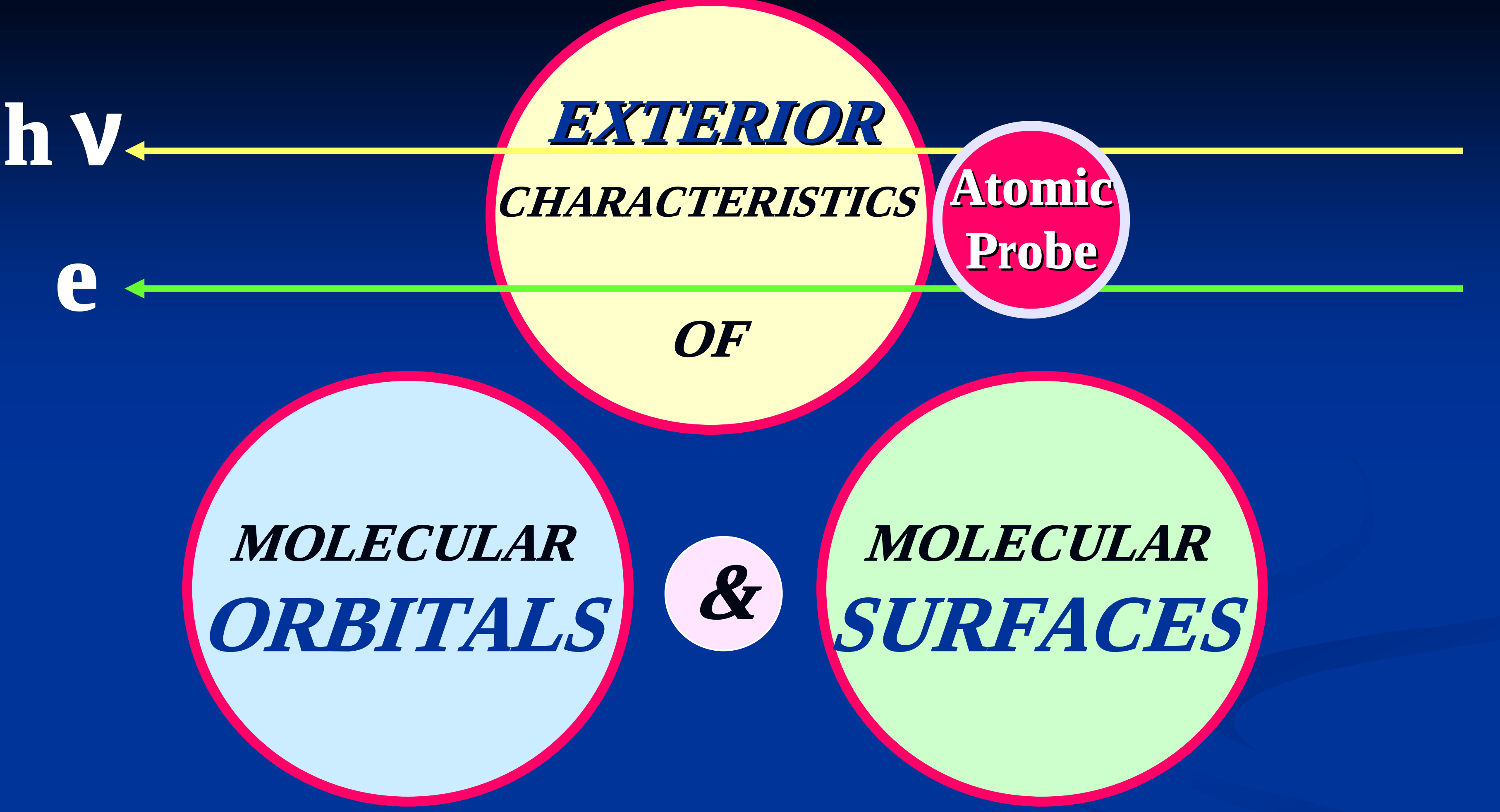
EXTERIOR CHARACTERISTICS OF MOLECULAR ORBITALS AND MOLECULAR SURFACES AS STUDIED BY ATOMIC PROBES

Koichi Ohno

Graduate School of Science
Tohoku University
JAPAN



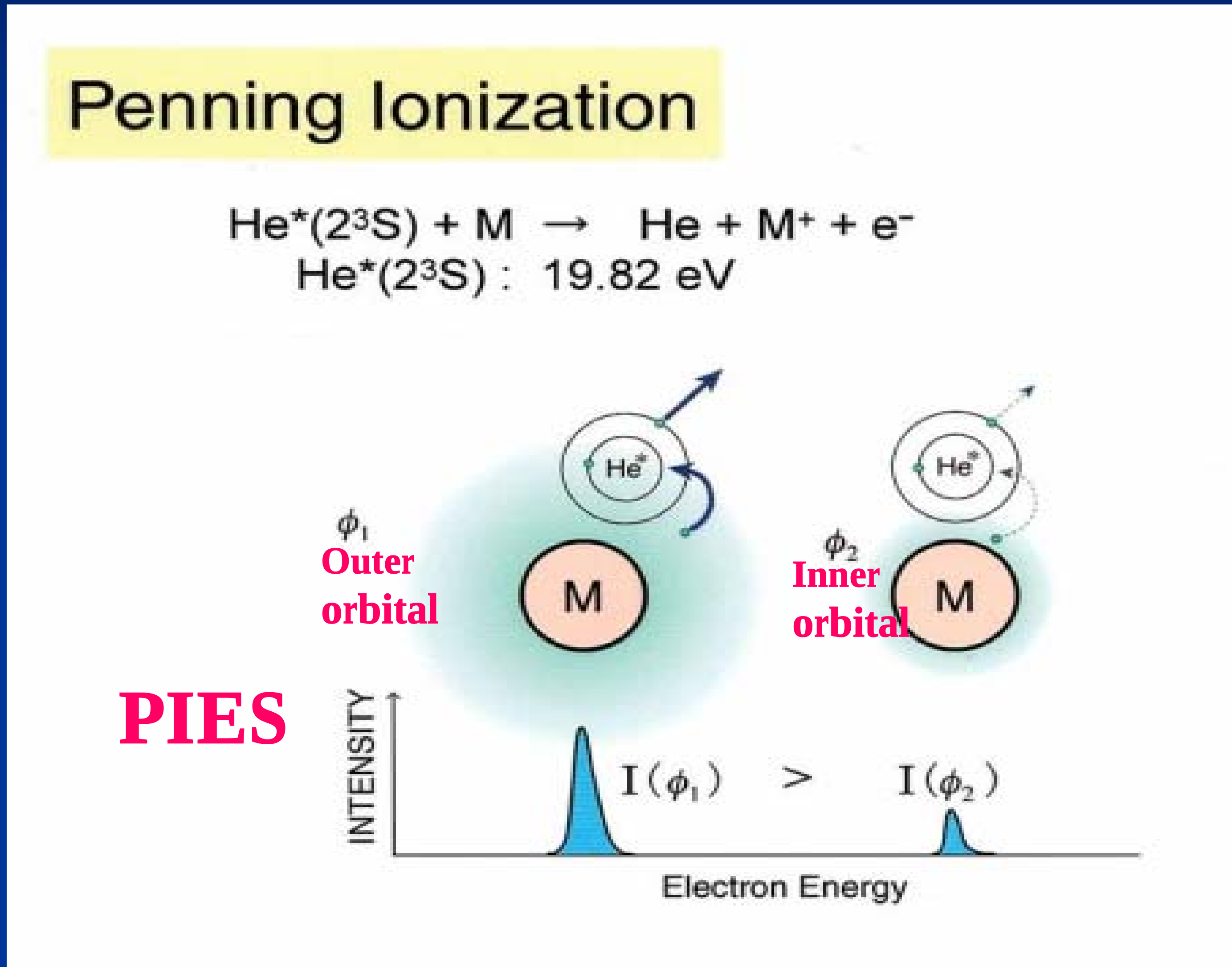
are important, because molecules and atoms interact with each other at *exterior* parts, not via interior parts.

Photons and electrons go through molecules, but atoms do not. Thus, atomic probes are most suitable.

An Excited Atom He* can be used to Probe Outer Properties of Molecules

K. Ohno,
H. Mutoh, &
Y. Harada

J.Am.Chem.Soc.
105, 4555, (1983)



