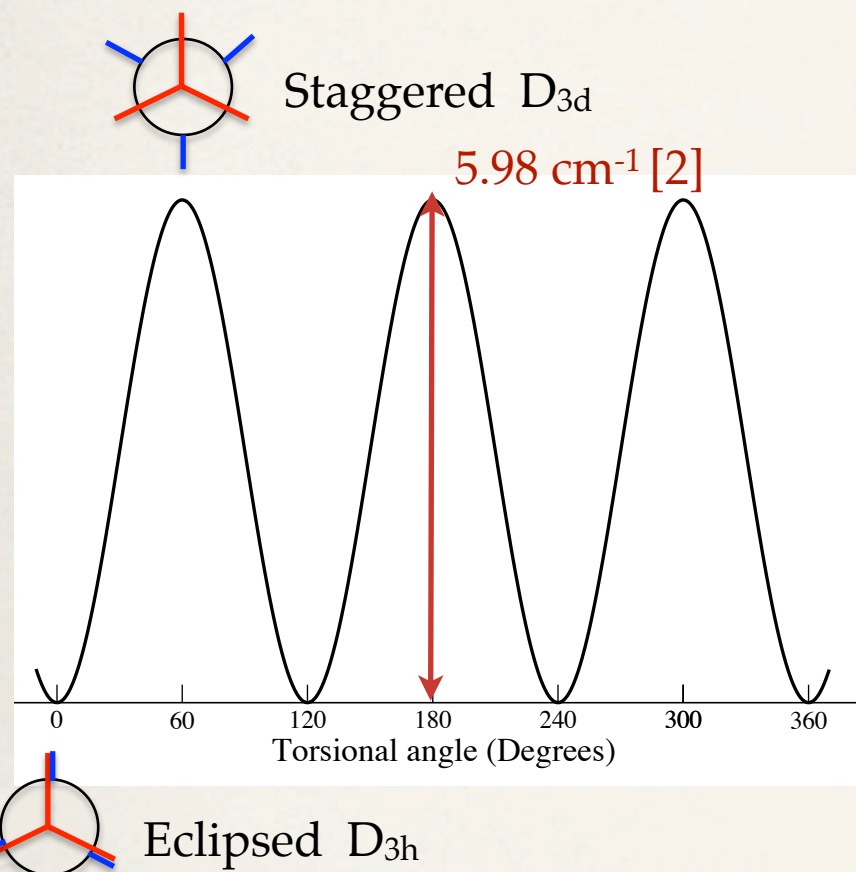
PHOTOELECTRON SPECTROSCOPY OF 2-BUTYNE (C_4H_6)



Photoelectron ejected from the $\text{C} \equiv \text{C}$ bond

Neutral ground state

«The ethane and dimethylacetylene molecules have been of great spectroscopic interest for more than 60 years because of their internal rotation and high symmetry.» from Bunker and Jensen [1].



Rotational structure :

Symmetric top

$$A = 2.66 \text{ cm}^{-1} [2]$$

$$B = 0.11189761(50) \text{ cm}^{-1} [2]$$

Quantum numbers : K angular momentum along top axis.

K_i associated to internal rotation.

N total angular momentum without spin.

MS group : G_{36} (EMS) [3]

Vibrational structure [2,4-6]:

15 modes :
4 $a_1(s)$
3 $a_4(s)$
4 $e_1(d)$
4 $e_2(d)$

[1] P. Bunker and P. Jensen, 2012. Molecular Symmetry and Spectroscopy. E-book edition. NRC Research Press, Ottawa, Ontario, Canada.

[2] C. Lauro, P. Bunker, J. Johns, and A. McKellar, J. Mol. Spectrosc. **184**(1), 177–185 (1997).

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[6] J. Plíva, A. S. Pine, and S. Civiš, J. Mol. Spectrosc. **180**, 15 – 25 (1996).

