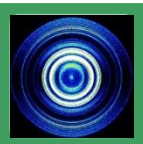
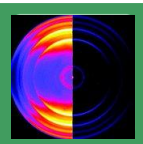
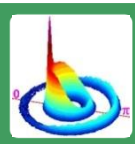




Cl-LOSS DYNAMICS OF VINYL CHLORIDE CATION IN B^2A'' STATE: ROLE OF C^2A' STATE

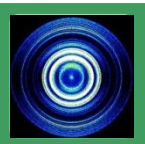
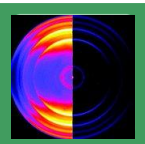
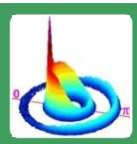
— **T**hreshold **P**hoto**e**lectron-**P**hoto**i**on **Co**incidence **V**elocity **M**ap **I**maging

Xiaoguo ZHOU, Lei Xing, Shilin Liu

Hefei National Laboratory for Physical Sciences at the Microscale and Department of Chemical Physics, University of Science and Technology of China

2017.06.20

Motivation

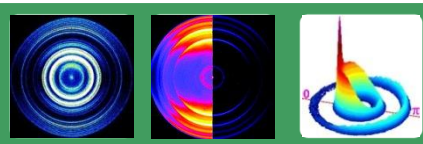
- **Spectroscopy and dynamics of molecular ions**
  - **open-shell system**
  - **accurate parameters**

    e.g. ionization potential (IP), appearance potential (AP)

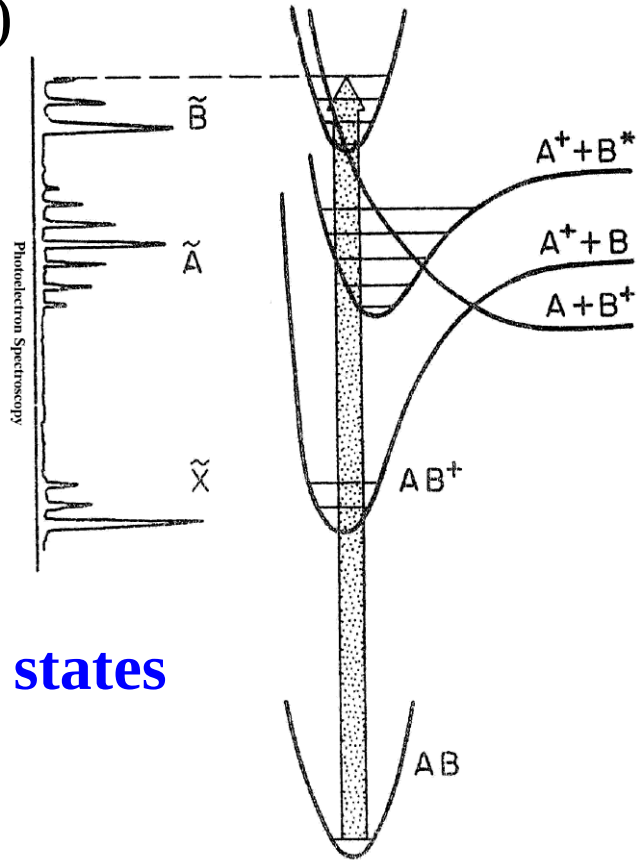
    bond dissociation energy (BDE)
  - **molecular interactions**

    e.g. conical intersection, internal conversion, Jahn-Teller
  - **benchmark for high-level theoretical calculation**

VUV photoionization or DPI



$$AB \xrightarrow{\text{tunable VUV}} AB^+(e, v'') + e\ (\text{spectrosc.})$$
$$\downarrow$$
$$A^+ + B\ \ (\text{disso. dynamics})$$



Energy conservation:

$$E_{AB+} = E_{AB} + h\nu - \mathrm{IP(AB)} - E_{el}$$

- $E_{el} = 0$, **TPEPICO**

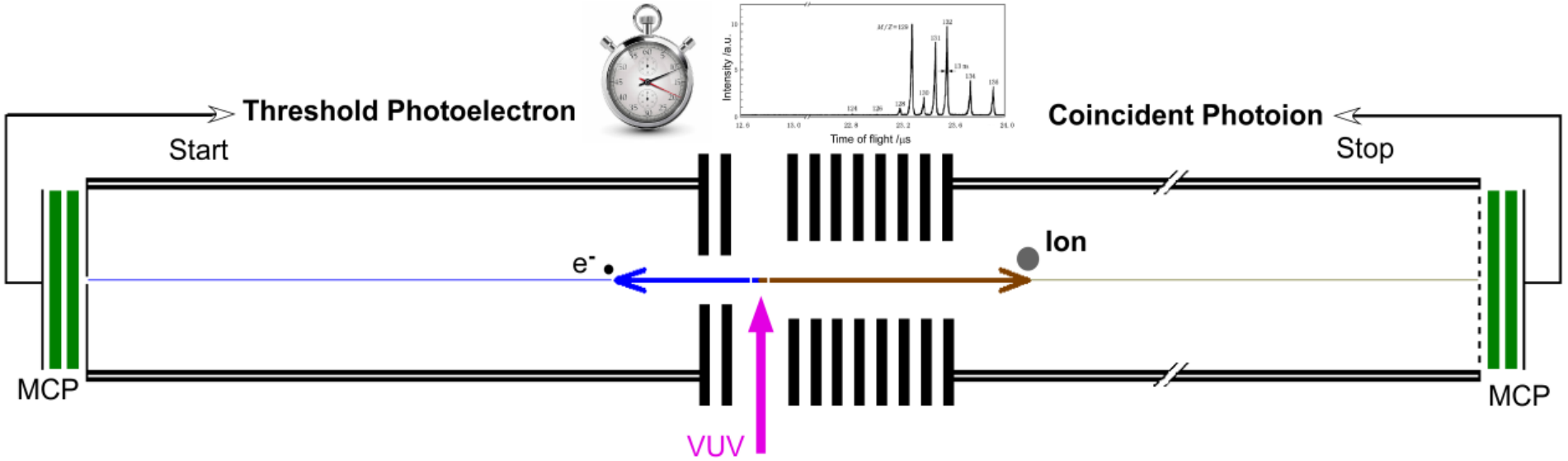
General method, suitable for all electronic states

In a dissociative photoionization event:

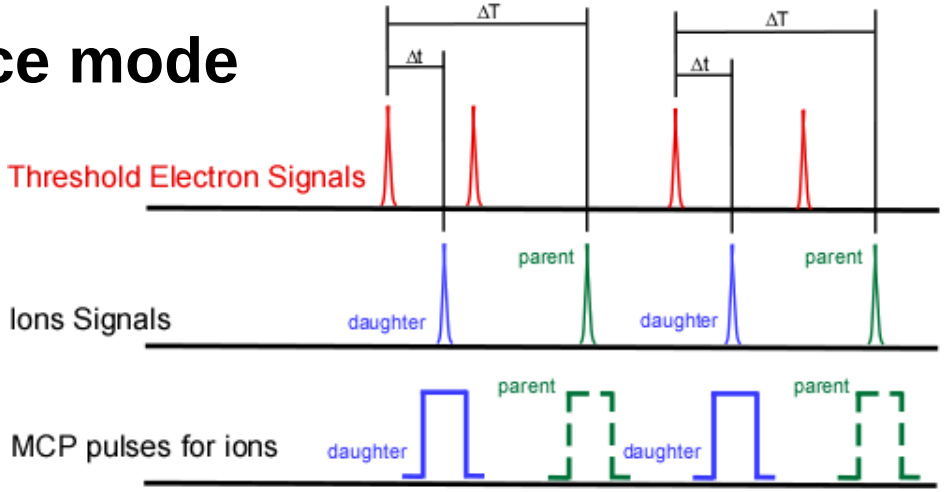
$$E_{in}(A^+) + E_{in}(B) + E_T = E_{AB} + h\nu - \mathrm{IP(AB)} - E_{el} - \underline{\mathrm{BDE}(AB^+)}$$

$E_T = E_T(A^+) + E_T(B)$: **kinetic energy released distribution (KERD)**

TPEPICO principle

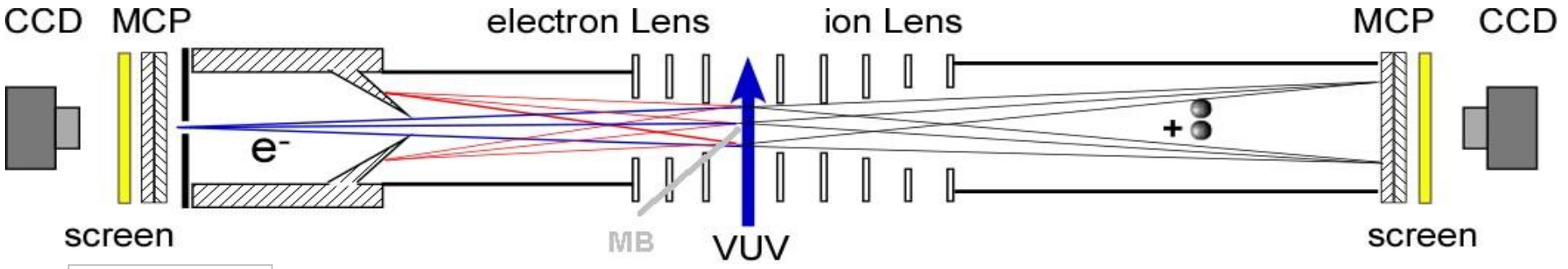


Time coincidence mode



New TPEPICO design at Hefei

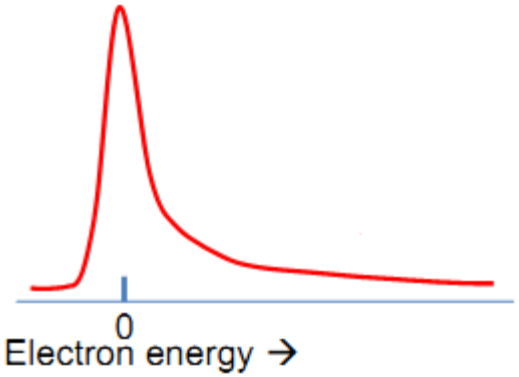
TPEPICO + double Velocity Imaging



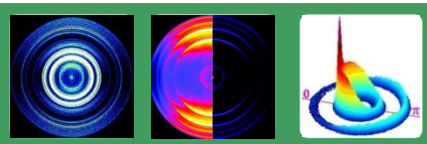
VMI of electron → Coincidence ← VMI of ion

