# Ionization energies of van der Waals clusters

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# Innsbruck

# Outline

- Motivation
- Experiment
- Results & Discussion
- Conclusion

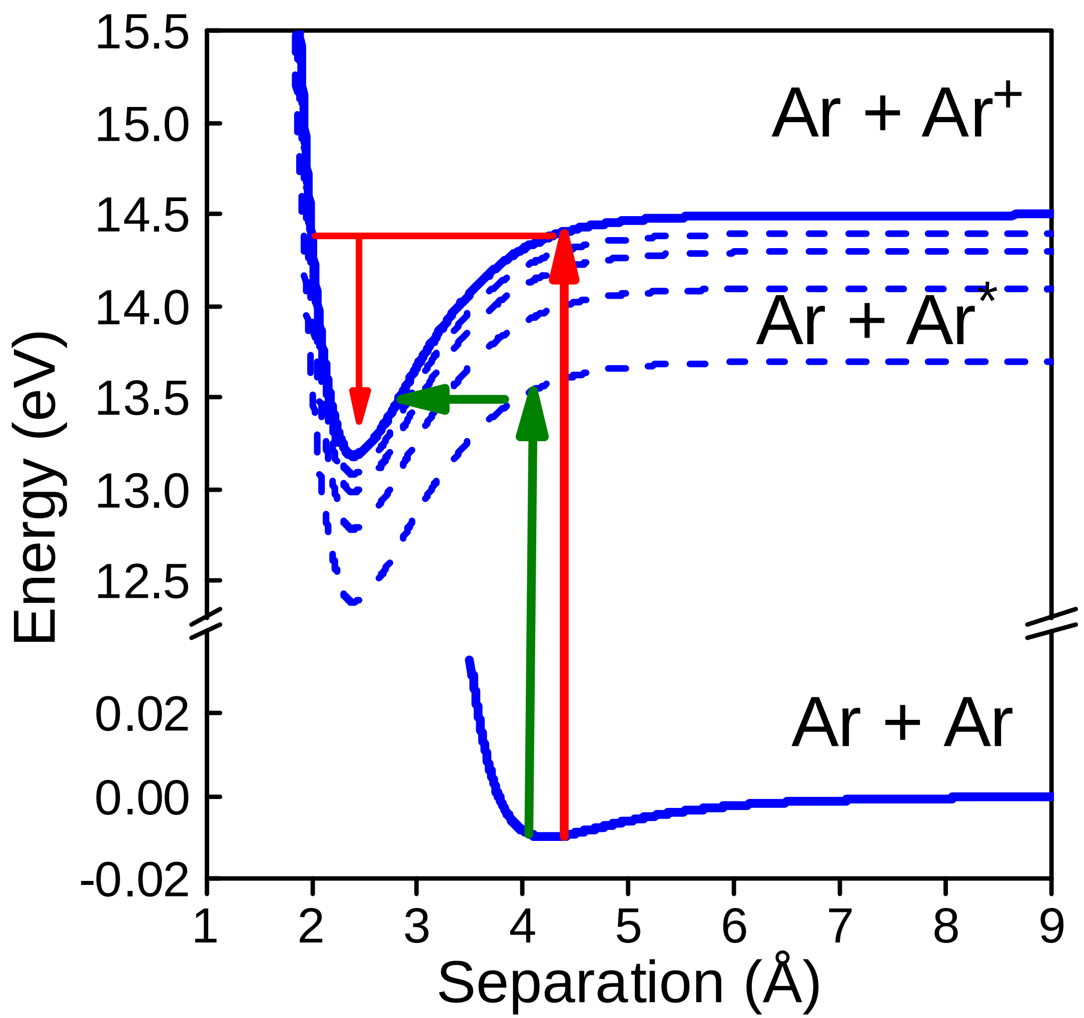
# Motivation

- Ionization mechanism?
- Structure of ionic core?
- Work function of solids?
- Dissociation energy of cluster ions?

# Ionization mechanism

Vertical ionization?
Adiabatic ionization?

Soft ionization via autoionizing states:
$Ar + Ar^* \rightarrow Ar_2^+$ ???