Cation ground state

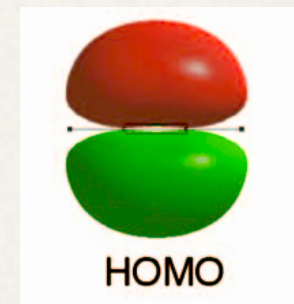
Cation ground state :

Vibronic ground state of the cation : ${}^2E_{2(d)}$.  Jahn-Teller active

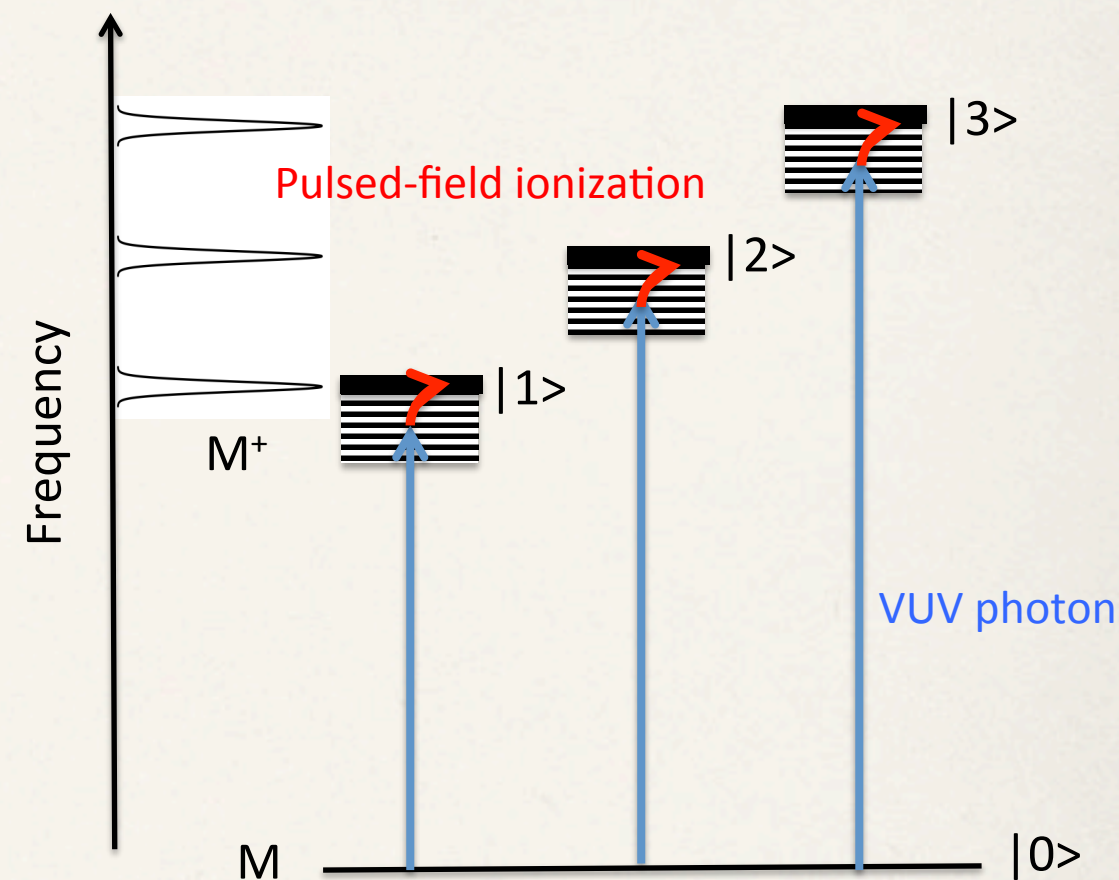
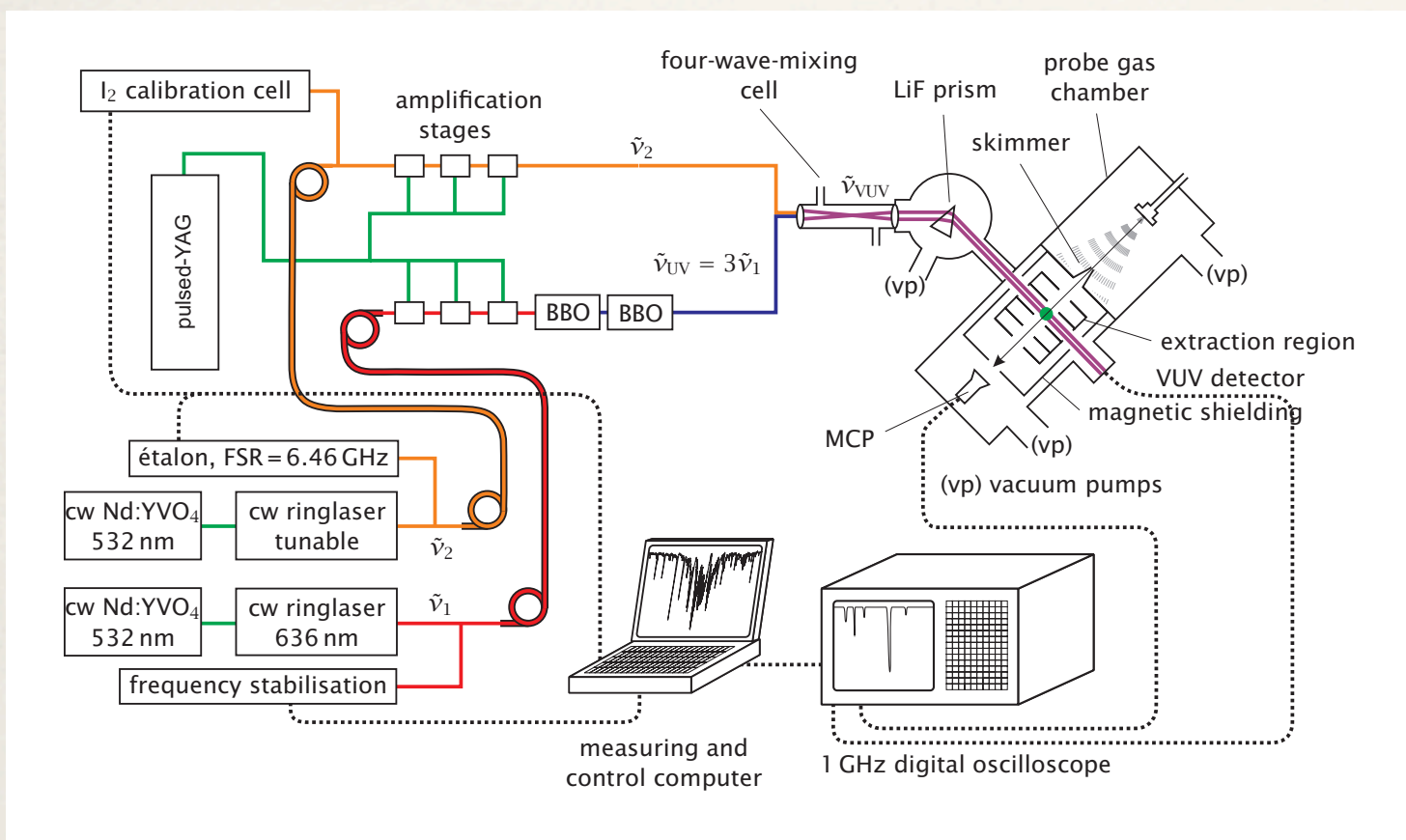
Active modes : $e_{1(d)}$ (4x)
 $e_{2(d)}$ (4x)