Key points:

- Hot electron tail in TPES;
- False coincidence measurement

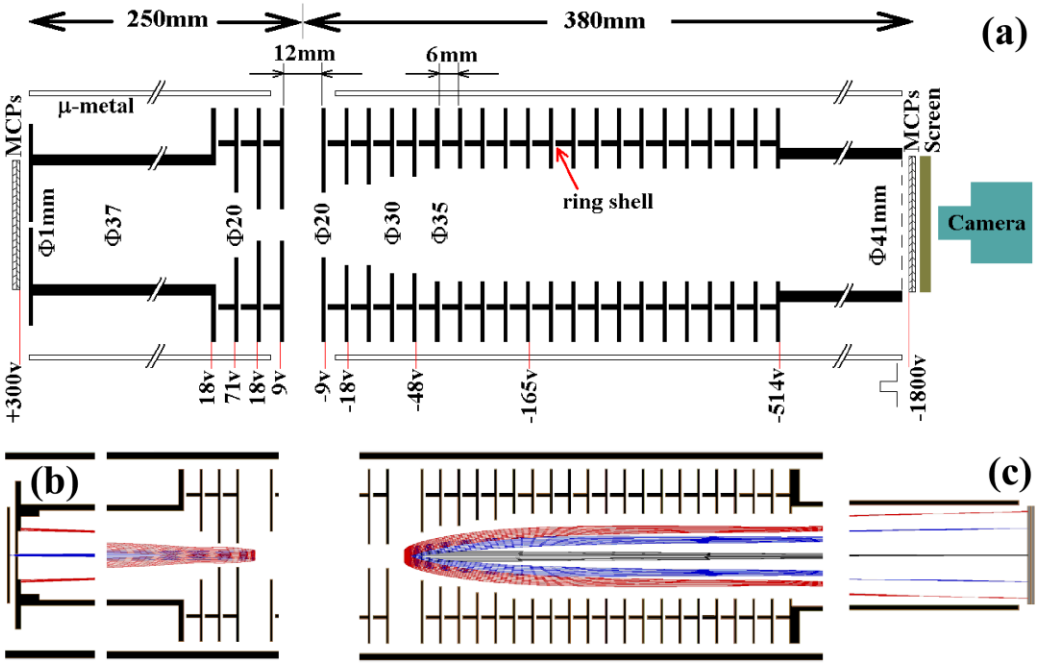


Key points in TPEPICO VMI



decelerated ion optics

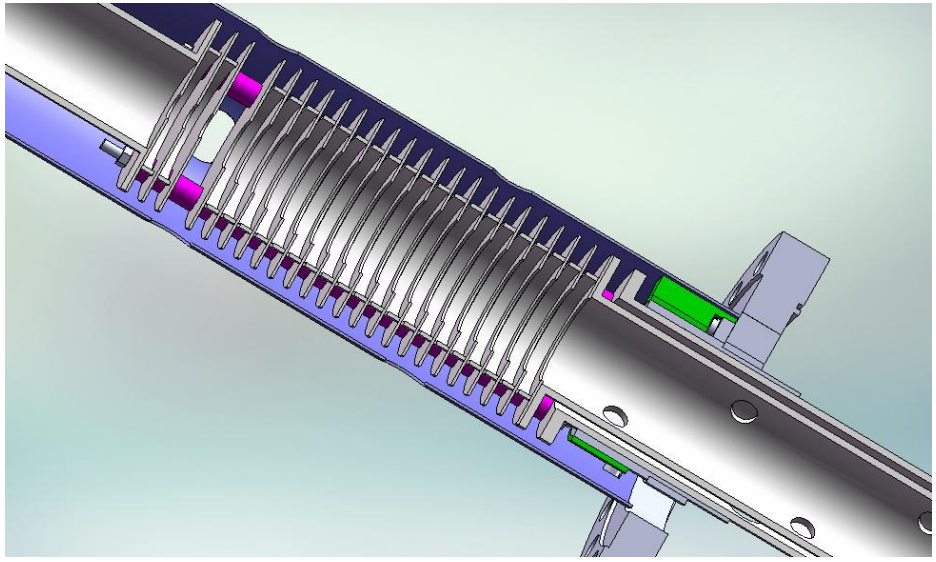
- Reduce the ratio of hot electrons falsely detected in coincidence measurement

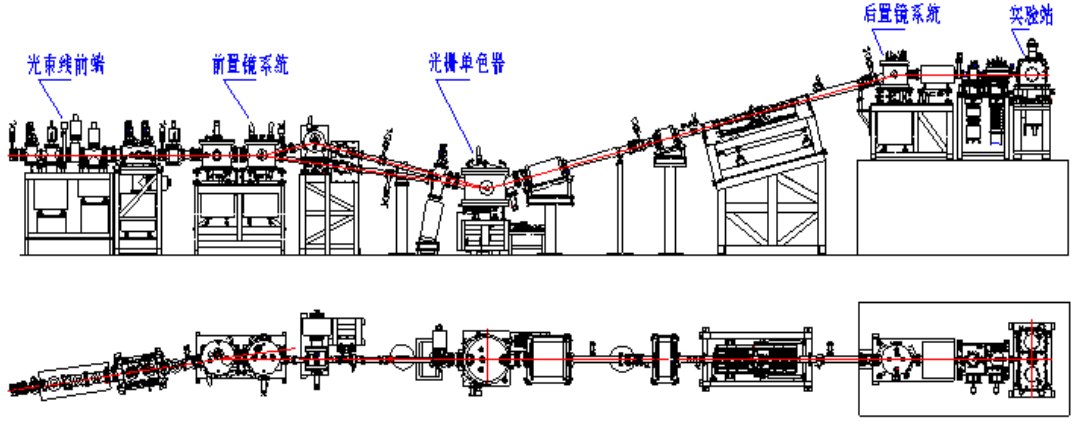


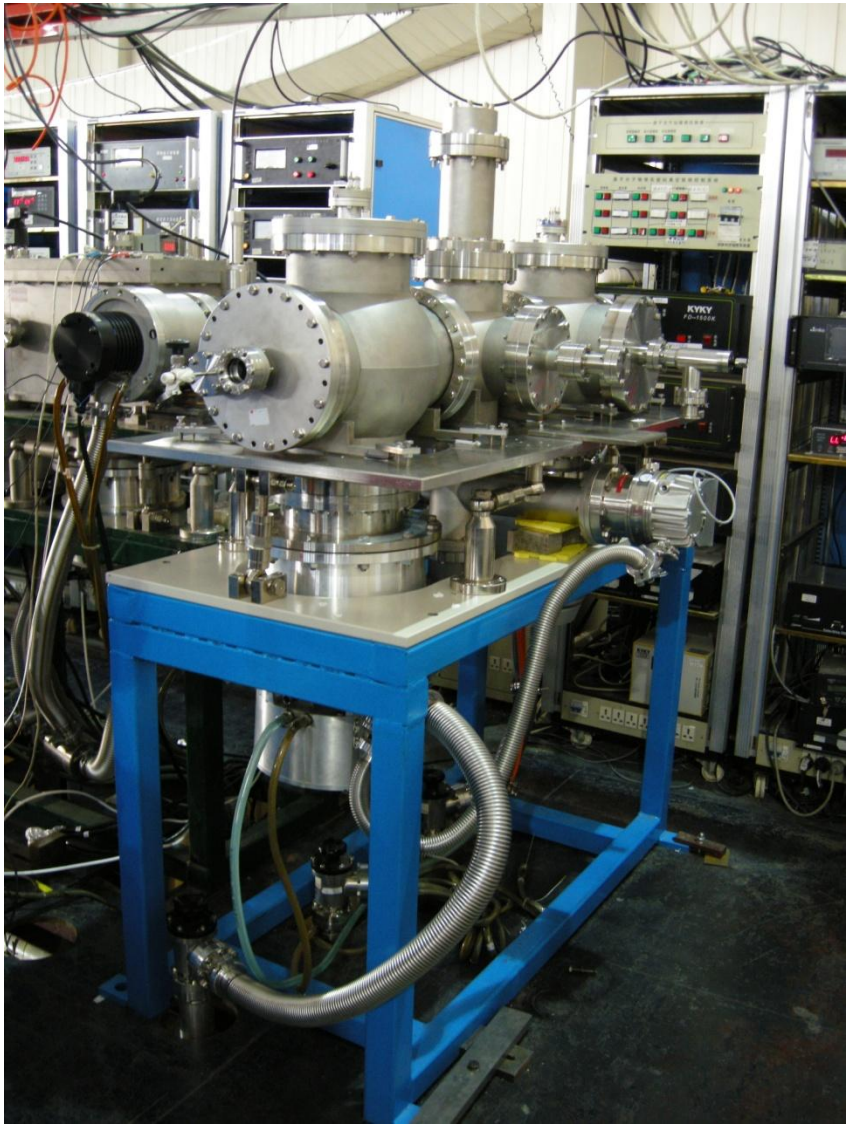
Ionization region /mm^3	Hot electron / meV	Ratio of collected hot electrons		
		Ref.1 in 2003	Ref.2 in 2002	Present
1 × 4 × 4	10	26.7%	36.7%	3.3%
	20	18.9%	25.6%	2.4%
	50	12.2%	15.5%	1.5%