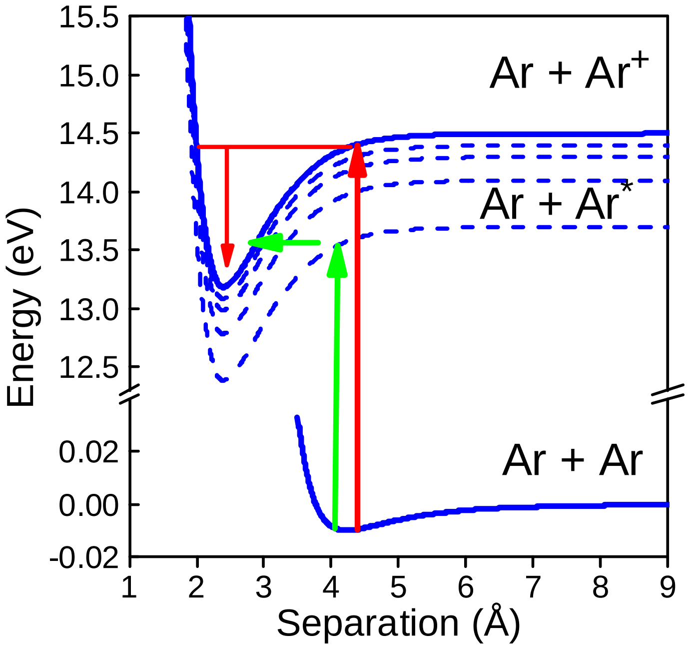


# Ionization mechanism: EI versus PI

**Electron impact (EI) vs. photoionization (PI)**

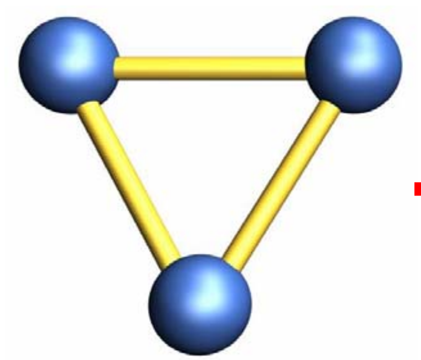
Is it really true that

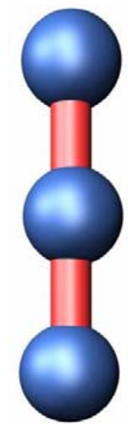
- ➢Resolution (EI) << Resolution (PI)?
- ➢EI is a vert. process while PI reaches adiab. values?
- ➢PI can distinguish between vert. and ad. thresholds?