Questions :

- Internal rotation ?
- Spin orbit coupling ? (Acetylene: $A_{so} = -30.86(44) \text{ cm}^{-1}$ [7])
- Role of Jahn-Teller effect ?



Experimental setup and PFI-ZEKE PES



cw ring dye laser
linewidth : $\approx 3.10^{-5} \text{ cm}^{-1}$
(1 MHz)

VUV laser linewidth : 0.008 cm^{-1} (240 MHz) [8]

PFI-ZEKE PES :

- Survey study 2 cm^{-1}
- High-resolution study 0.15 cm^{-1}

Photoelectron spectrum overview of the 2-butyne

Vibrational selection rules :

$$\Gamma_{\text{vib}} \otimes \Gamma_{\text{vib}^+} \supset A_{1(s)}$$

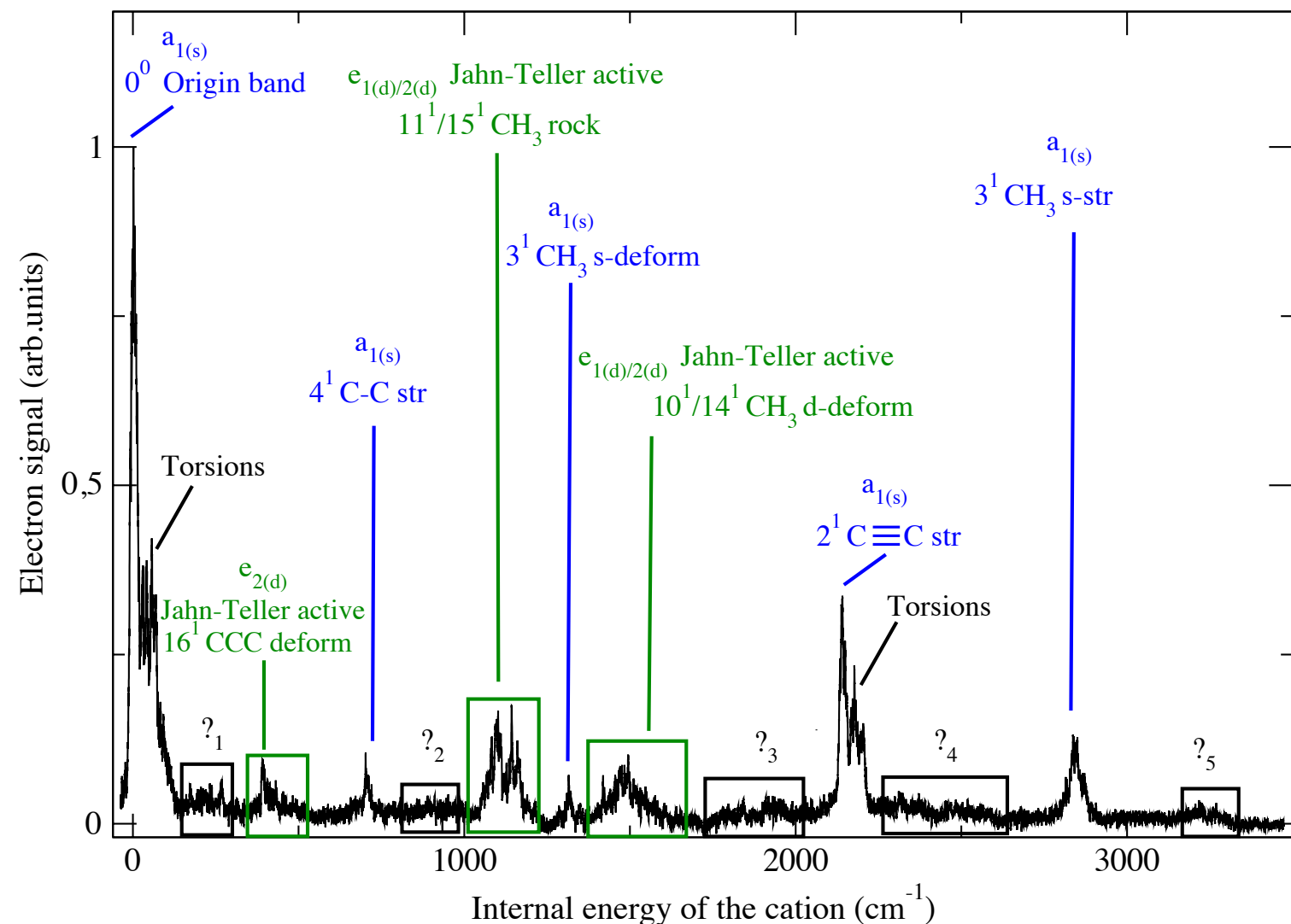
$$(A_{1(s)})^n \leftarrow A_{1(s)}$$

$$(A_{4(s)})^{2n} \leftarrow A_{1(s)}$$

$$(E_{1(d)})^{2n} \leftarrow A_{1(s)}$$

$$(E_{2(d)})^{2n} \leftarrow A_{1(s)}$$

With n integer and n>0



First assignments of the overview spectrum

Mode	Type	Symmetry	Frequency observed (cm ⁻¹) (G ₃₆ (EMS))	Frequency calculated (cm ⁻¹) [9]
1	CH ₃ s-str	a _{1(s)}	2850	2946
2	C≡C str	a _{1(s)}	2142	2149
3	CH ₃ s-deform	a _{1(s)}	1315	1275
4	C—C str	a _{1(s)}	703	694
10/14	CH ₃ d-deform	e _{1(d)} /e _{2(d)}	1440-1540	1385-1389
11/15	CH ₃ rock	e _{1(d)} /e _{2(d)}	1090-1150	877-977
16	CCC deform	e _{2(d)}	405	350-418

Rotortional selection rules

In the approximations of :

Free internal rotation.