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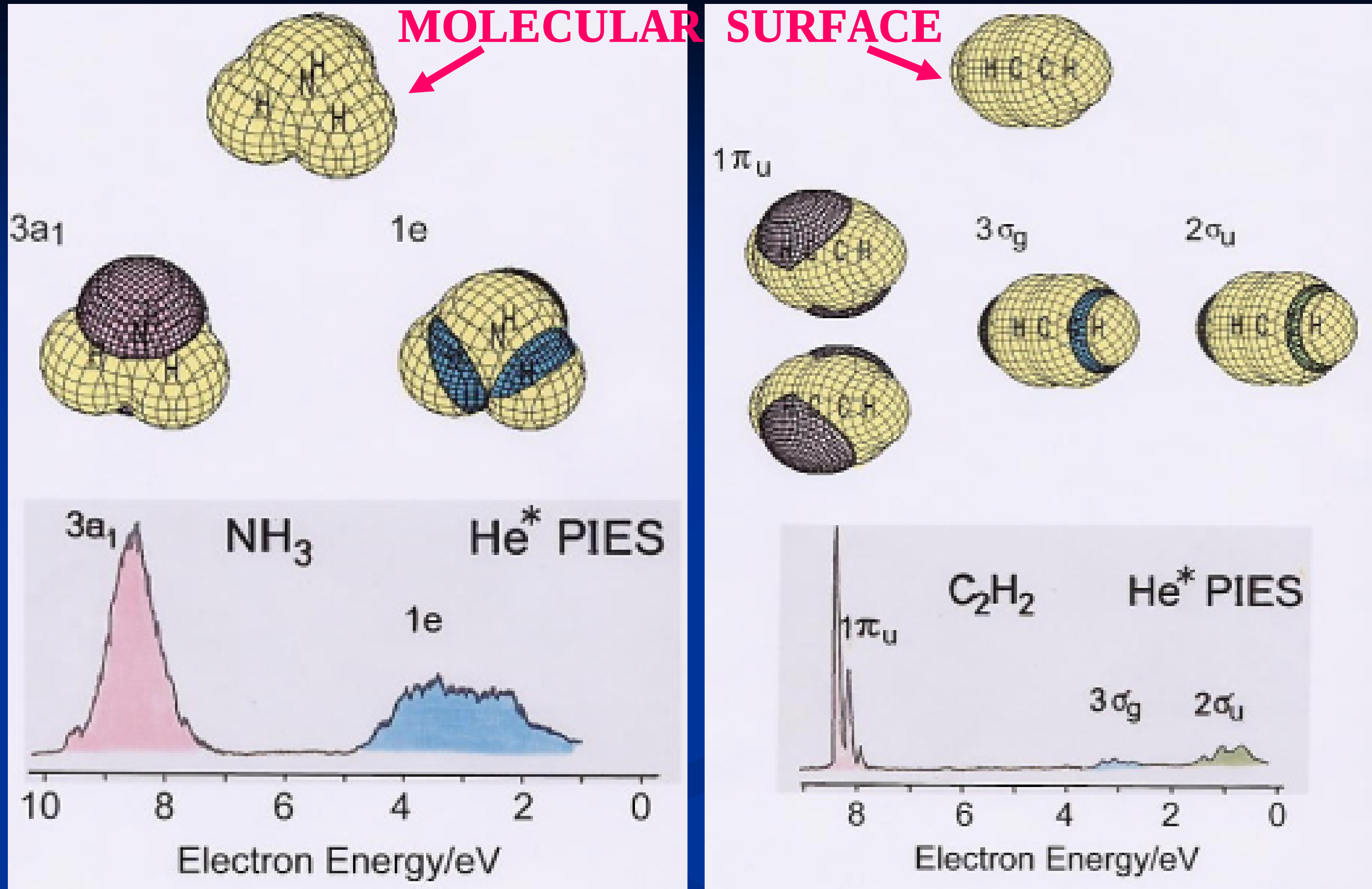
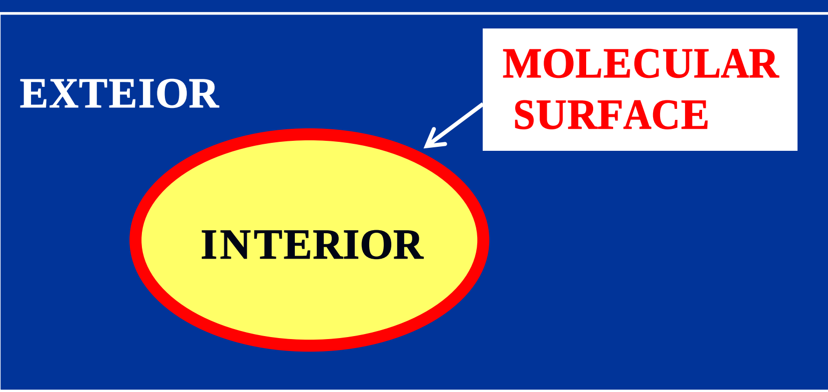
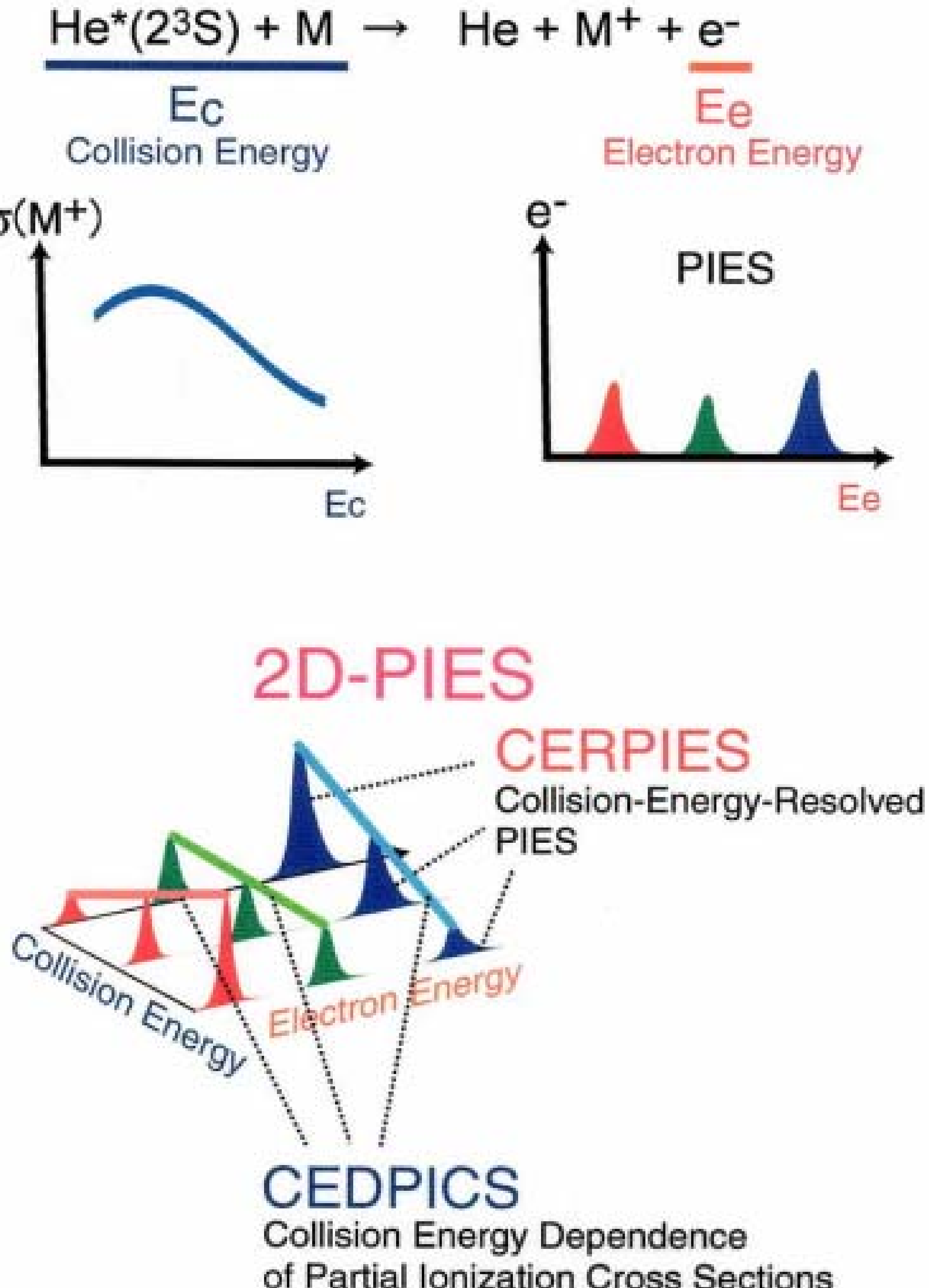




Molecular Surface is important, because it divides chemically activ exterior parts from inactive interio parts.

Development of 2D-PIES

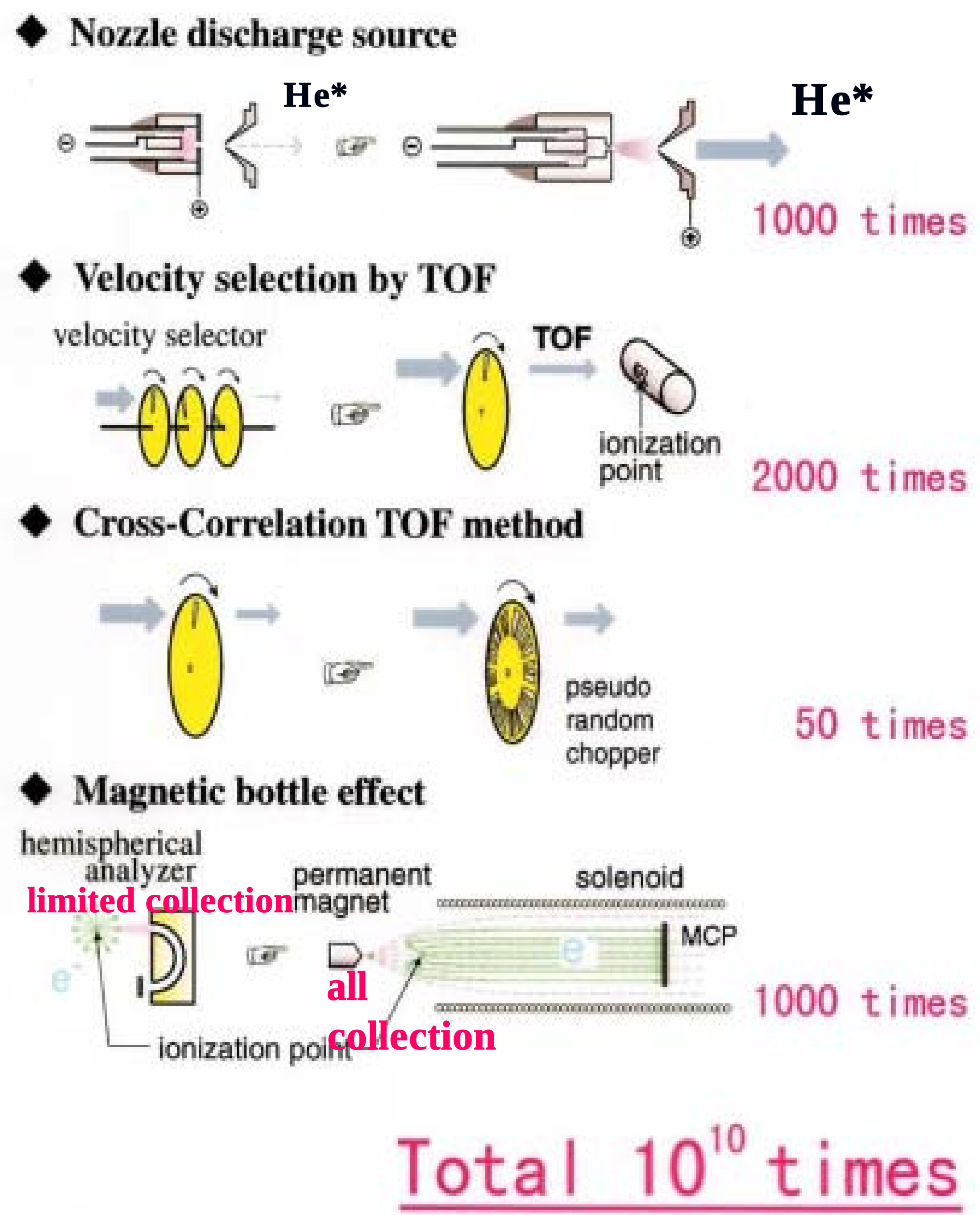


Simultaneous Analyses of Reactants & Products result in 5 orders of Signal Reduction !