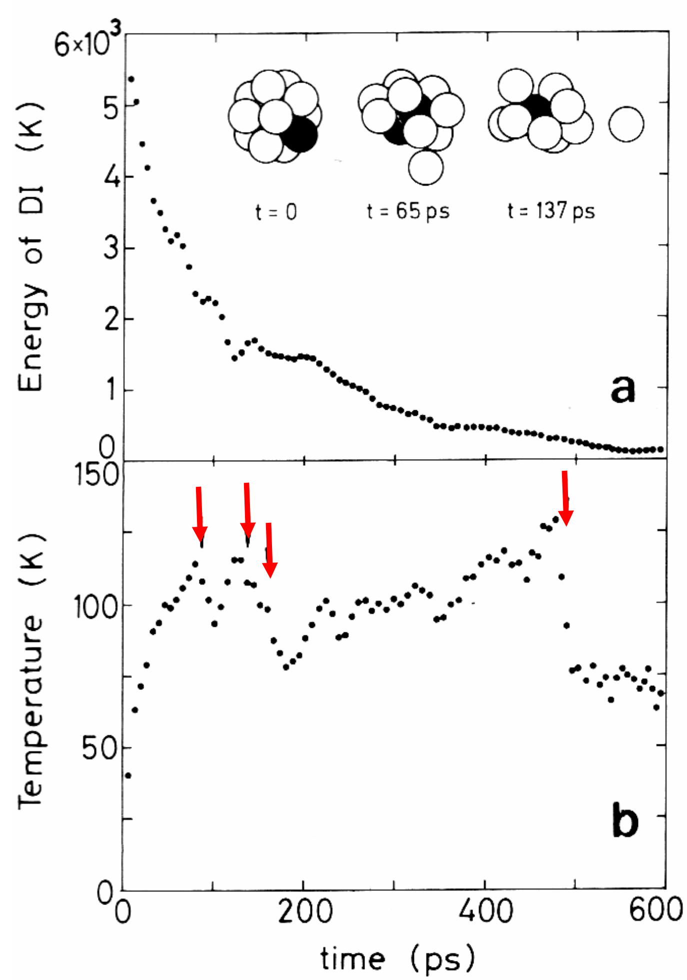


# Consequences of non-adiabatic ionization: fragmentation

$Ar_3 \rightarrow Ar_3^+$








Soler et al., CPL 109, 1994

# Ionic core

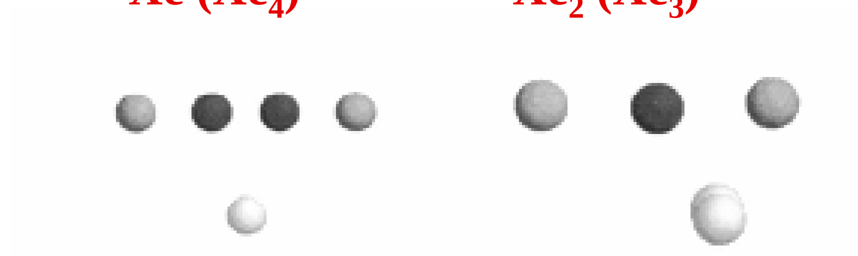
**From theory & experiment:**

**small *n* (> 2): trimer or tetramer**

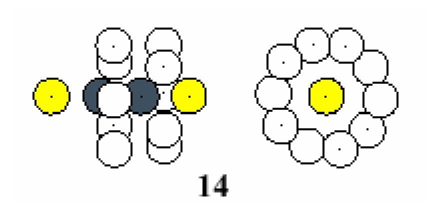
**large *n*: dimer**

**$Xe_5^+$: structural isomers**
Gascon et al., JCP 117 (2002)

**Xe $(Xe_4)^{+}$`** **$Xe_2$ $(Xe_3)^+$**



**$Ar_{14}^+$**
Doltstinis and Knowles, 1998

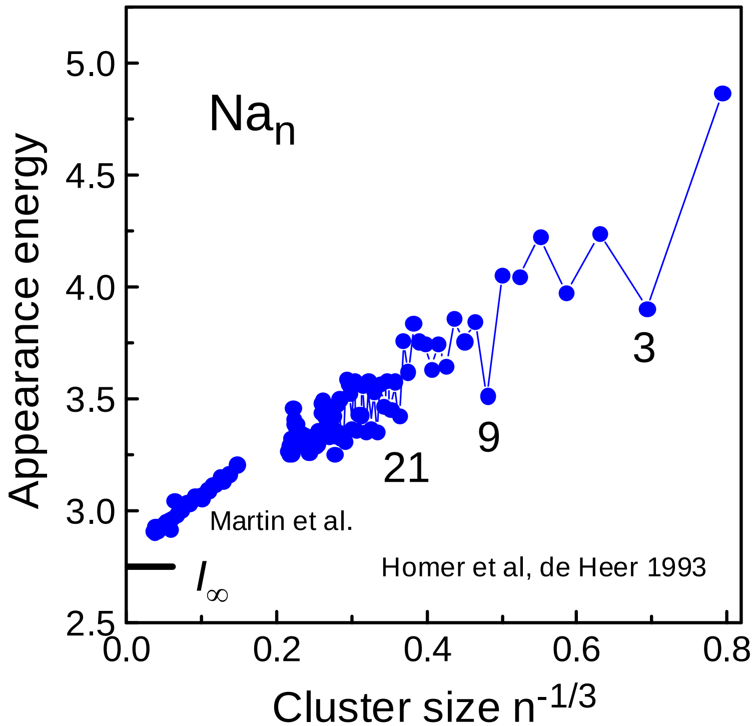


# Size dependence and "workfunction"

$$I_n = I(\infty) + \frac{e^2}{2r_n}\left[1-\frac{1}{\varepsilon}\right] = I(\infty) + \frac{e^2}{2r_0\sqrt[3]{n}}\left[1-\frac{1}{\varepsilon}\right]$$