No perturbation for the origin band by Jahn-Teller effect.

Energy levels : $E_{\text{rotor}} = E_{\text{rot}} + E_{\text{tor}} = B(N(N+1)-K^2) + AK^2 + AK_i^2$ and $\pm A_{\text{so}}/2$ for the cation.

Photoionization selection rules [10-11],

$$\Gamma_{\text{rve}}(\text{neutral}) \otimes \Gamma_{\text{rve}}(\text{ion}) \supset \Gamma^* \text{ if } \ell \text{ even}$$

$$\Gamma_{\text{rve}}(\text{neutral}) \otimes \Gamma_{\text{rve}}(\text{ion}) \supset \Gamma^{(s)} \text{ if } \ell \text{ odd}$$

$$\left. \begin{array}{l} \Delta K = \pm 1, \pm 5 \text{ for } K'' = 6n \pm 1 \text{ and } 6n \pm 2 \text{ and } 6n \pm 6 \\ \Delta K = \pm 1, \pm 3 \text{ for } K'' = 0 \text{ and } 6n \pm 3 \end{array} \right\} n \text{ nonnegative integer}$$

$$\Delta K_i = 0 \text{ for all values of } K_i''$$

$$\left. \begin{array}{l} \Delta K_i = -2 \text{ for } K_i'' = 3m + 1 \\ \Delta K_i = +2 \text{ for } K_i'' = 3m - 1 \\ \Delta K_i = -4 \text{ for } K_i'' = 3m + 2 \\ \Delta K_i = +4 \text{ for } K_i'' = 3m - 2 \end{array} \right\} m \text{ integer } > 0$$

$$\Delta K_i = \pm 6 \text{ for all values of } K_i''$$

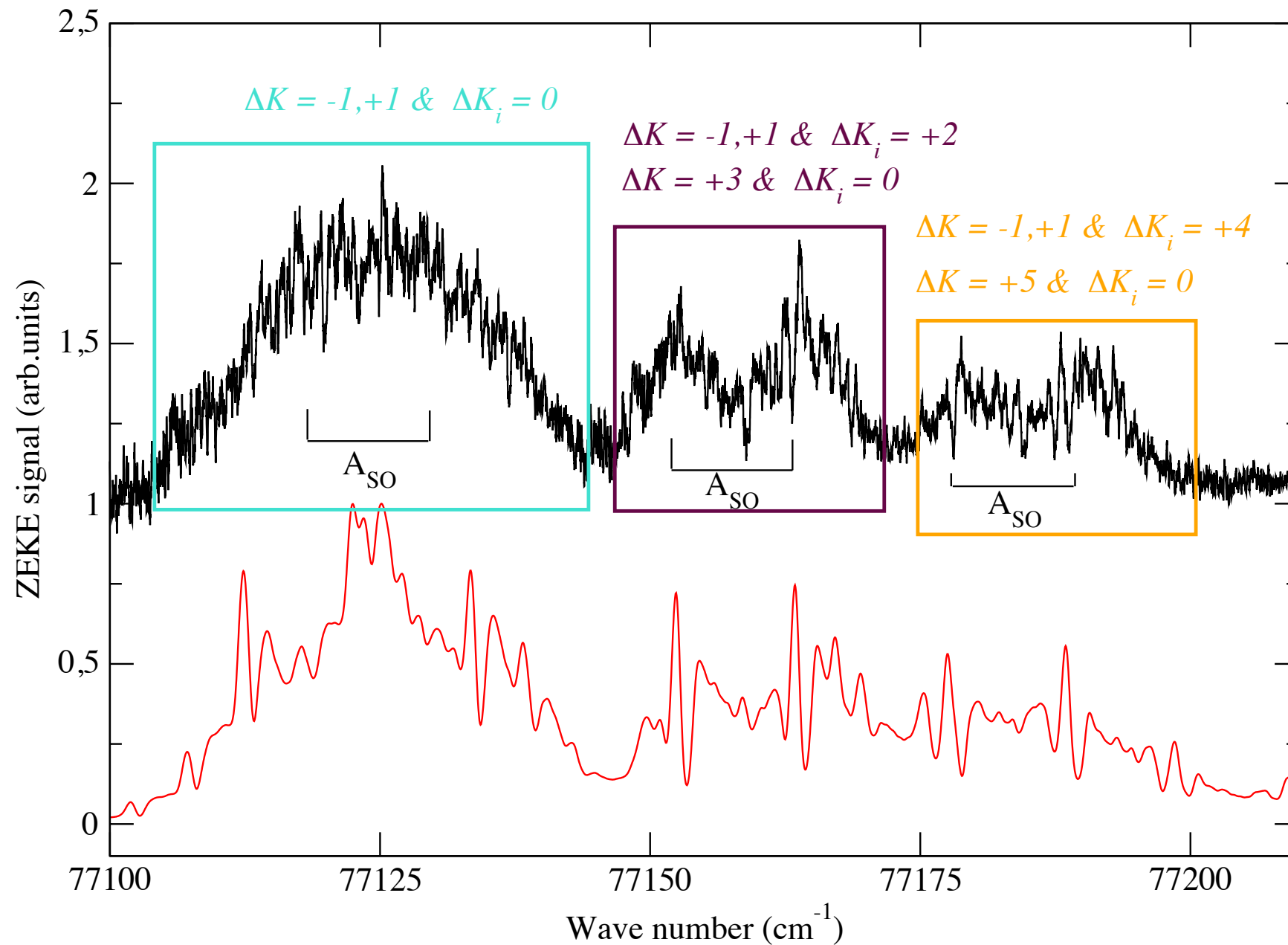
[10] R. Signorell and F. Merkt, Mol. Phys. **92**(5), 793–804 (1997).