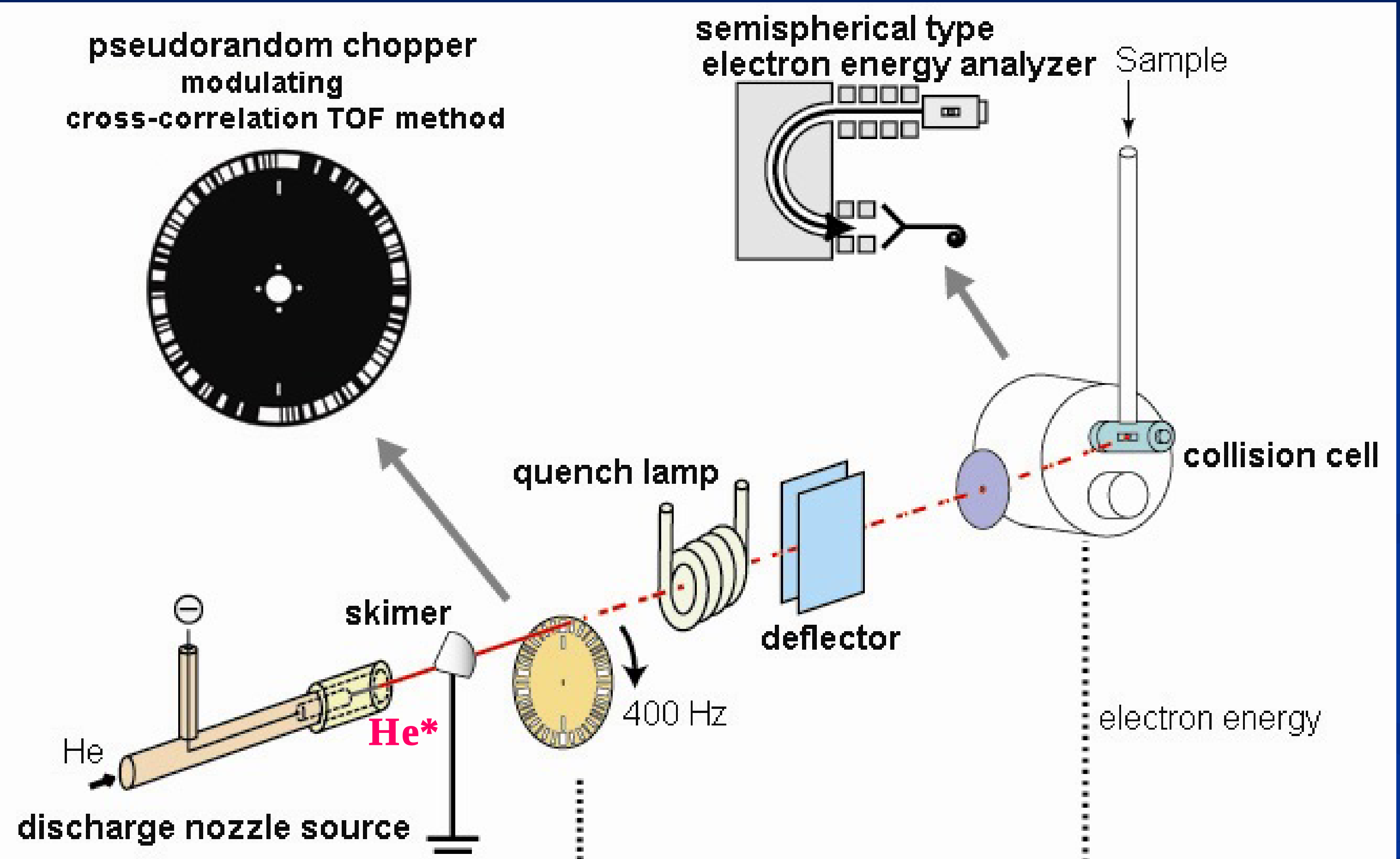
1D-PIES **2D-PIES**

3 hrs → 34 years !

Improvements of Experimental Techniques made it possible to do 2D-PIES experiments without waiting 34 years !

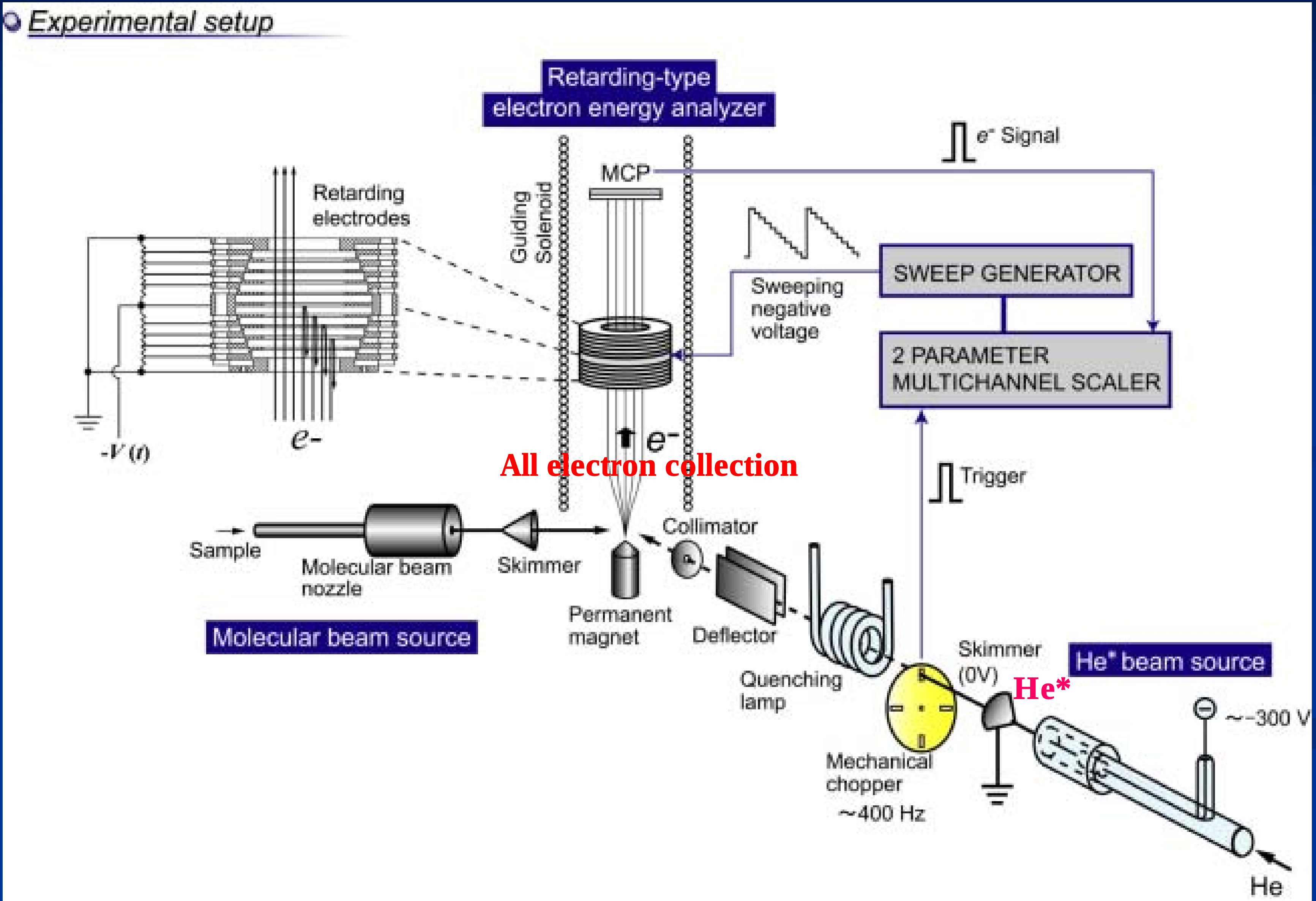


2D-PIES Apparatus



ca. 10^{15} atoms $s^{-1}sr^{-1}$

Crossed Molecular Beam 2D-PIES



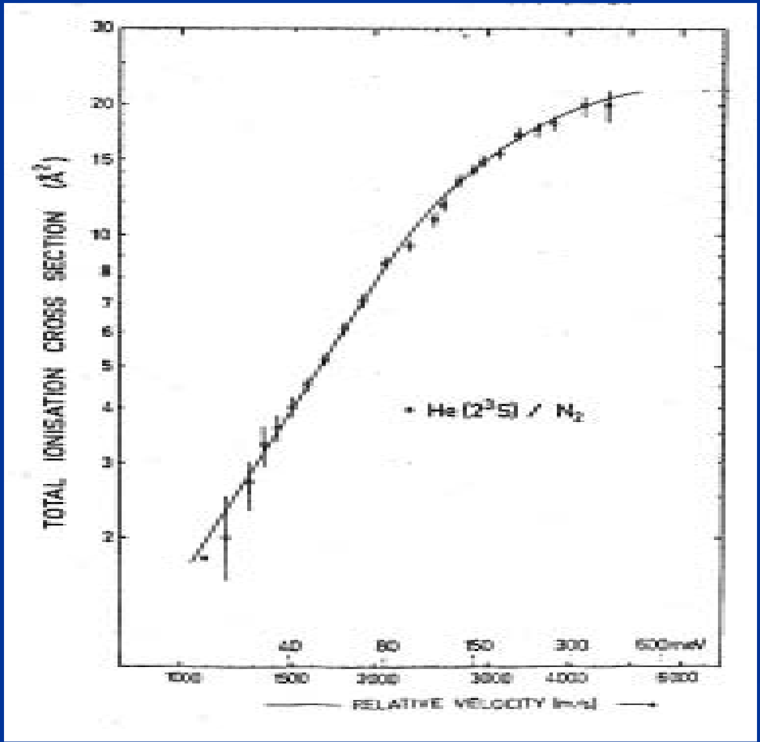
2D-PIES made it possible to observe

Collision Energy Dependence of Partial Ionization Cross Sections (CEDPICS)

Ionic States-Unresolved

Total Ionization Cross Section :

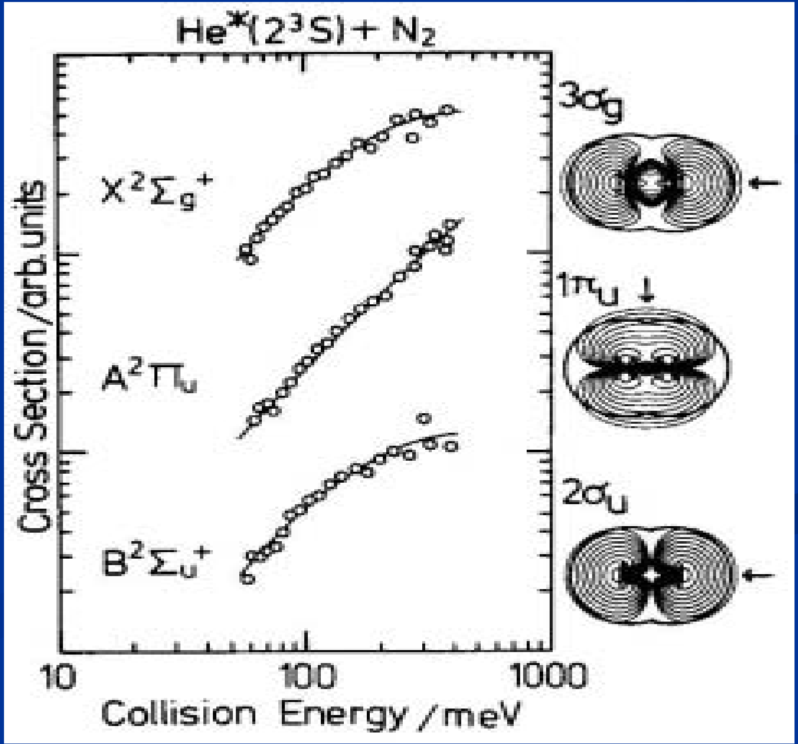
Illenberger & Niehaus (1975)