X. F. TANG, X. G. ZHOU, … Rev. Sci. Instrum. 80 (2009), 113101*

TPEPICO VMI at Hefei



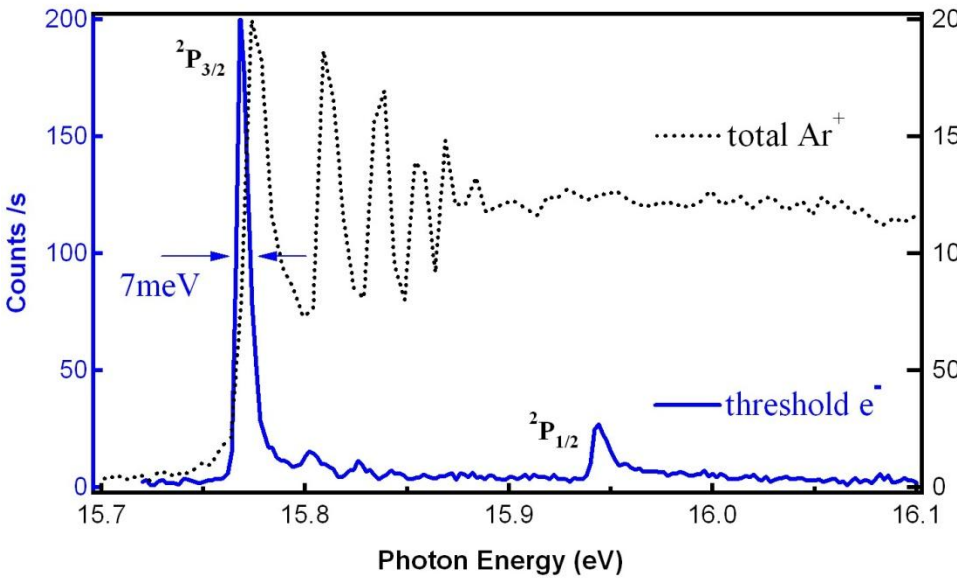


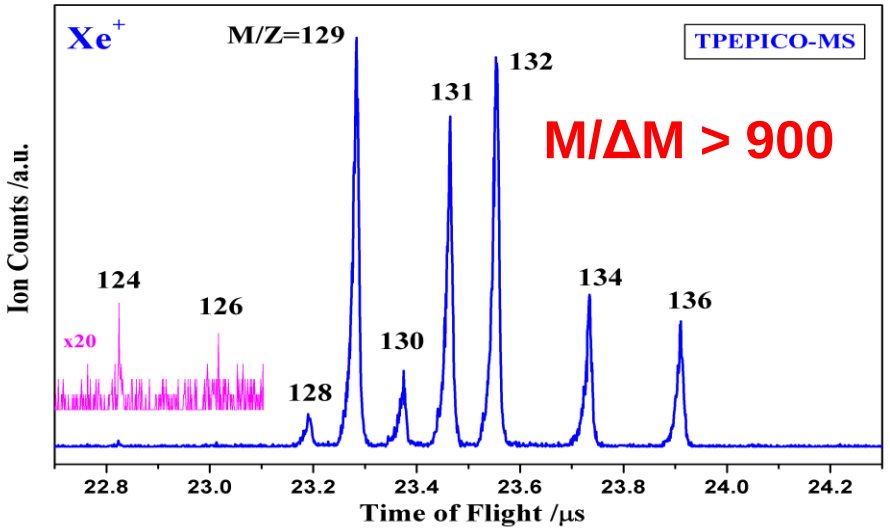


U14A in Hefei Synchrotron Radiation Lab.

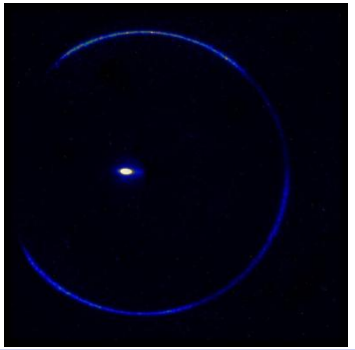
X. F. TANG, X. G. ZHOU, … Rev. Sci. Instrum. 80 (2009), 113101*

TPEPICO VMI performance





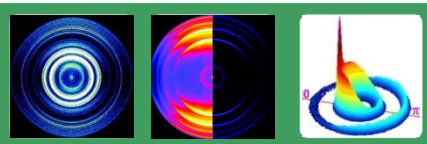
Performance	Hefei
Coincidence counts/s	~ 300
Energy resolution of Threshold e^-	7 meV Vibrational
Velocity map imaging, $\Delta E_t / E_t$	~ 2%



$$\frac{\Delta E_T}{E_T} = 2 \times \frac{\Delta v}{v} = 2.2\%$$

X. F. TANG, X. G. ZHOU, … Rev. Sci. Instrum. 80 (2009), 113101*

TPEPICO + double VMI



O_2^+ ion:

$B^2\Sigma_g^-$ vibrational dependence	*J. Phys. Chem. A*, 115, 6339 (2011)
$^2\Sigma_u^-$ dark ionic state	*J. Phys. Chem. A*, 116, 9459 (2012)

N_2O^+ ion:

$C^2\Sigma^+$ NO^+ formation pathways	*J. Chem. Phys.* 134, 54312 (2011)
N^+ formation pathways	in analysis
$D^2\Pi$ dissociation dynamics	*J. Electron Spectrosc. Relat. Phenom.* (2014)

CH_3Cl^+ ion:

A^2A_1 & B^2E internal conversion	*J. Chem. Phys.* 136, 34304 (2012)

CH_3Br^+ ion:

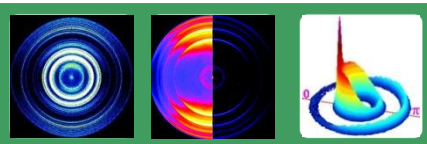
A^2A_1 & B^2E spin-orbit coupling	*J. Chem. Phys.* 140, 44321 (2014)

CF_4^+ ion:

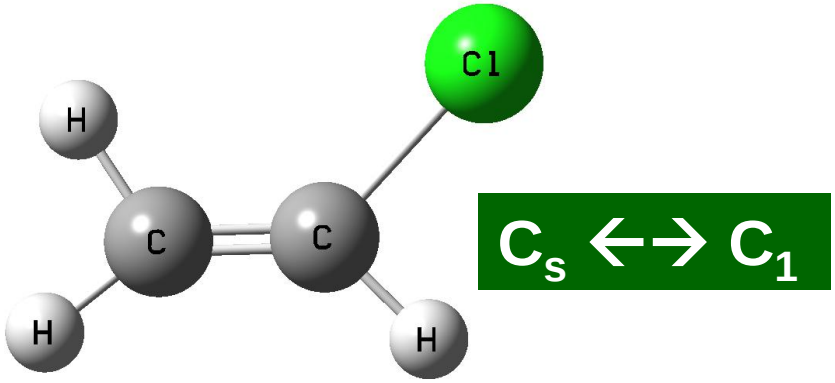
$AP_0(CF_3^+/CF_4)$ = 14.709 eV	*J. Chem. Phys.* 138, 94306 (2013)

……

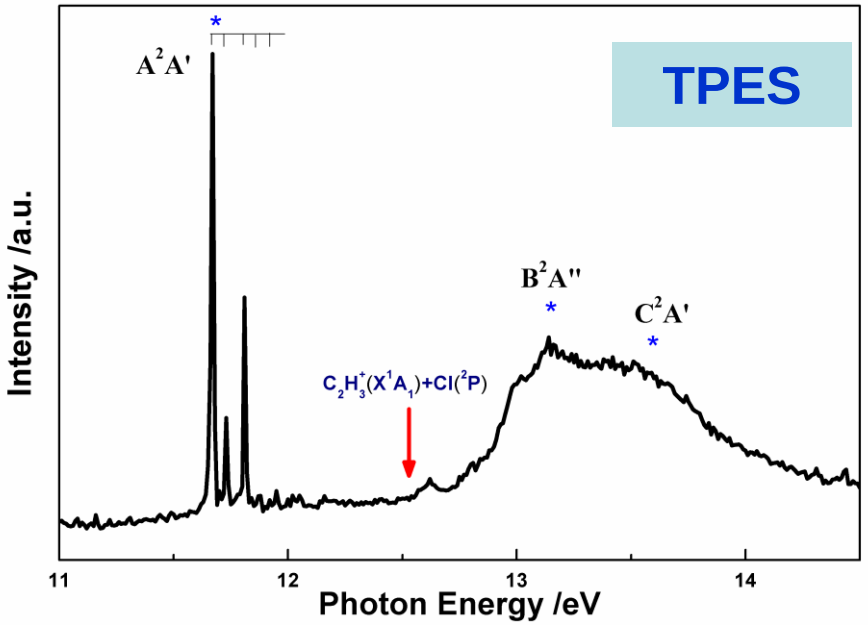
Cl-loss of $C_2H_3Cl^+$



$C_2H_3Cl^+ \rightarrow C_2H_3^+(X^1A_1) + Cl$ $\quad D_e = 12.53$ eV



$C_s \leftrightarrow C_1$



A^2A' state:

a series of vibrational bands

B^2A'' state:

from 12.5 eV;

center at 13.14eV;

no vibrational structure, except for the lowest vibronic band

C^2A' state:

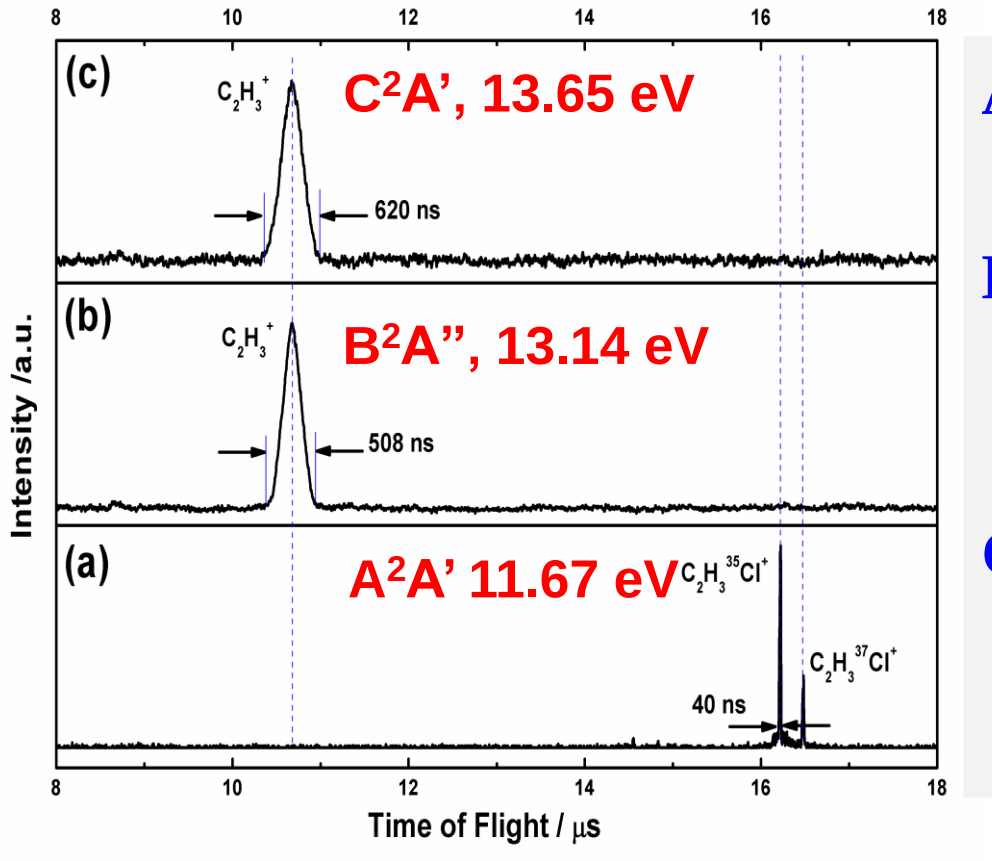
center at ~ 13.65 eV;

no vibrational structure;

serious overlapping

TPEPICO TOF-MS

TPEPICO TOF Mass Spectra



A^2A' state: bound

only $C_2H_3{}^{35}Cl^+$ & $C_2H_3{}^{37}Cl^+$

B^2A'' state: dissociative

no $C_2H_3{}^{35}Cl^+$;

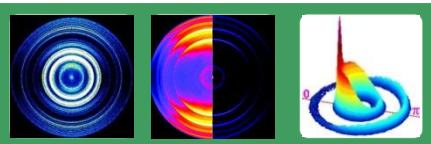
$C_2H_3^+$ with 240 ns FWHM

C^2A' state: dissociative

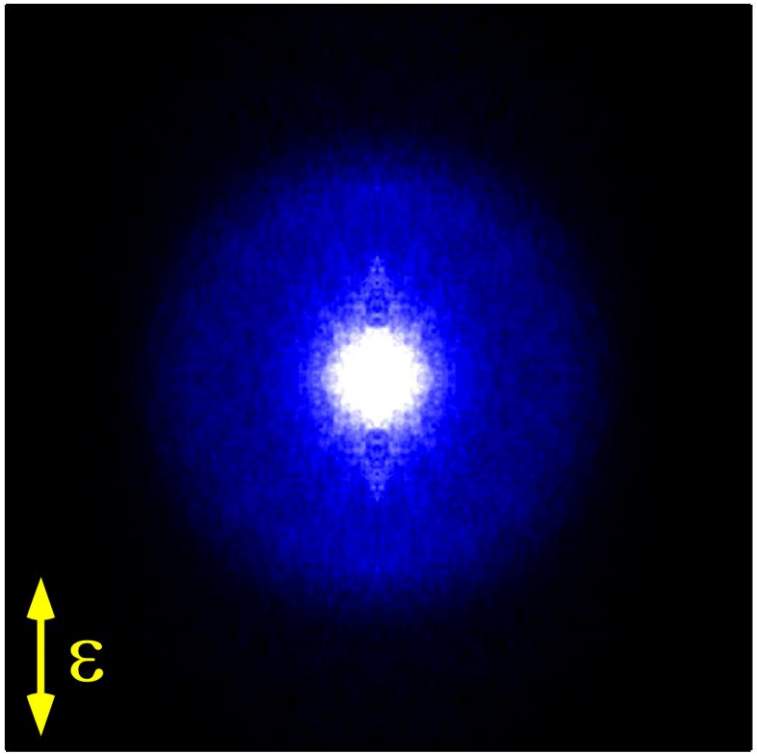
no $C_2H_3{}^{35}Cl^+$;