[11] S. Willitsch and F. Merkt, Int. J. Mass. Spectrom. **245**(1-3), 14–25 (2005).

PFI-ZEKE PE spectrum of the origin band at high resolution

Intensity for ΔK branches: ± 1 ; 3 ; 5 (1 ; 1.5 ; 2)

Intensity for ΔK_i branches: 0 ; ± 2 ; 4 (1 ; 2 ; 0.4)



IP = 77123.5(20) cm⁻¹

$A_{\text{SO}} = -11(1)$ cm⁻¹

$T_{\text{rot}} = 16$ K

Conclusions and outlook

Answers :

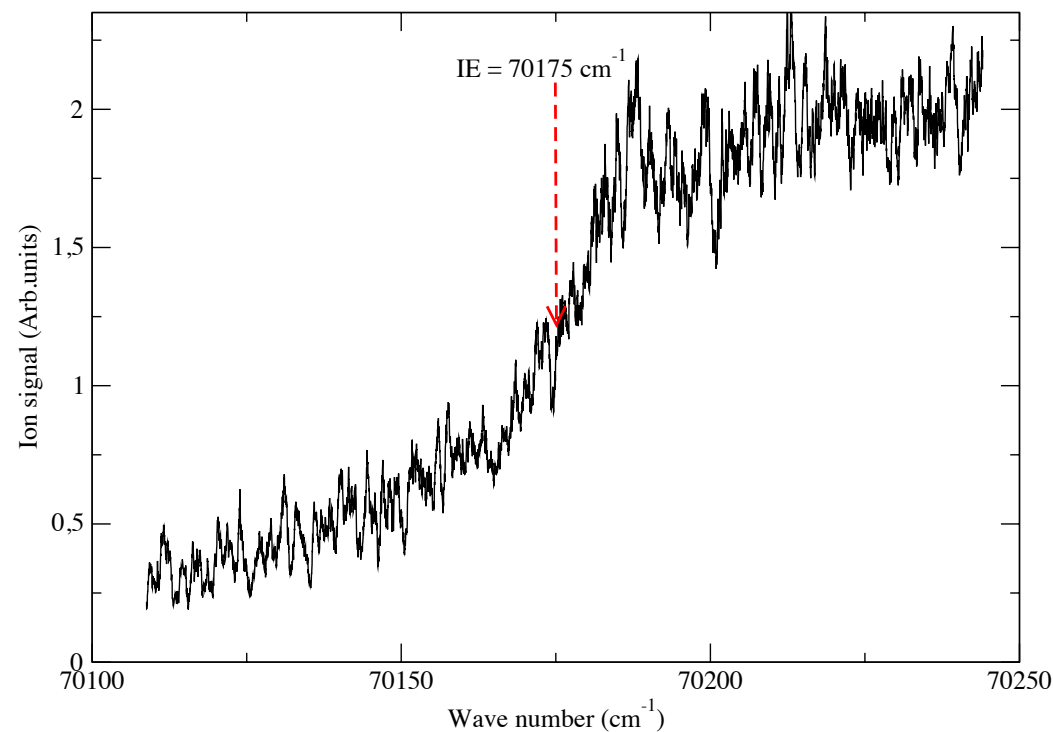
- Cation is subject to free internal rotation ($K_i^+ = 1,2,3,4,5$).
- Spin orbit coupling $|A_{so}| = 11(1) \text{ cm}^{-1} < 30.86(44) \text{ cm}^{-1}$ in acetylene.
- Role of Jahn-Teller: active Jahn-Teller modes have been observed.