Ionic States-Resolved

Partial Ionization Cross Sections :

Ohno et al. J.Chem.Phys.94,2675 (1991)



2D-PIES made it possible to observe

Collision Energy Resolved Penning Ionization Electron Spectra (CERPIES)

Collision-Energy Unresolved PIES :
Ohno et al. (1983)

4560 J. Am. Chem. Soc., Vol. 105, No. 14, 1983

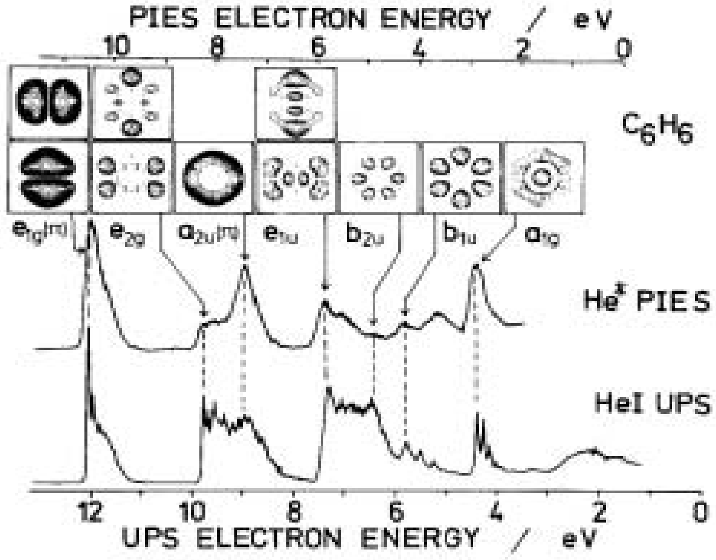


Figure 10. Transmission-corrected He*(2^3S) PIES (upper) and He I UPS (lower) for C_6H_6, and electron density maps for MO. The maps are drawn for a plane 1.7 Å above the molecular plane.

Collision-Energy Resolved PIES :
Takami & Ohno (1992)

J.Chem.Phys.96,6523(1992)

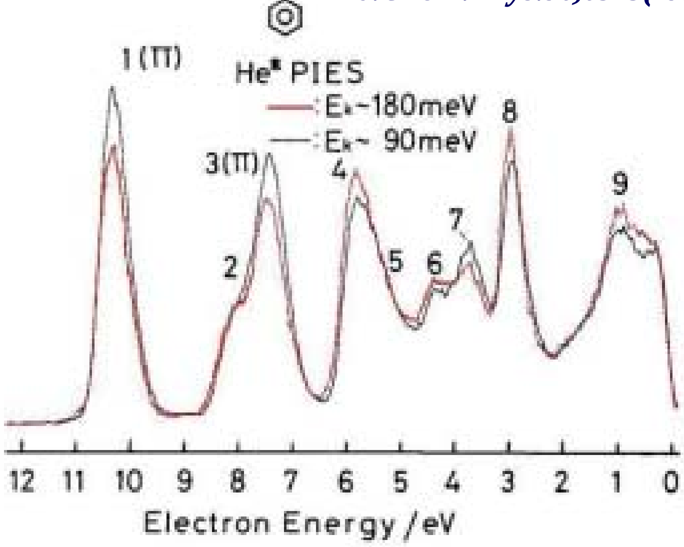
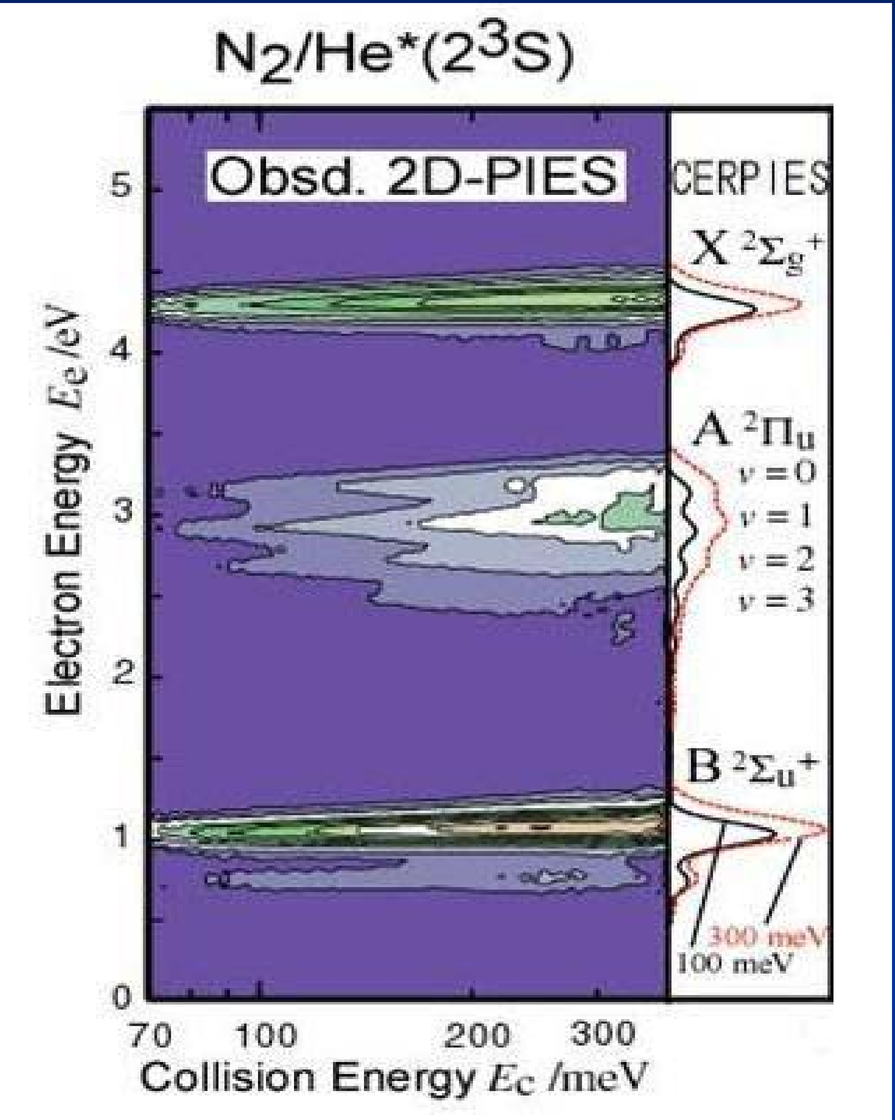


FIG. 5. Collision-energy-resolved He*($2\ ^3S$) Penning ionization electron spectra of benzene (— 50—110 meV, average 90 meV; — 170–300 meV, average 180 meV).

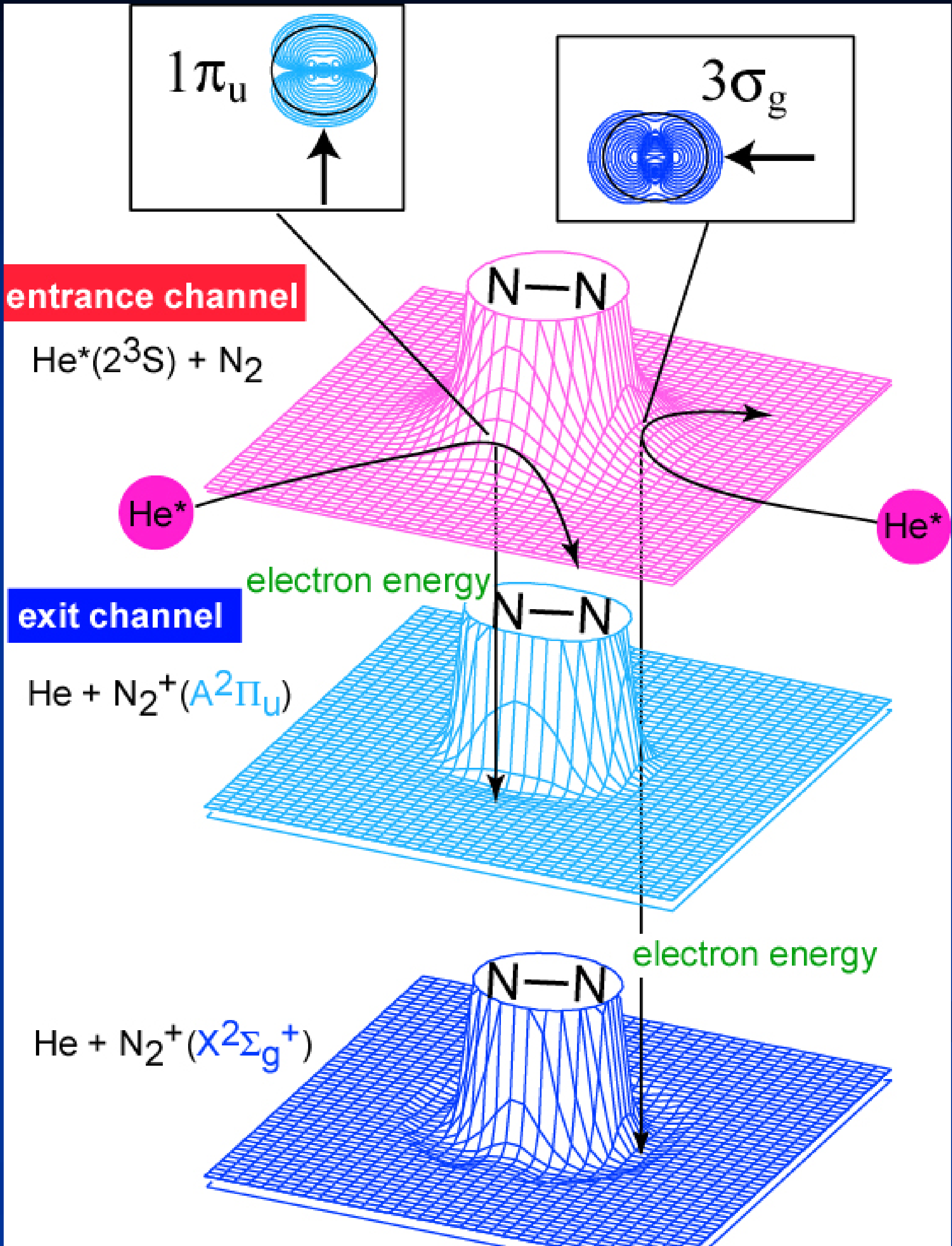
2D-PIES of N_2/ He*(2^3S)