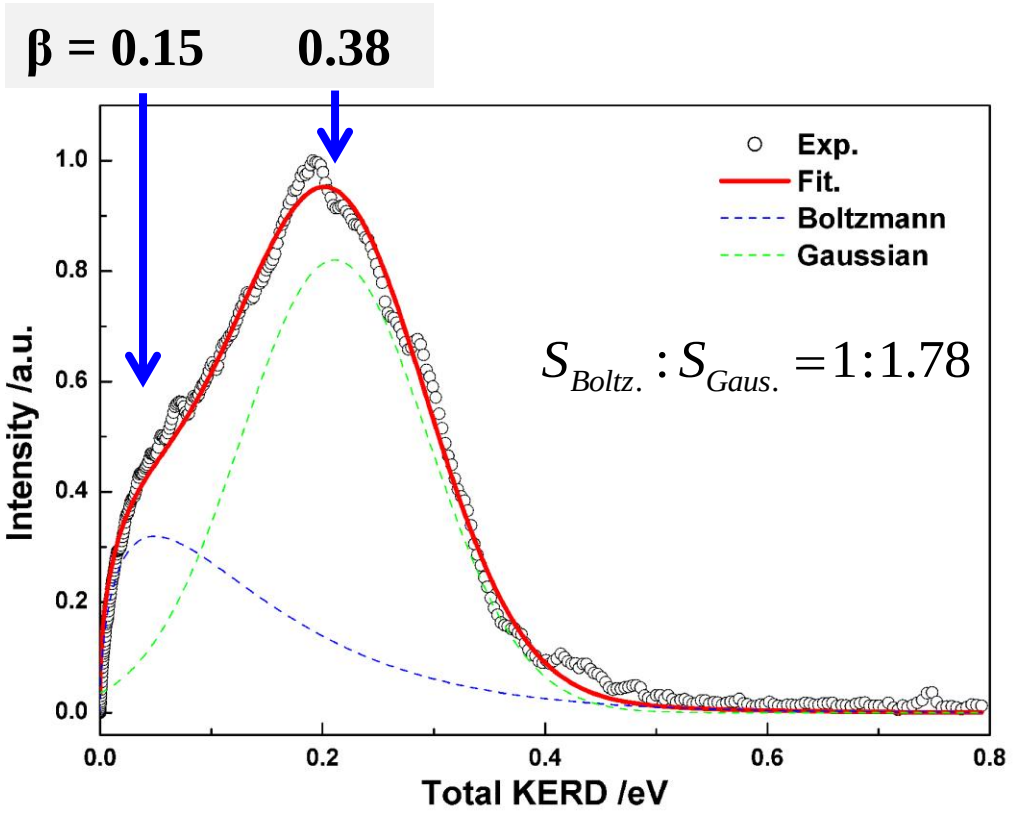
$C_2H_3^+$ with 280 ns FWHM

TPEPICO imaging



B^2A'', 13.14 eV

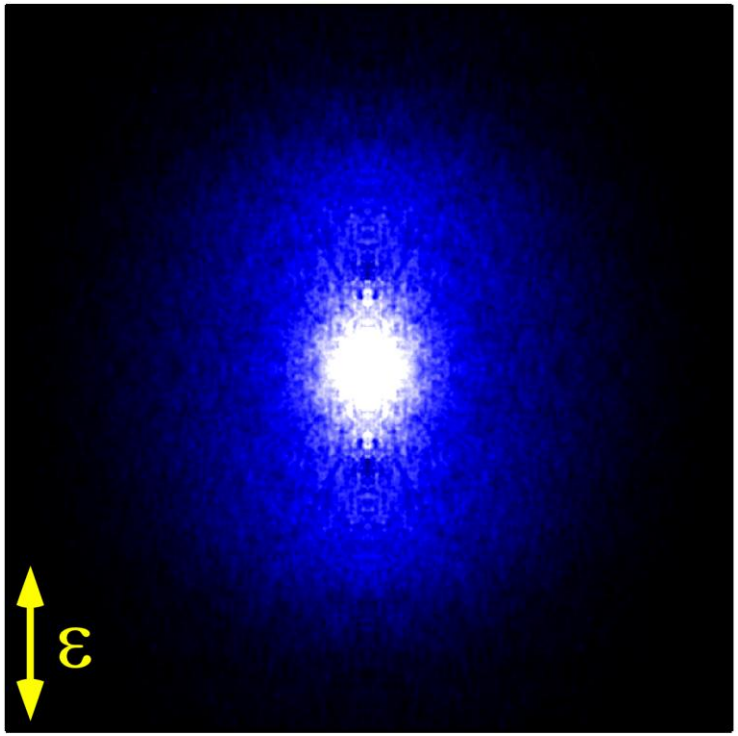


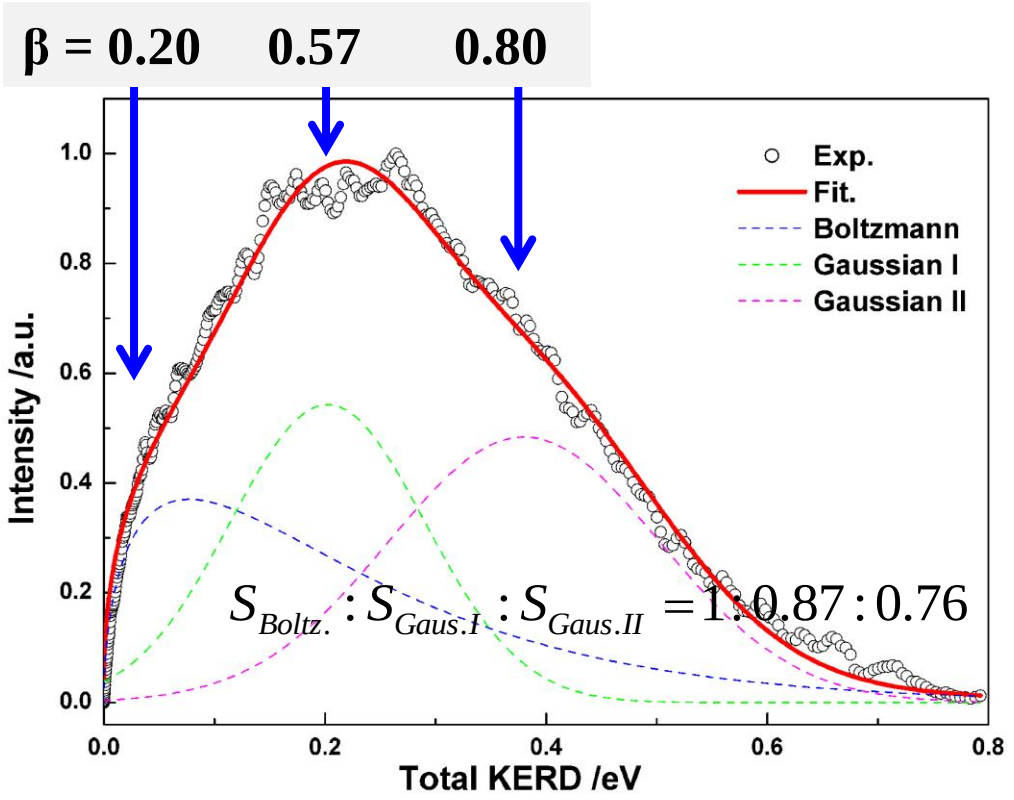


- Bimodal distribution of $C_2H_3^+$
- Boltzmann (statistic) + Gaussian (direct dissociation)

TPEPICO imaging

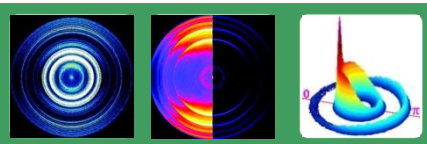
C^2A', 13.65 eV





- Triplet internal energy distribution of $C_2H_3^+$
- Boltzmann (statistic) + 2 Gaussian (2 fast dissociation)
- A new $C_2H_3^+$ formation pathway besides those similar to B^2A''

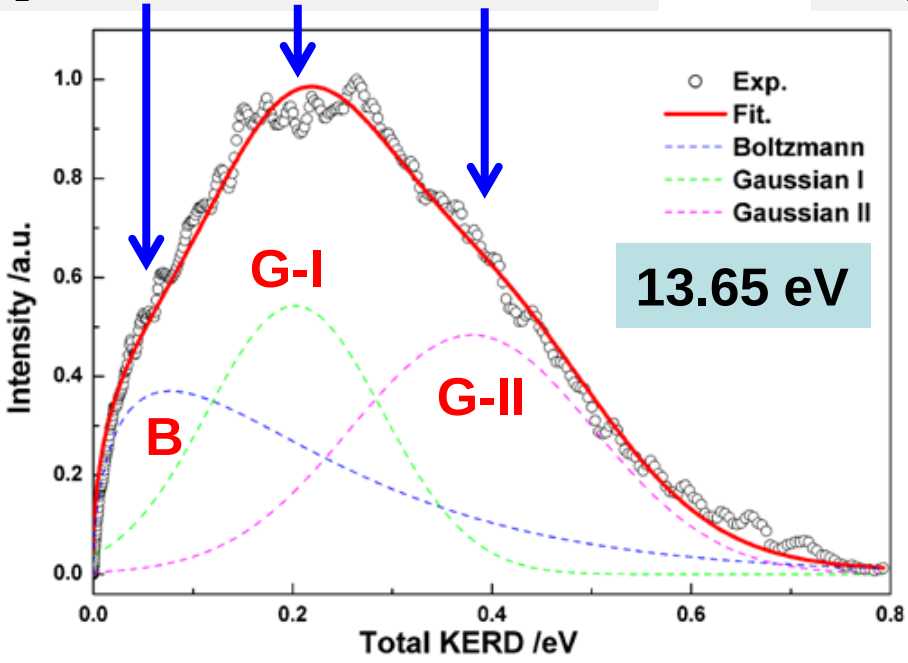
TKERD curves



$$f_T = \frac{< E_T >}{E_{avail}}$$

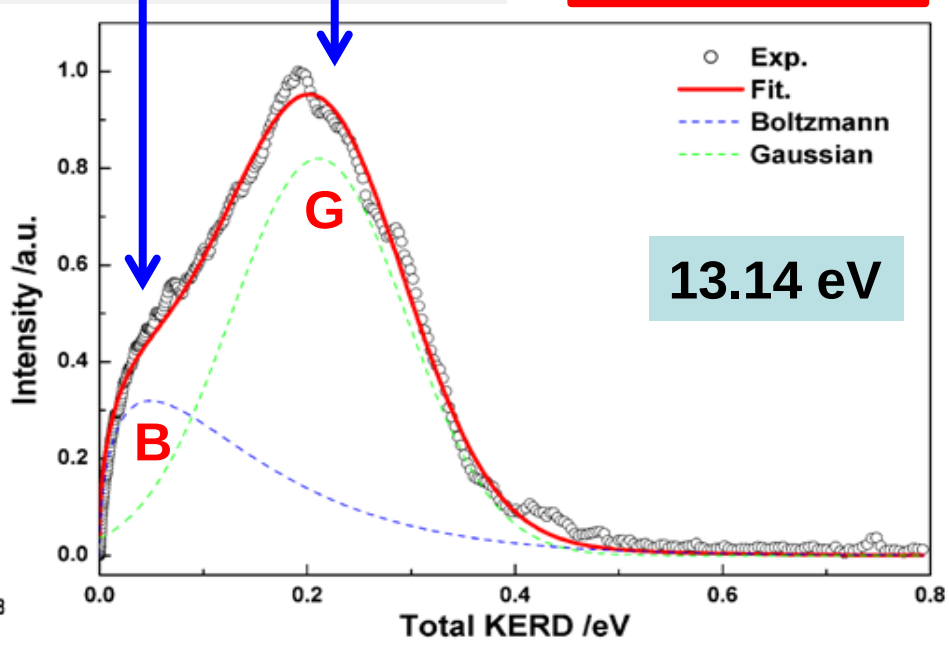
$<E_T>$ = 0.15 0.20 0.38 eV

f_T = 0.13 0.18 0.34



$<E_T>$ = 0.10 0.21 eV

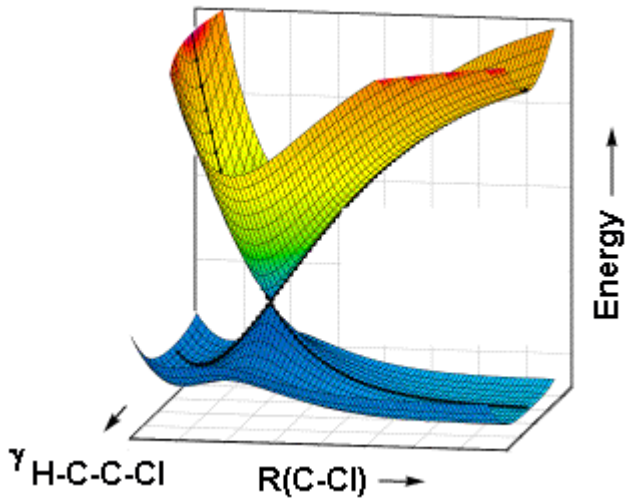
f_T = 0.16 0.34



At 13.65 eV, Gauss-II distribution has the same pathway as at 13.14 eV

What is the Gauss-I population?

Potential Energy Surface

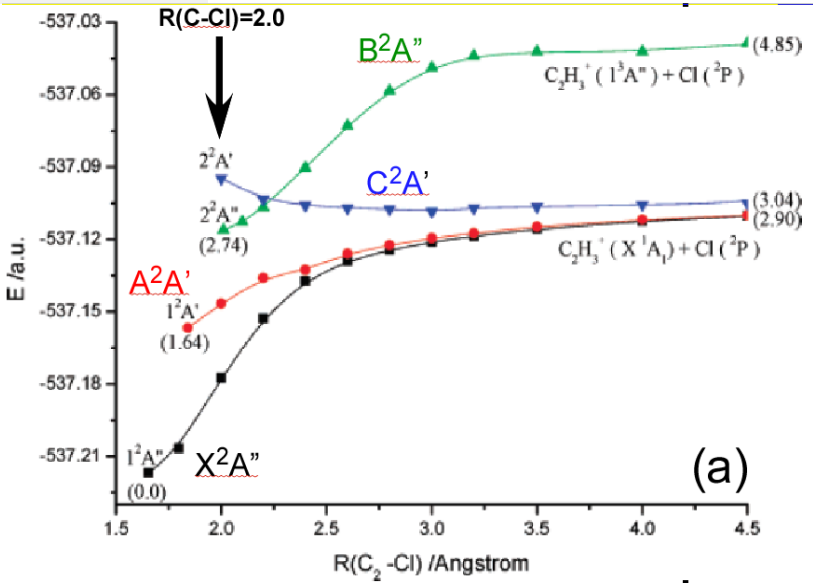


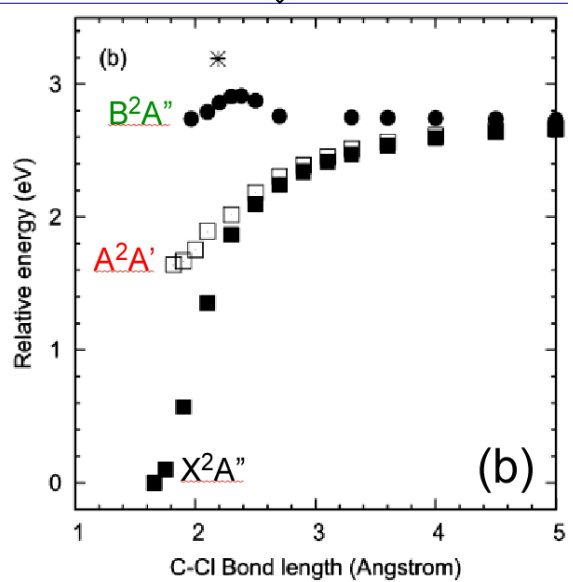
Conical Intersection
between B & C states