Outlook :

- Record spectrum of the fully deuterated 2-butyne isotope.
- Ab-initio calculation including Jahn-Teller effect would be desirable.

Short communication on the propargyl (C_3H_3) radical

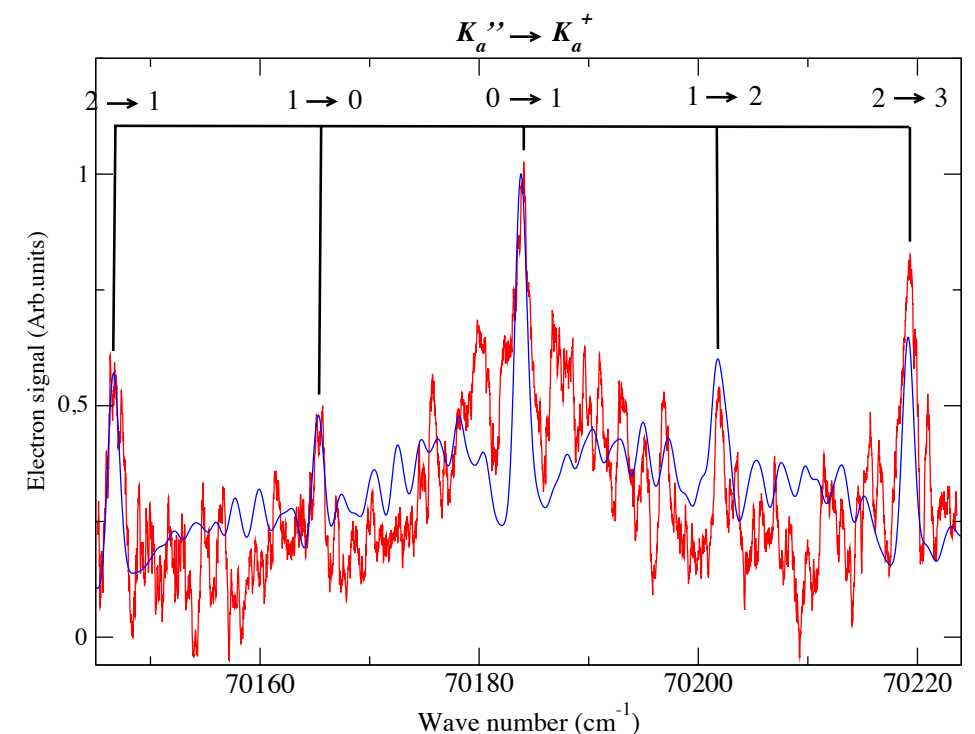
Controversy in literature for the value of the adiabatic ionization energy.



E_I/hc (cm^{-1})	Ref	Method
70156(4)	[12]	VUV-VMI-TPE
69961(8)	[13]	VUV-PIE
70170(160)	[14]	MT-RPMS
70251(160)	[15]	TPES
69928(160)	[16]	PES
70138-70210	[17]	ab-initio
70001	[14]	ab-initio
70174.7(20)	This work	PFI-ZEKE PE

Adiabatic ionization energy : 70174.7(20) cm^{-1}

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 [15] P. Hemberger, M. Lang, B. Noller, I. Fischer, C. Alcaraz, B.K. Cunha de Miranda, G.A. Garcia and H. Soldi-Lose, J. Phys Chem. A. **115** (11), 2225 (2011).
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 [17] P. Botschwina and R. Oswald, Chemical Physics **378** (13), 4 (2010).



Thank you for your attention