In order to elucidate collisional ionization dynamics,
we have developed
a new method for ***theoretical construction of 2D-PIES*** **by trajectory calculations.**

Theoretical Construction of 2D-PIES

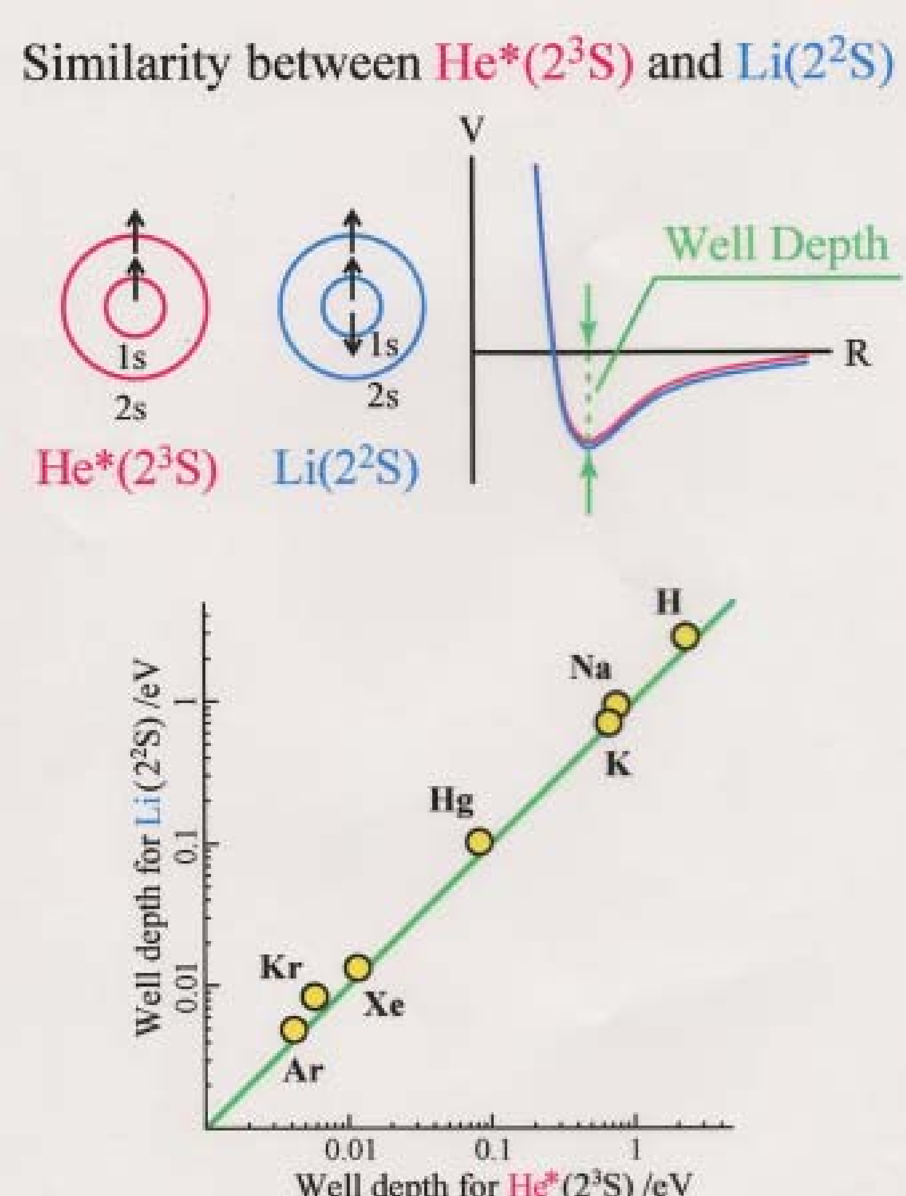
requires Entrance and Exit Potentials together with Transition Rates



Entrance Potential for Reactants

can be obtained as ab initio model potentials using a Li atom in place of an excited He* atom, based on the well known similarity between He* and Li.

Both of them show very similar well depths



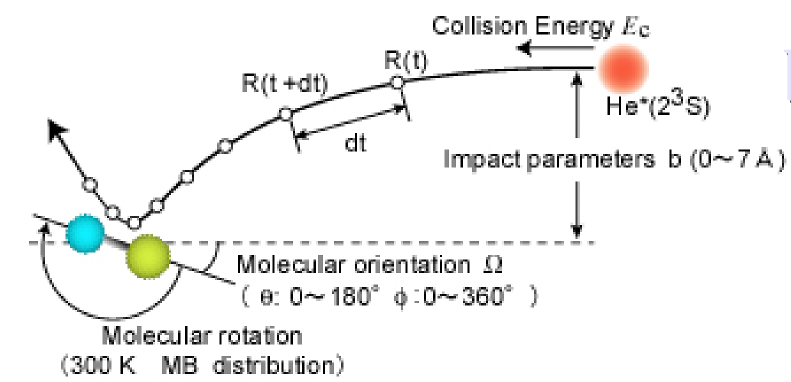
rajectory calculations are
hen performed for various
nitial conditions more than
10,000, based on calculated
otential energy surfaces and
ransition rates.

Here, it is important to note
hat transition rates are
elated with MO functions.

Trajectory Calculations fo

by

Classical trajectory calculations



Transition probability into ionic state i in the interval dt :

$$P_{b,\Omega}^{(i)}(t)dt = S_{b,\Omega}(t)W^{(i)}(t)dt$$

Survival fraction of He* : $S_{b,\Omega}(t) = 1 - \int_{-\infty}^{t} P_{b,\Omega}^{(i)}(t')dt'$

Transition rate into ionic state i :

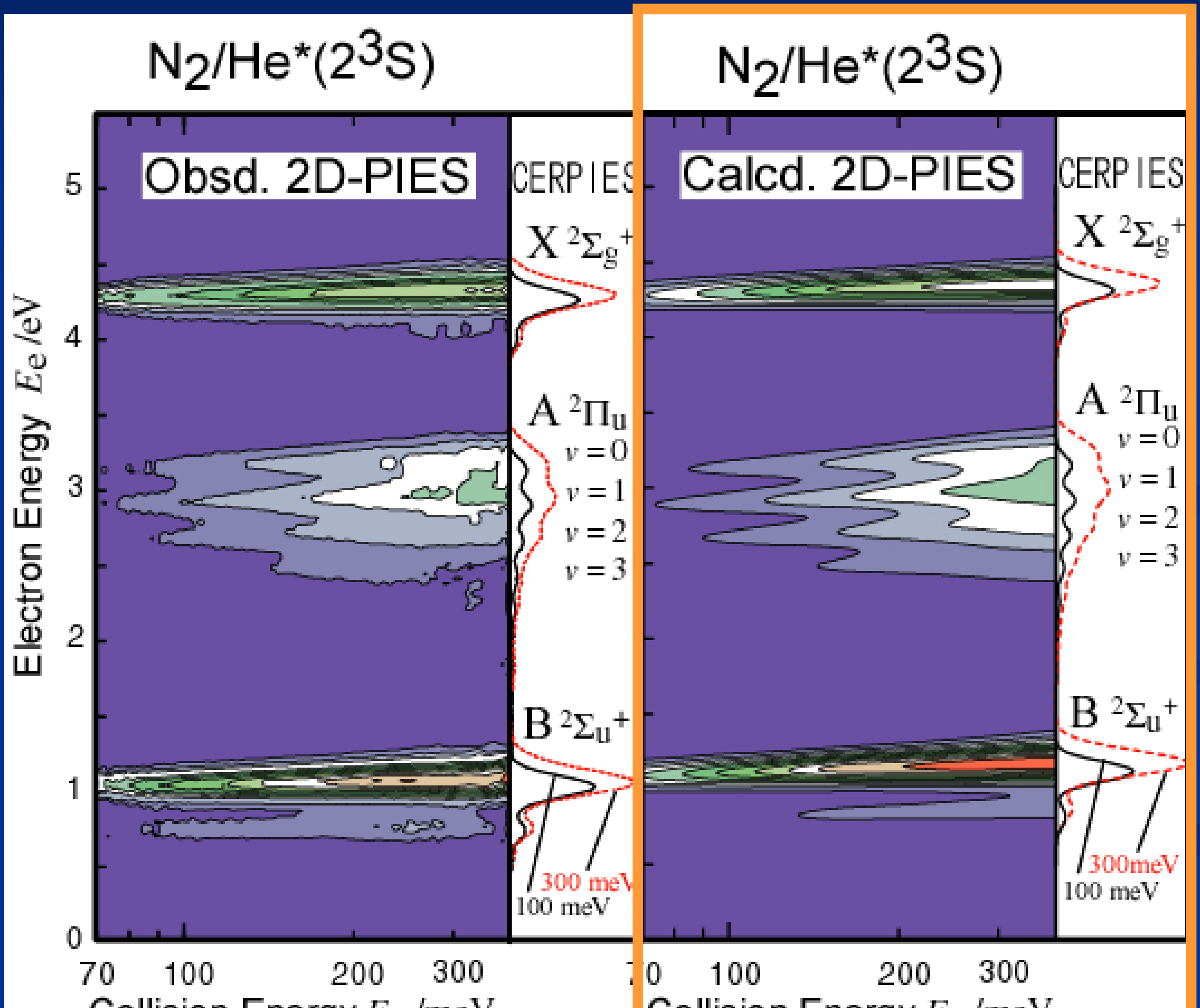
$$W^{(i)} = k^{(i)} \left| \langle \phi_{\mathrm{He1s}} | \boxed{\phi_{M_i}} \rangle \right|^2$$