- **C_s symmetry:**
  B^2A'' bound & C^2A' repulsive
- **No symmetry C_1:**
  B^2A'' predissociative
  C^2A' unknown

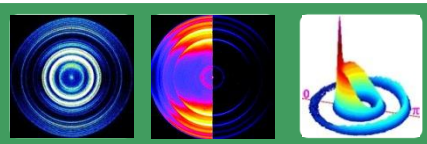
In plane: *J. Phys. Chem. A* 2008, *112,* 1688

Out of plane: J. Phys. Chem. A 2010, *114,* 7937

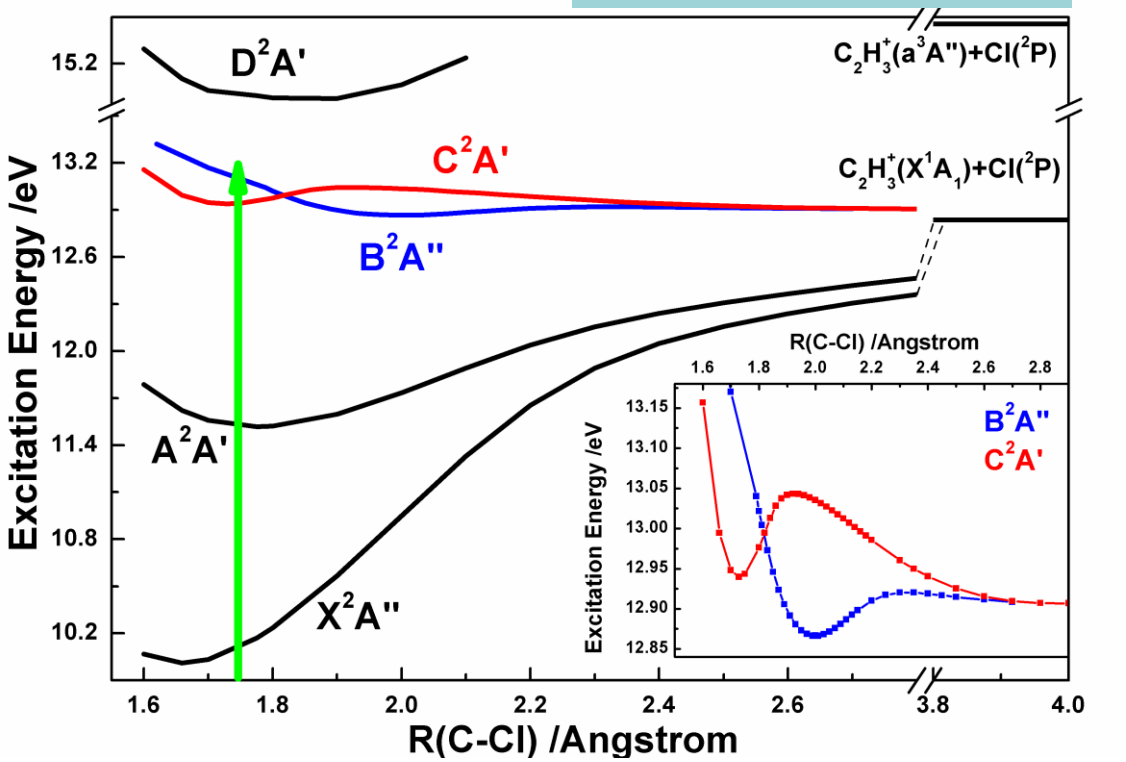




Potential Energy Surface



at TD-B3LYP/6-311+G(d,p)



- **No symmetry C_1:**

  B^2A'' & C^2A' predissociative

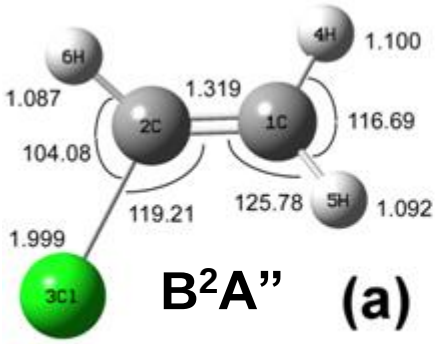
- **Geometries:**

  B^2A'' bent

  C^2A' planar

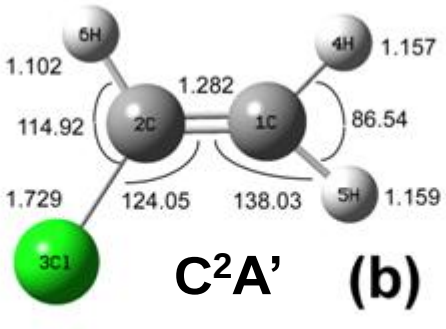
- **CI between B & C:**

  0.13 eV above B^2A''



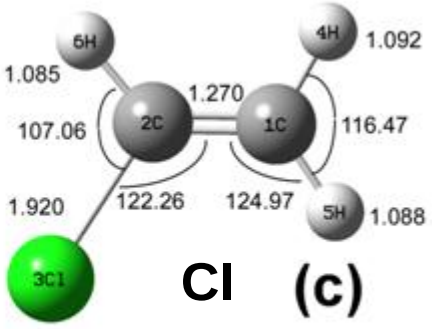
B^2A'' (a)

D(^{3}Cl-^{2}C-^{1}C-^{4}H)=161.2



C^2A' (b)

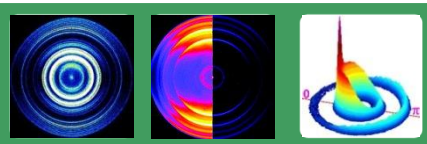
D(^{3}Cl-^{2}C-^{1}C-^{4}H)=180.0



CI (c)

D(^{3}Cl-^{2}C-^{1}C-^{4}H)=180.0

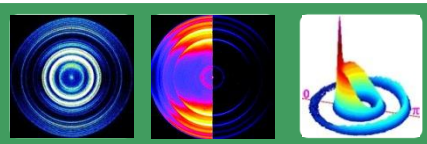
Potential Energy Surface



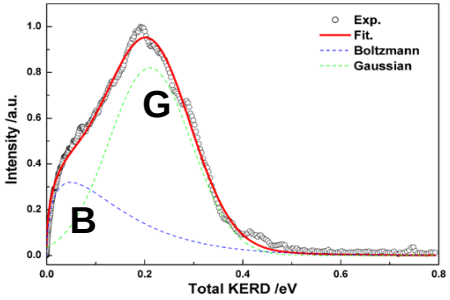
State	R(C-C) /Å	R(C-Cl) /Å	A(^{1}C-^{2}C-^{6}H) [a]	T_v /eV [b]		T_0 /eV [b]	
				Cal.	Exp.	Cal.	Exp.
$X^2A''(C_s)$	1.395	1.659	122.54	10.10	10.005[d]	9.81	10.0062[e]
	1.405[c]	1.657[c]	122.5[c]	9.631[c]			
	1.392[e]	1.657[e]	122.4[e]				
	1.391[f]	1.640[f]	122.6[f]				
$A^2A'(C_s)$	1.326	1.775	128.41	11.75	11.664[d]	11.74	11.6667[e]
	1.327[f]	1.752[f]	131.2[f]	11.141[c]			
$B^2A''(C_1)$	1.319	1.999	135.74	13.07	13.13[d]	12.84	12.7518[e]
	1.368[c]	1.964[c]	131.6[c]	12.596[c]			
	1.316[e]	1.991[e]	135.6[e]				
	1.354[f]	1.937[f]	131.4[f]				
$C^2A'(C_s)$	1.282	1.729	121.03	13.57	13.56[d]	13.17	--
				13.422[c]			
$X^1A'(C_s)$	1.324	1.752	124.40	--	--	--	--
	1.332[g]	1.726[g]	123.8[g]				

a. C=C-H bond angle (degrees) in vinyl cation moiety.
b. ionization energies were calculated with the optimized geometry of ground neutral molecule.
c. SA-CASSCF optimized geometries and MRCISD energies from Ref. 21.
d. from He(I) photoelectron spectra of Ref. 9.
e. from MATI-PFY spectra of Ref. 12.
f. CASPT2 geometries from Ref. 20.
g. experimental data from Ref. 42.