MO

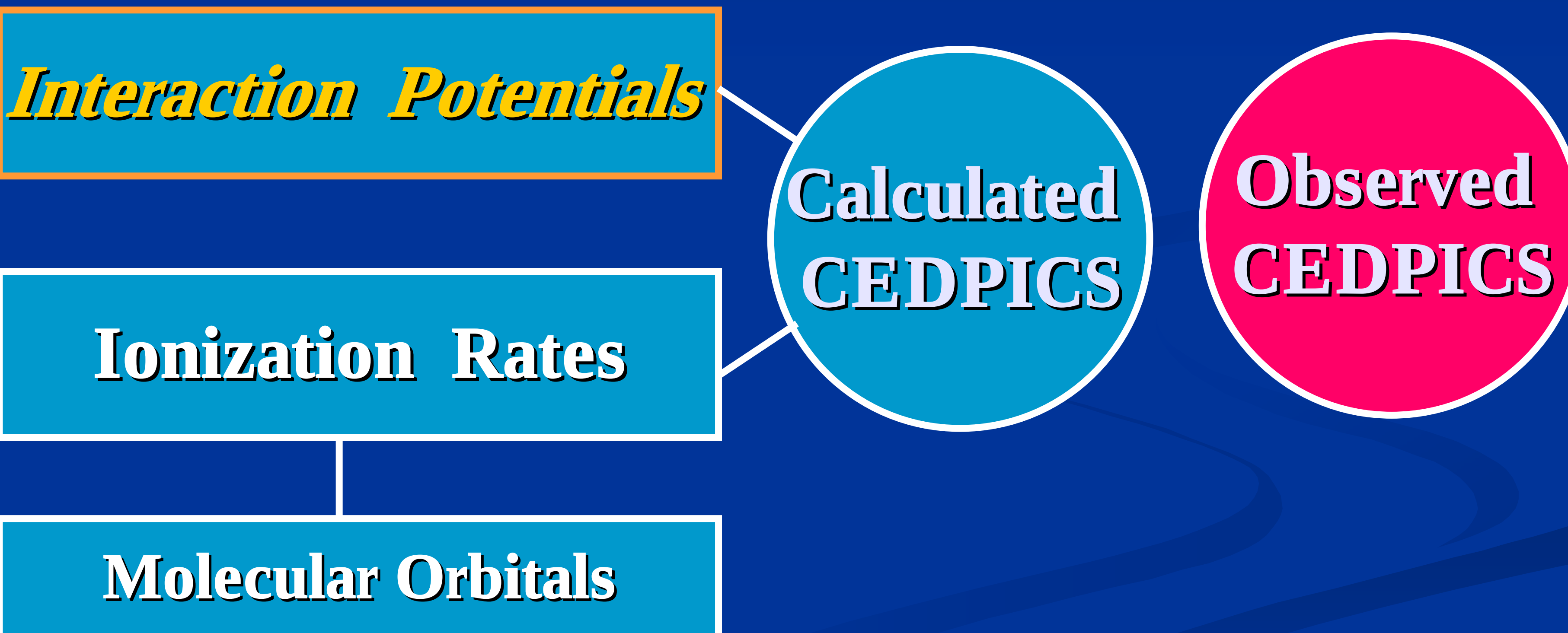
Partial transition probability : $P_{b,\Omega}^{(i)} = \int_{-\infty}^{+\infty} P_{b,\Omega}^{(i)}(t)dt$

Partial ionization cross section : $\sigma^{(i)}(E_c) = \int 2\pi b P^{(i)}(b)db$

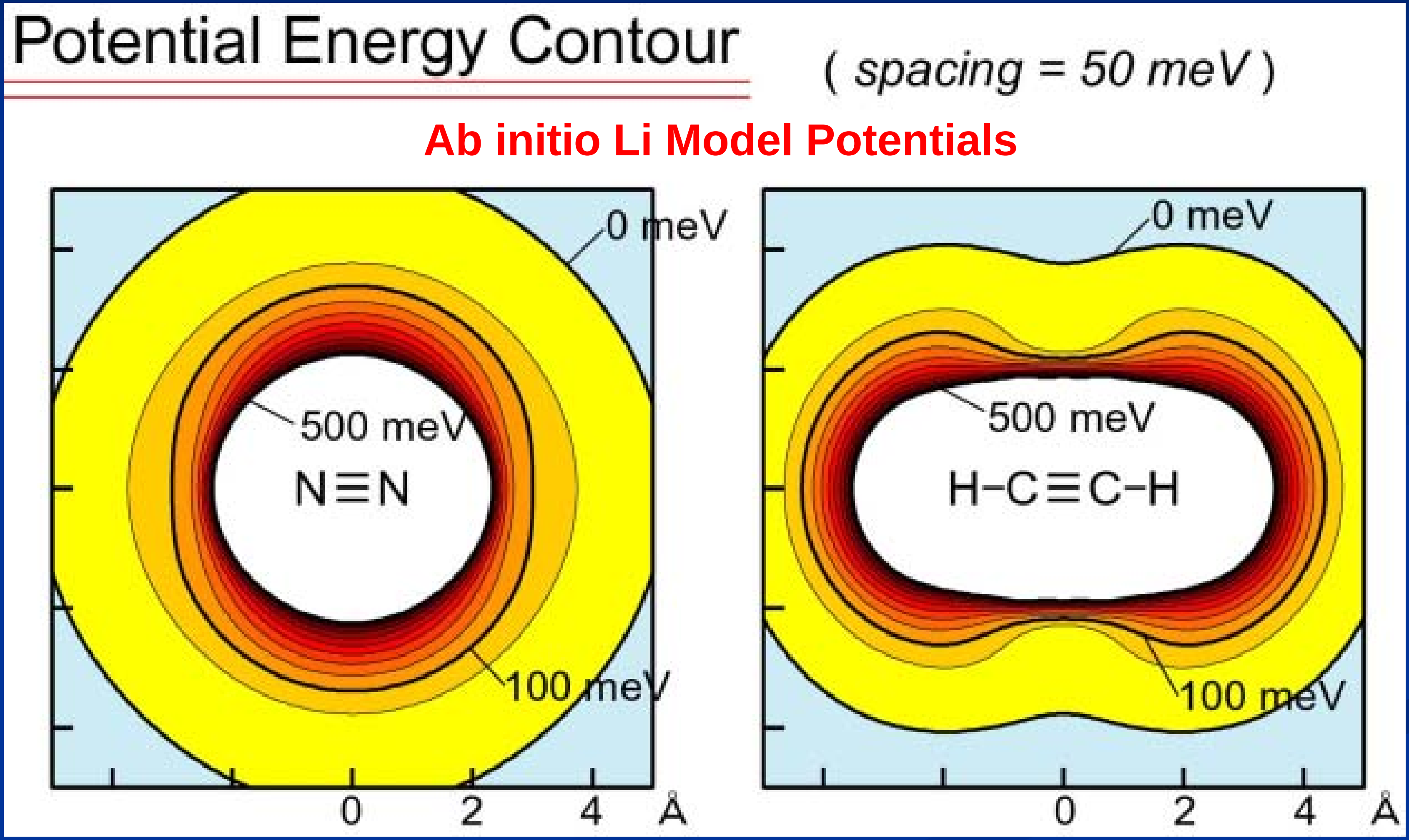
Comparison of *Observed* and *Calculated* 2D-PIES of N_2 / $He^*(2^3S)$



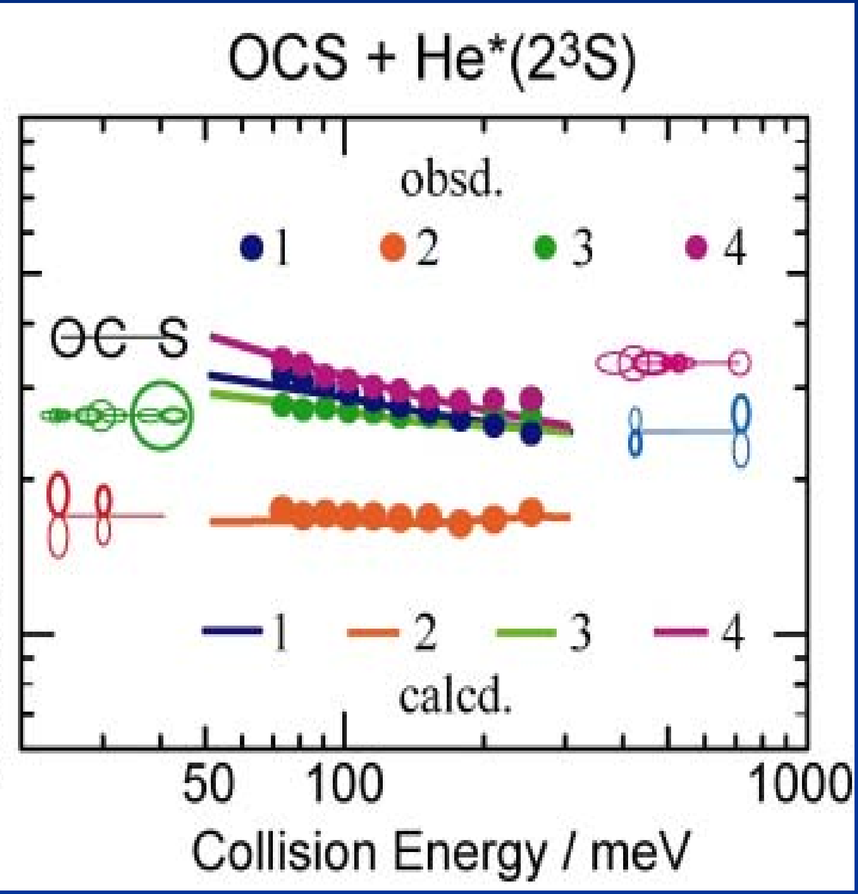
Optimization of Theoretical Simulations to Observed CEDPICS leads to Determination of *Interaction Potentials*

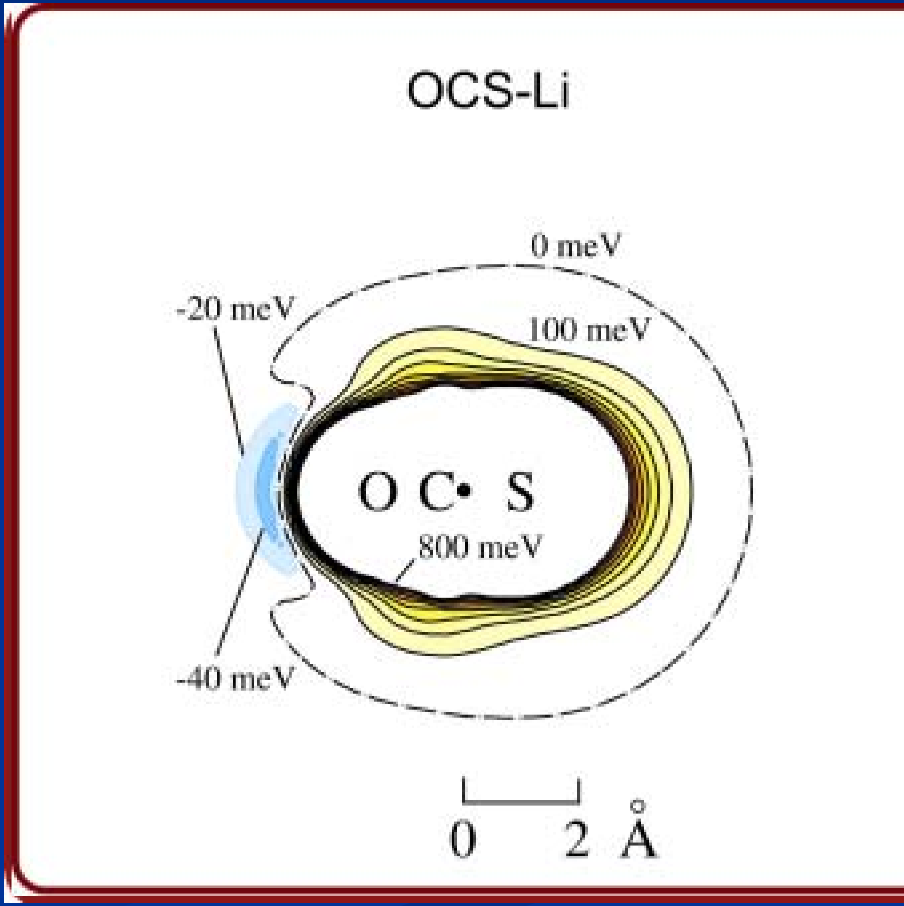


Interaction Potentials for N_2 , C_2H_2 /Li, He*

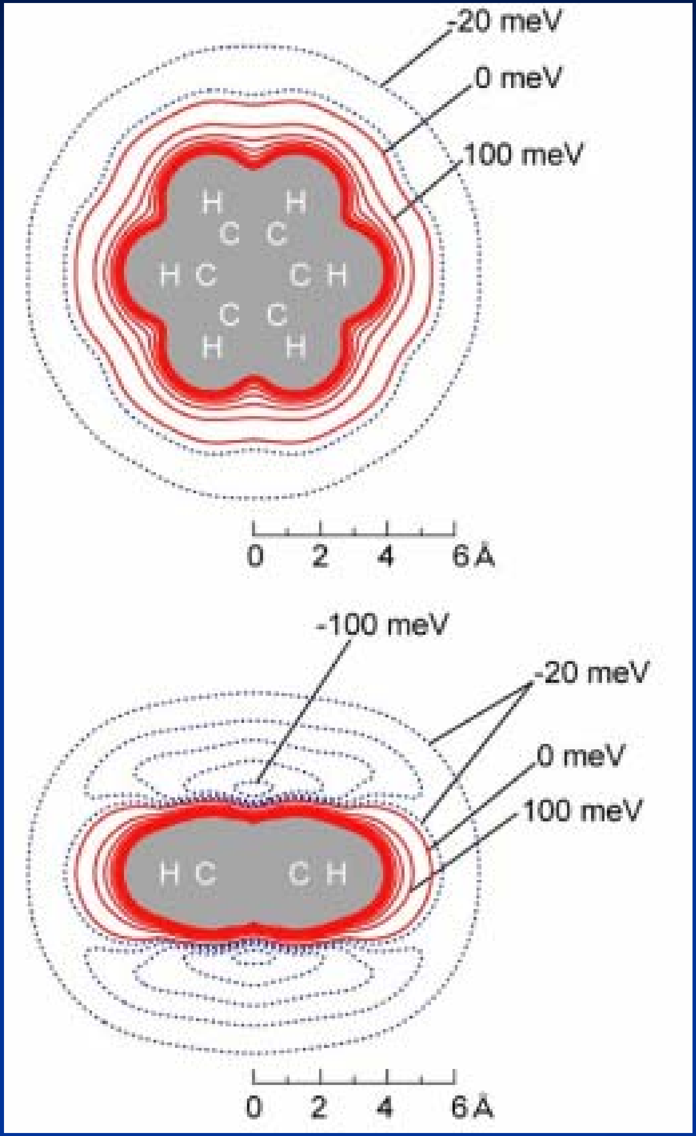


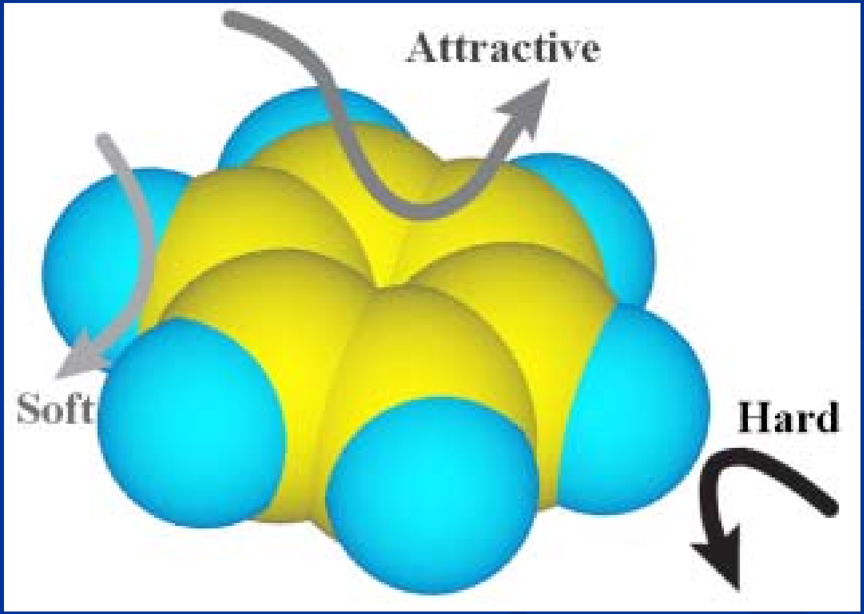
Interaction Potential for OCS /Li, He*





Interaction Potential for C_6H_6 / He*





Determination of *Molecular Orbitals* via Optimization of Theoretical Simulations to Observed CEDPICS

Interaction Potentials

Ionization Rates

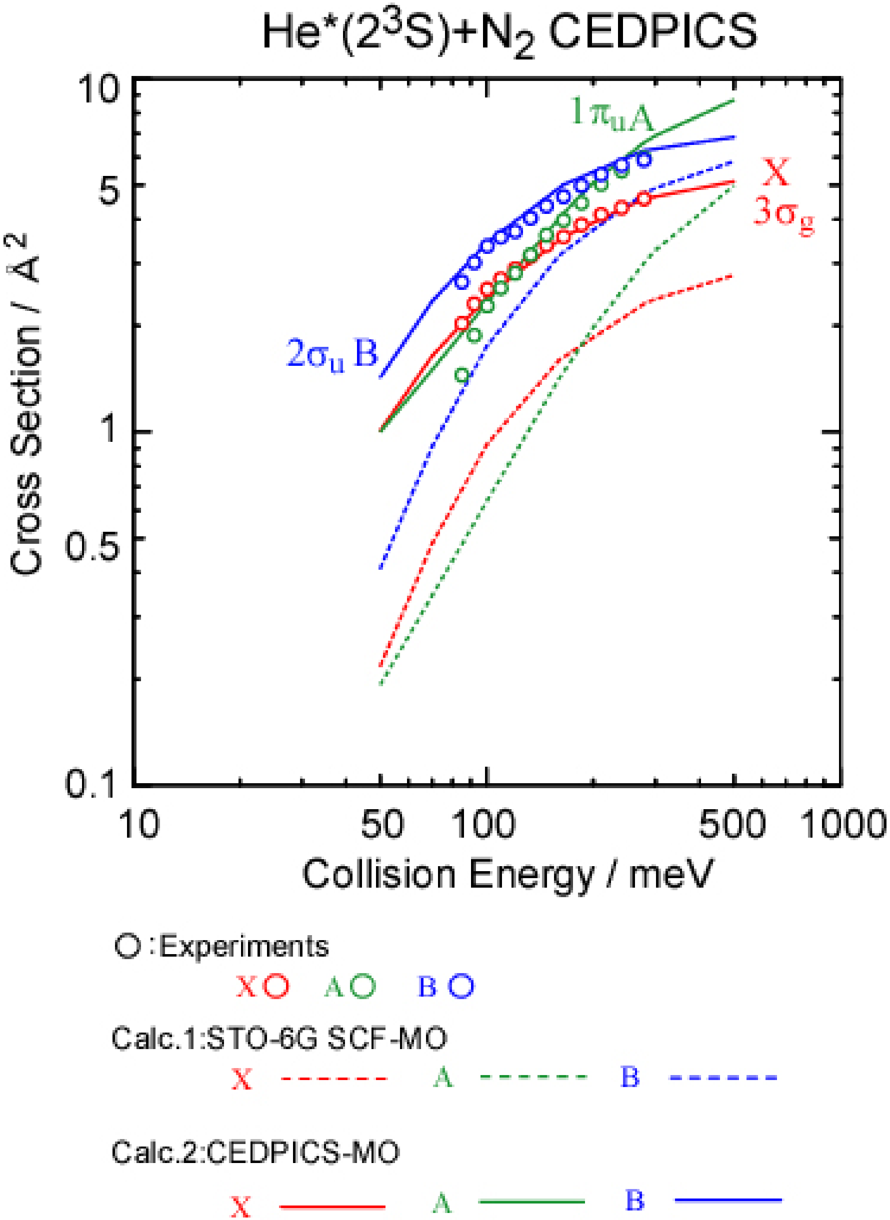
Molecular Orbitals

Calculated CEDPICS

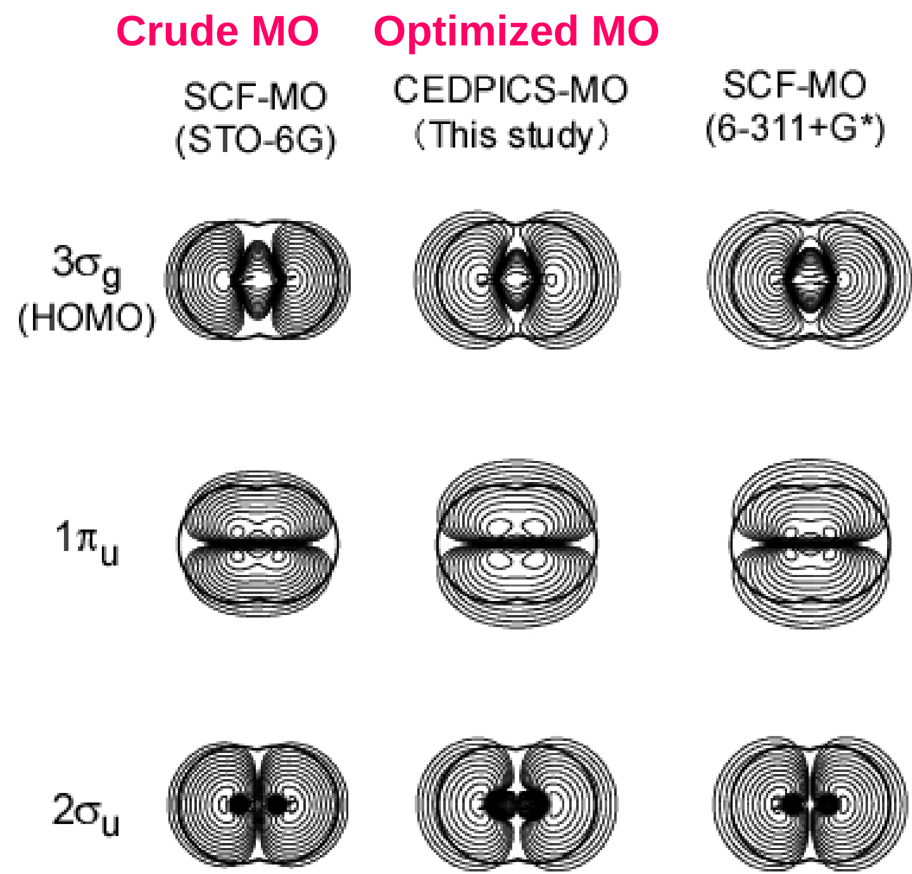
Observed CEDPICS

Determination of ***Molecular Orbitals***

- Input Data
  - Experimental 2D-PIES / CEDPICS DATA
  - Entrance Potential for Reactants
- Molecular Orbitals
  - Initial guess : SCF-LCAO-MOs in a Minimal Basis
  - Optimization : MO Coefficients & Exponents