Dissociative Photoionization Mechanism

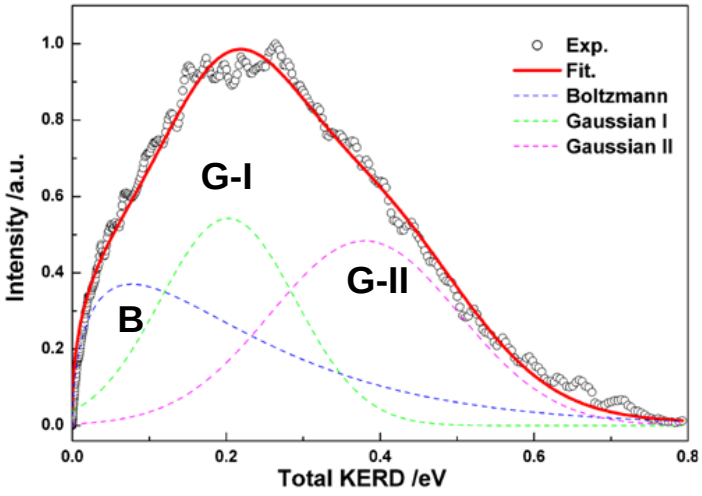


- **at 13.14 eV: B^2A'' no contribution from C^2A'**
  - **Boltzmann:** IC to lower state + statistical, slow
  - **Gauss**: direct dissociate along B^2A'', fast

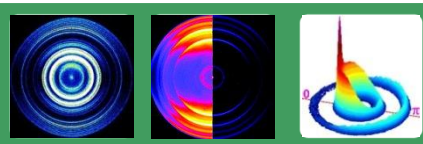


- **at 13.65 eV: B^2A'' with high v^+ & C^2A' due to overlap**
  - **Boltz. & Gauss-II**: similar to 13.14eV
  - **Gauss-I**: coupling from C^2A' to B^2A'' by conical intersection, slow

IVR in the following IC process to cause some excess energy redistributed to ro-vibrational excited $C_2H_3^+$



Conclusions



- **at 13.14 eV: B^2A''**

$$C_2H_3Cl + h\nu(13.14eV) \xrightarrow{\text{ionization}}$$

$$C_2H_3Cl^+(B^2A'') \begin{cases} \xrightarrow{IC} C_2H_3Cl^+(X^2A'' \text{ or } A^2A', v^+) \xrightarrow{statis.} C_2H_3{}^+(X^1A_1) + Cl(^2P) \\ \xrightarrow{direct} C_2H_3{}^+(X^1A_1) + Cl(^2P) \end{cases}$$

- **at 13.65 eV: B^2A'' with high v^+ & C^2A'**

$$C_2H_3Cl + h\nu(13.65eV) \xrightarrow{\text{ionization}}$$

$$C_2H_3Cl^+(C^2A' \text{ or } B^2A'', v^+) \begin{cases} \xrightarrow{IC} C_2H_3Cl^+(X^2A'' \text{or } A^2A', v^+) \xrightarrow{statis.} C_2H_3{}^+(X^1A_1) + Cl(^2P) \\ \xrightarrow{direct\ along\ B^2A''} C_2H_3{}^+(X^1A_1) + Cl(^2P) \\ \xrightarrow{CI\ from C^2A'\ to B^2A''} C_2H_3{}^+(X^1A_1) + Cl(^2P) \end{cases}$$

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  - ***Prof.*** **Shilin Liu, *Dr.* Xiaofeng Tang**
  - ***Mr.*** **Mingli Niu, *Ms.* Manman Wu**
- **Collaborators**
  - ***Prof.*** **Liusi Sheng, *Dr.* Fuyi Liu, *Mr.* Xiaobin Shan**

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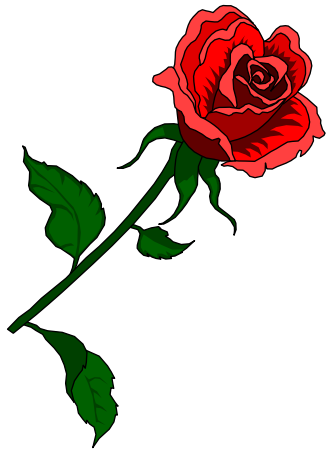
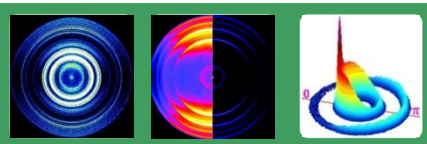
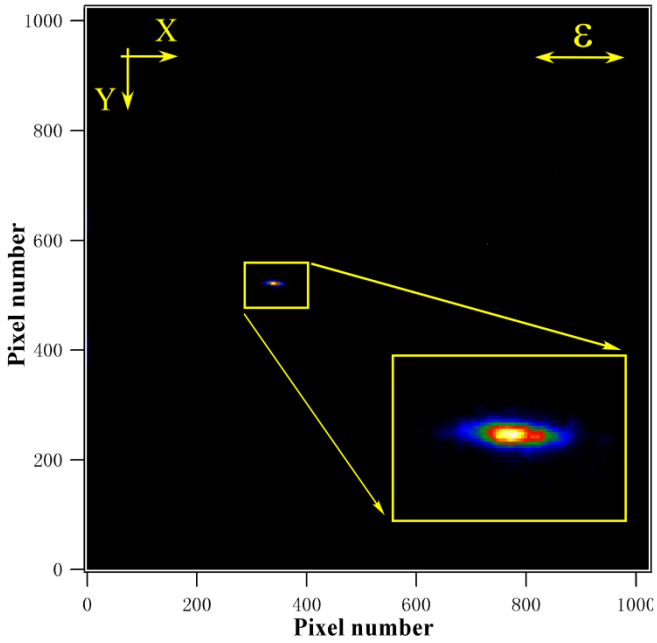
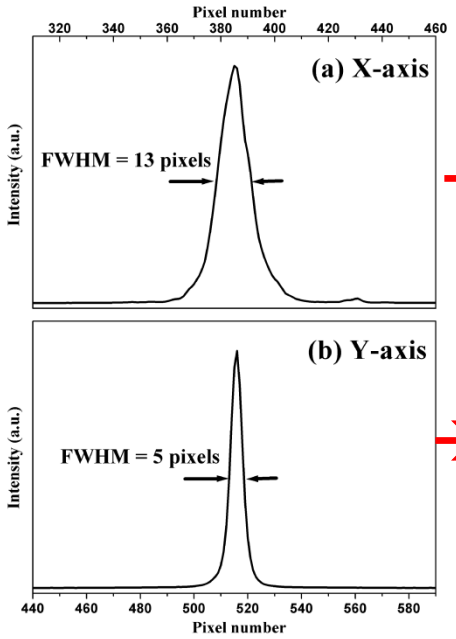