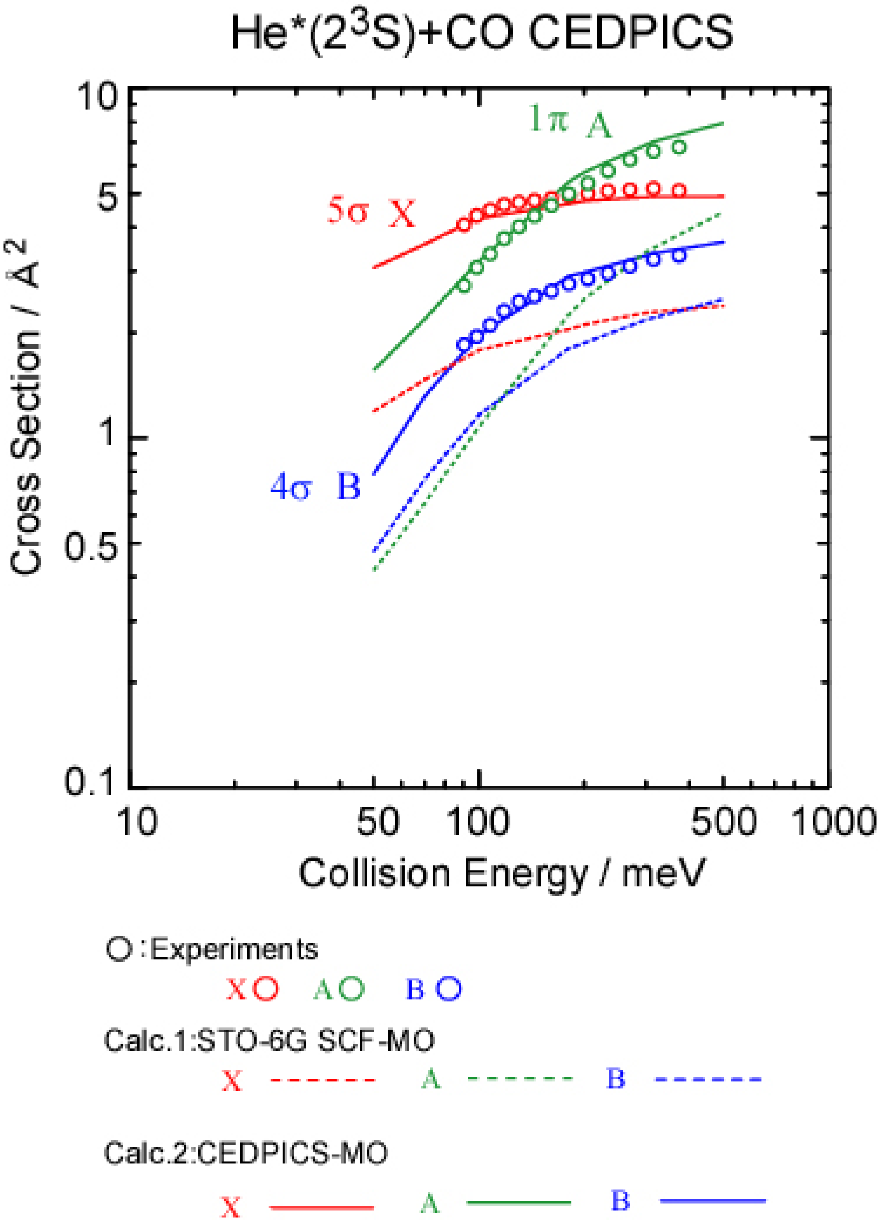


He*(2³S)+N₂ CEDPICS
Cross Section / Å²
Collision Energy / meV
10
5
1
0.5
0.1
10
50
100
500
1000
1πu A
X
3σg
2σu B
○:Experiments
X○ A○ B○
Calc.1:STO-6G SCF-MO
X A B
Calc.2:CEDPICS-MO
X A B

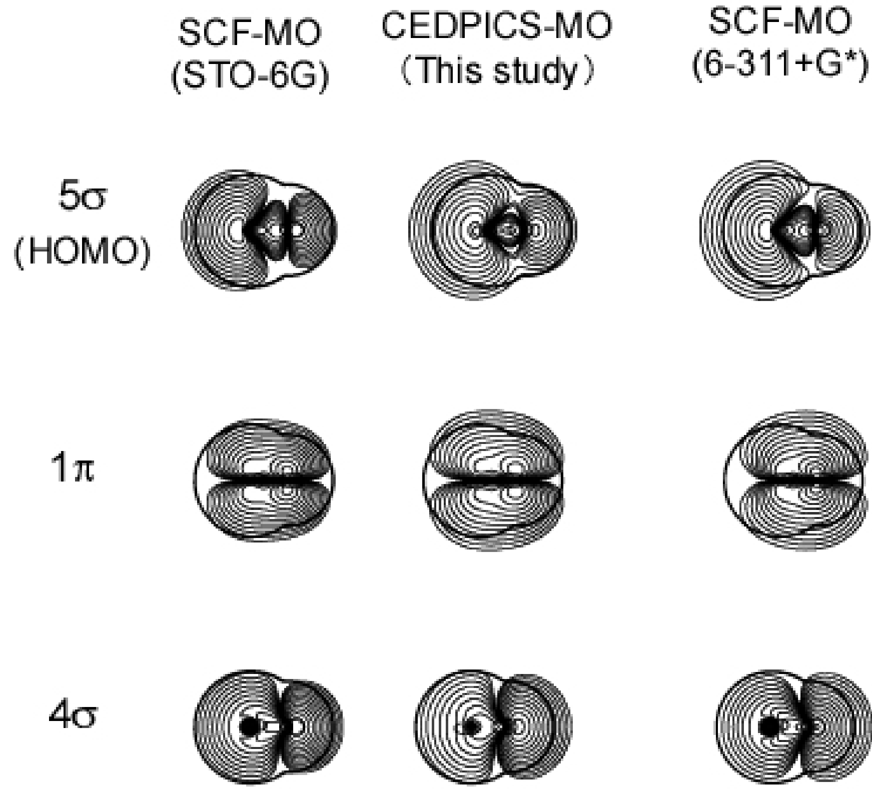


Crude MO
Optimized MO
SCF-MO
(STO-6G)
CEDPICS-MO
(This study)
SCF-MO
(6-311+G*)
3σg
(HOMO)
1πu
2σu

ζ (N) = 1.95 **ζ (N) = 1.63**



Crude MO **Optimized MO**



ζ (C) = 1.72 **ζ (C) = 1.42**

ζ (O) = 2.25 **ζ (O) = 1.92**

Summary & Conclusions

- 10^{10} times of improvements were made for constructing a crossed-beam 2D-PIES apparatus.
  - Ionic-state resolved CEDPICS became observable.
  - Collision-energy resolved PIES became observable.
- A theoretical simulation method was established.
  - Anisotropic interaction potentials between He* and molecules could be determined.
  - Spatial distributions of molecular orbitals could be obtained based on the observed CEDPICS.

Collaborators

1D-PIES (Univ. Tokyo)

Y. Harada, T. Munakata, K. Kuchitsu,

S. Fujisawa, H. Mutoh, K. Imai,

S Matsumoto, T. Veszpremi, S. Masuda

2D-PIES (Univ. Tokyo : Tohoku Univ.)

K. Mitsuke, T. Takami, T. Ishida, H. Yamakado,

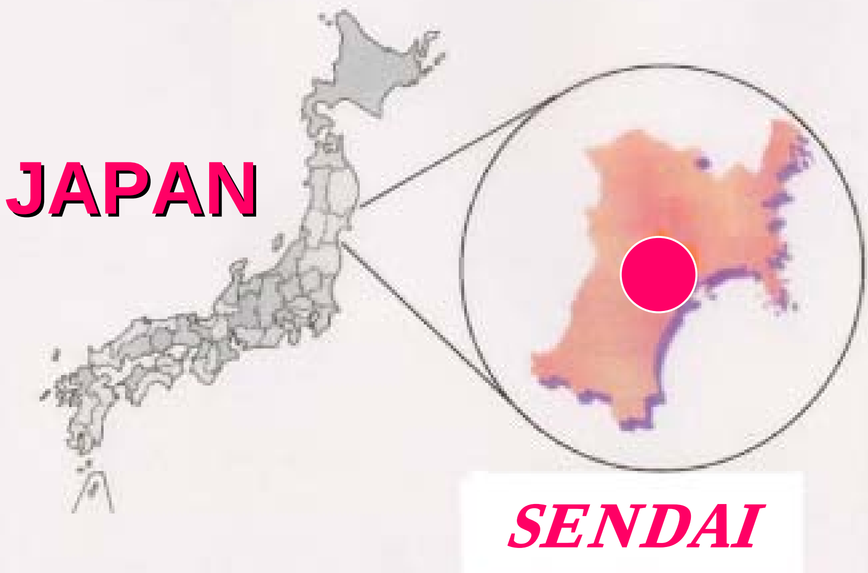
N. Kishimoto, S. Hoshino, T. Ogawa, T. Yamata,

T. Pasinszki, F. Misaizu, Y. Yamakita, H. Tanaka,

M. Yamazaki, S. Maeda, R. Maruyama, T. Horio



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SENDAI