Deconvolution of image



Ar^+

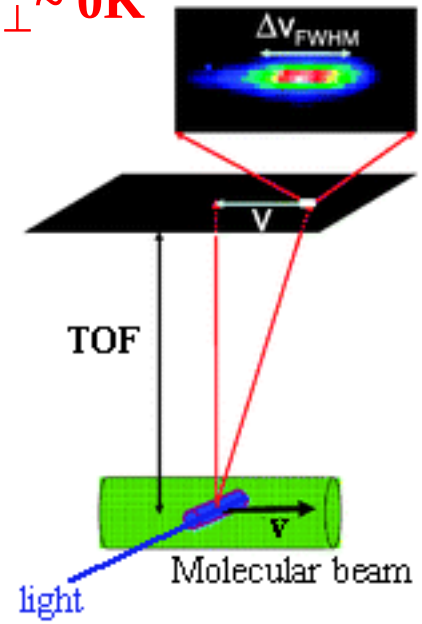




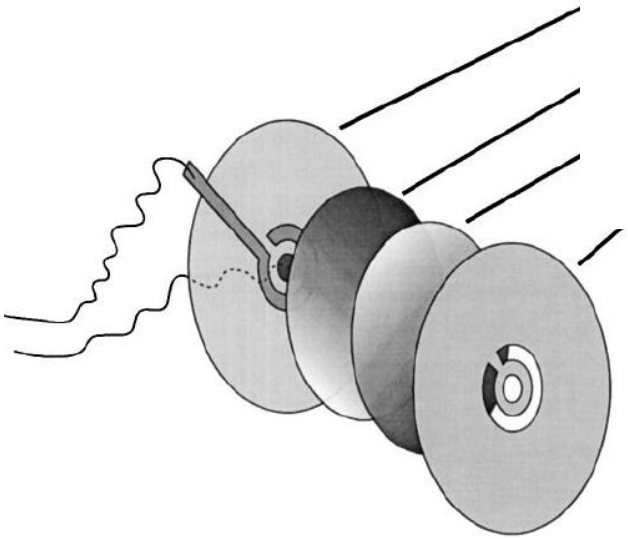
→ $T_{//} \sim 7K$

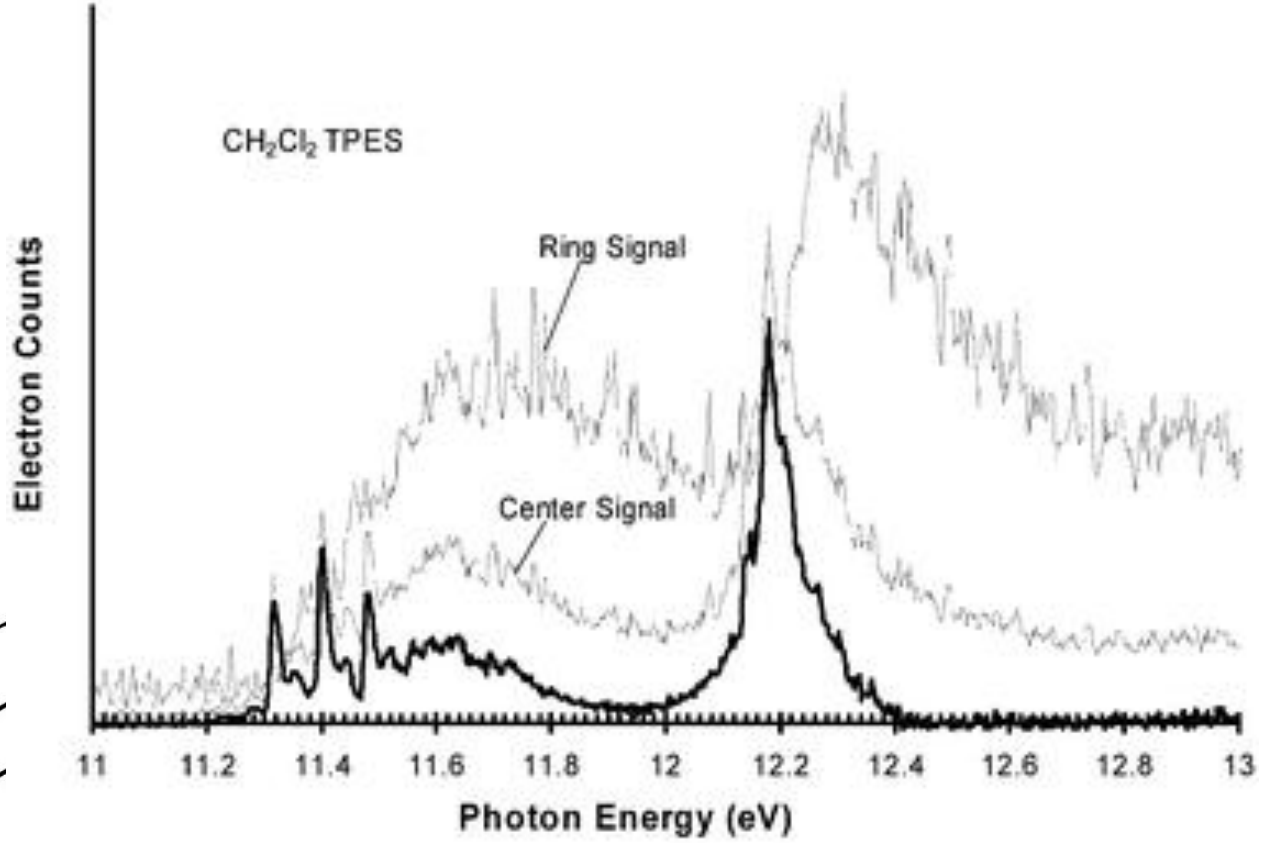
→ $T_{\perp} \sim 0K$

Molecular beam direction



Subtraction mode





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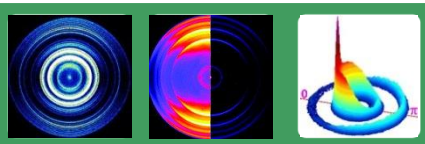
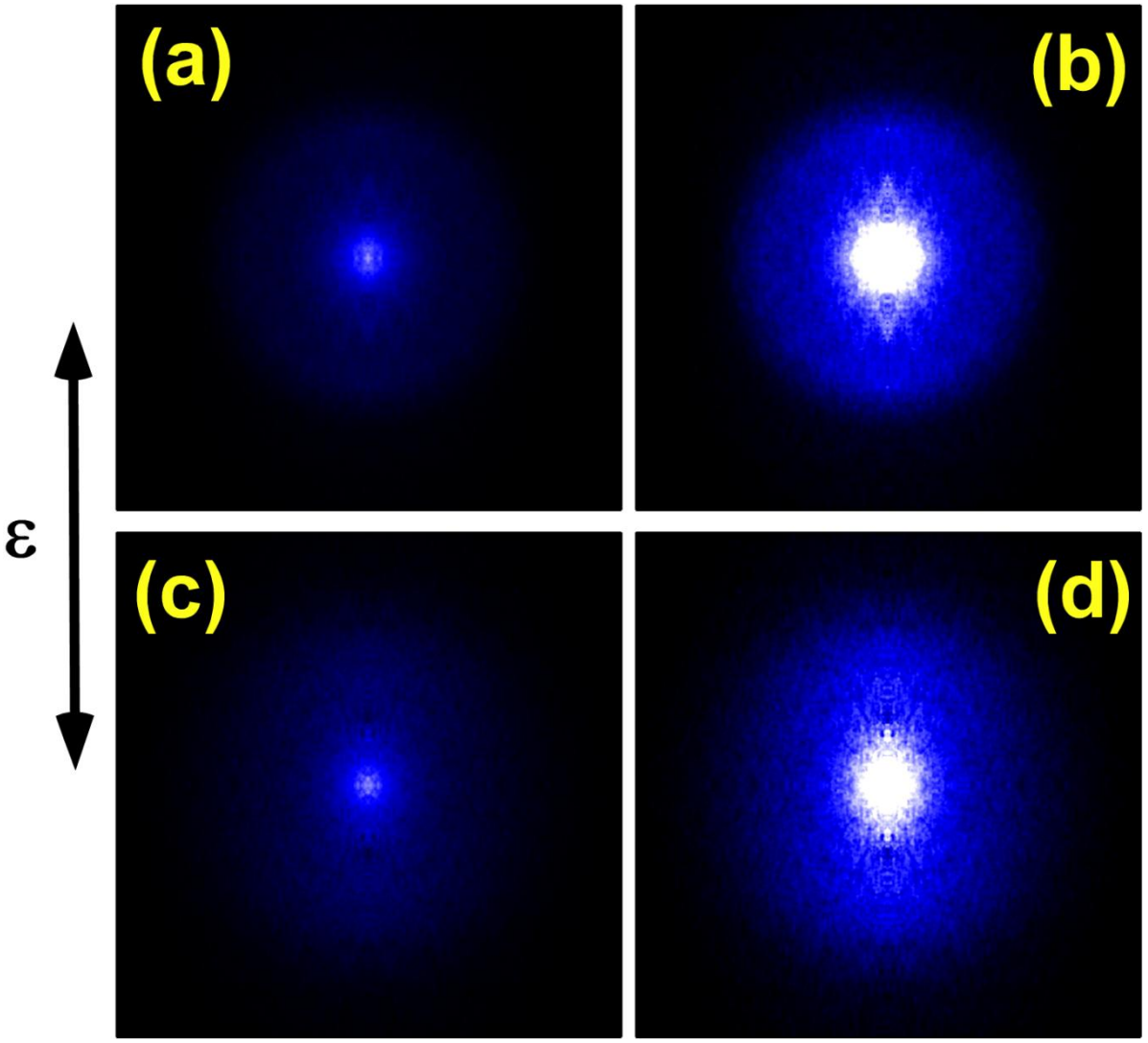
$CF_4^+ \rightarrow CF_3^+ + F$ （AP_0）

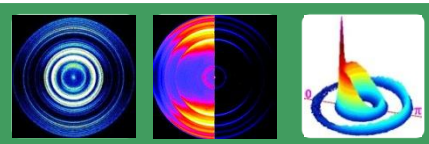




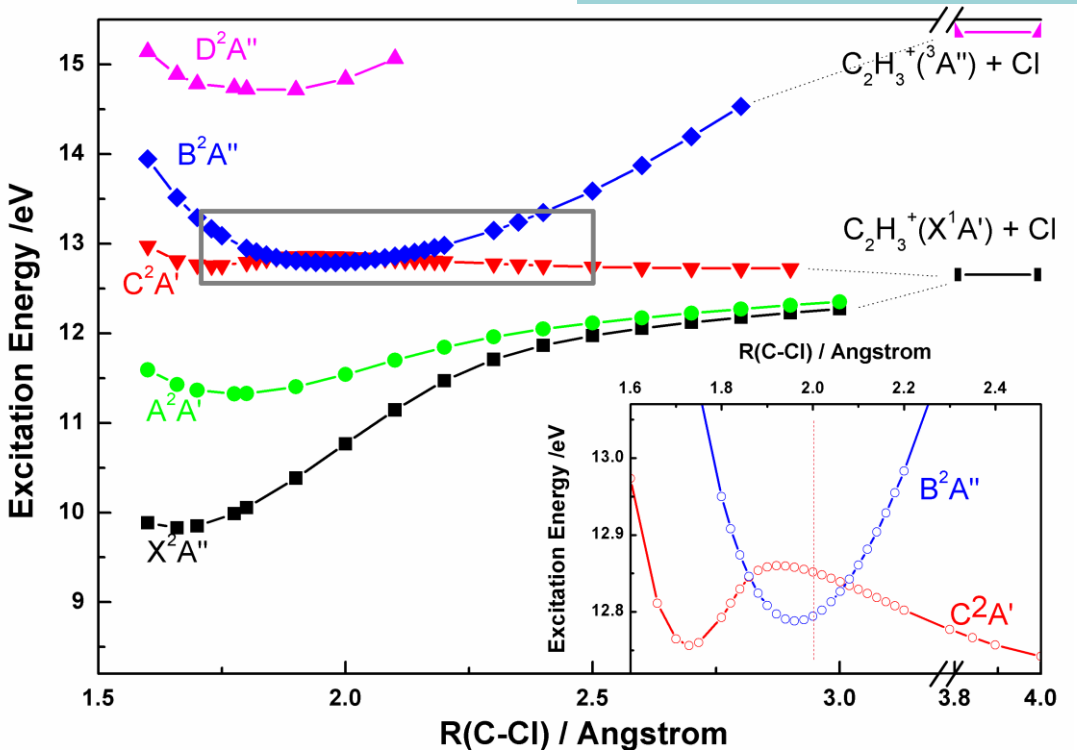
B^2A'', 13.14 eV

C^2A', 13.65 eV

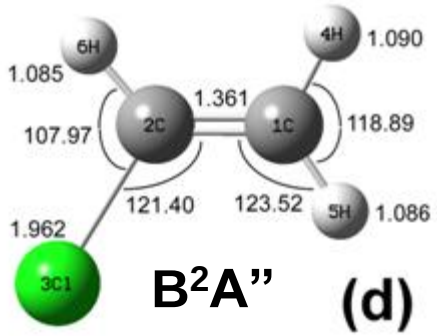
Potential Energy Surface



at TD-B3LYP/6-311+G(d,p)

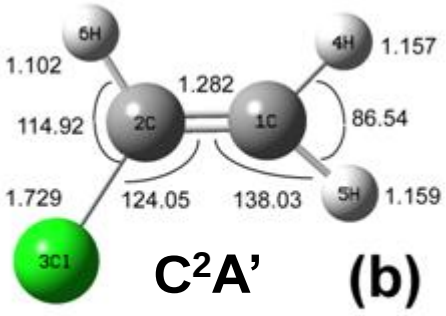


- **C_s symmetry:**
  - **B^2A'' bound**
  - **C^2A' predissociative**
- **Geometries:**
  - **B^2A'' & C^2A' planar**



B^2A'' (d)

$D(^3Cl\text{-}^2C\text{-}^1C\text{-}^4H)=180.0$



C^2A' (b)

$D(^3Cl\text{-}^2C\text{-}^1C\text{-}^4H)=180.0$