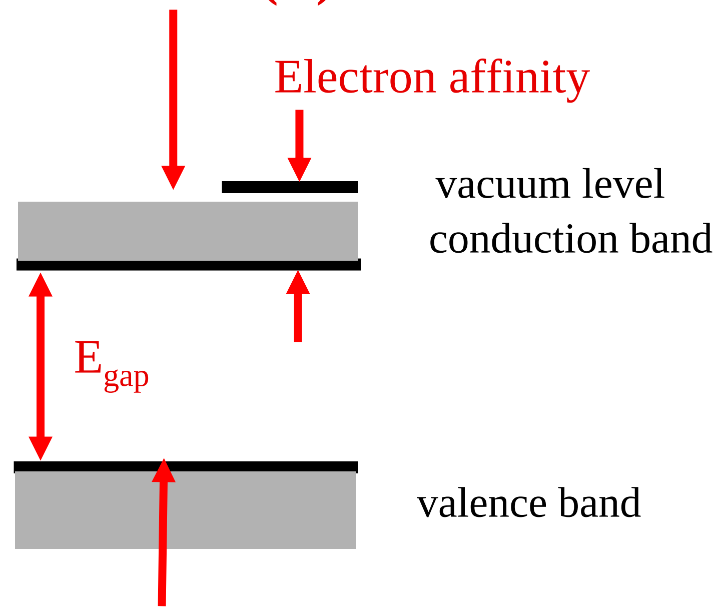
**bulk**

**$r_n$ = cluster radius**
**$r_o$ = eff. monomer radius**
**$n$ = cluster size**
**ε = dielectric const.**




Sodium work function
old: 2.28 eV    new: 2.75 eV

**Insulator: I(∞)**



# Dissociation energy of cluster ions

$$A_n \xrightarrow{D_n} A_{n-1} + A \xrightarrow{I_{n-1}} A_{n-1}^+ + A + e$$

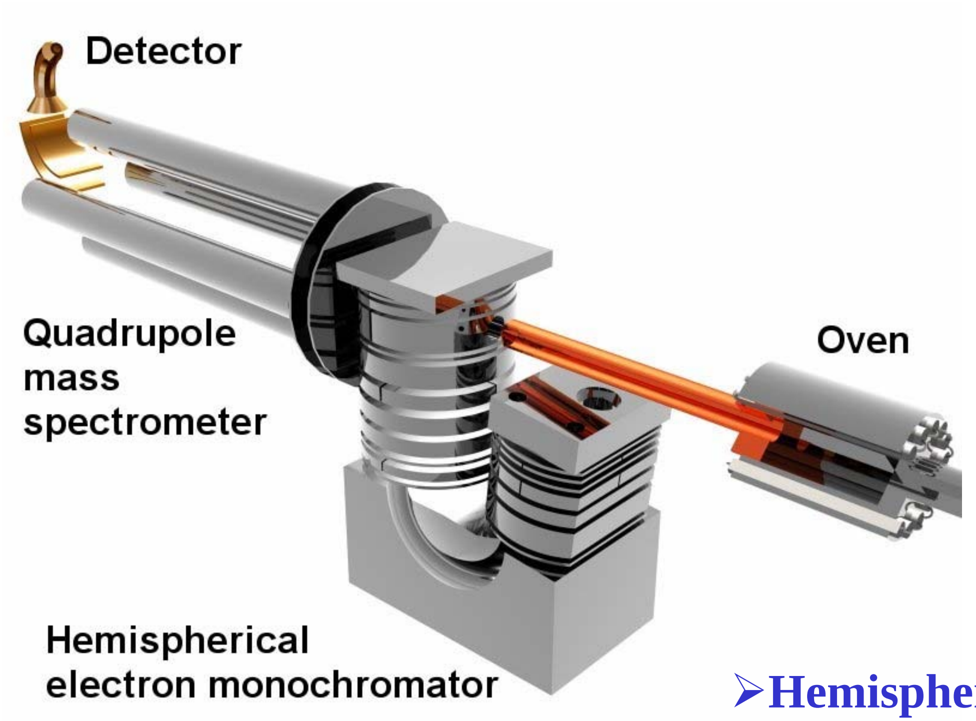
$$A_n \xrightarrow{I_n} A_n^+ + e \xrightarrow{D_n^+} A_{n-1}^+ + A + e$$

$$\rightarrow \boldsymbol{D_n^+ = D_n + I_{n-1} - I_n}$$

**small & easily estimated**

**Need adiabatic ionization energies!**

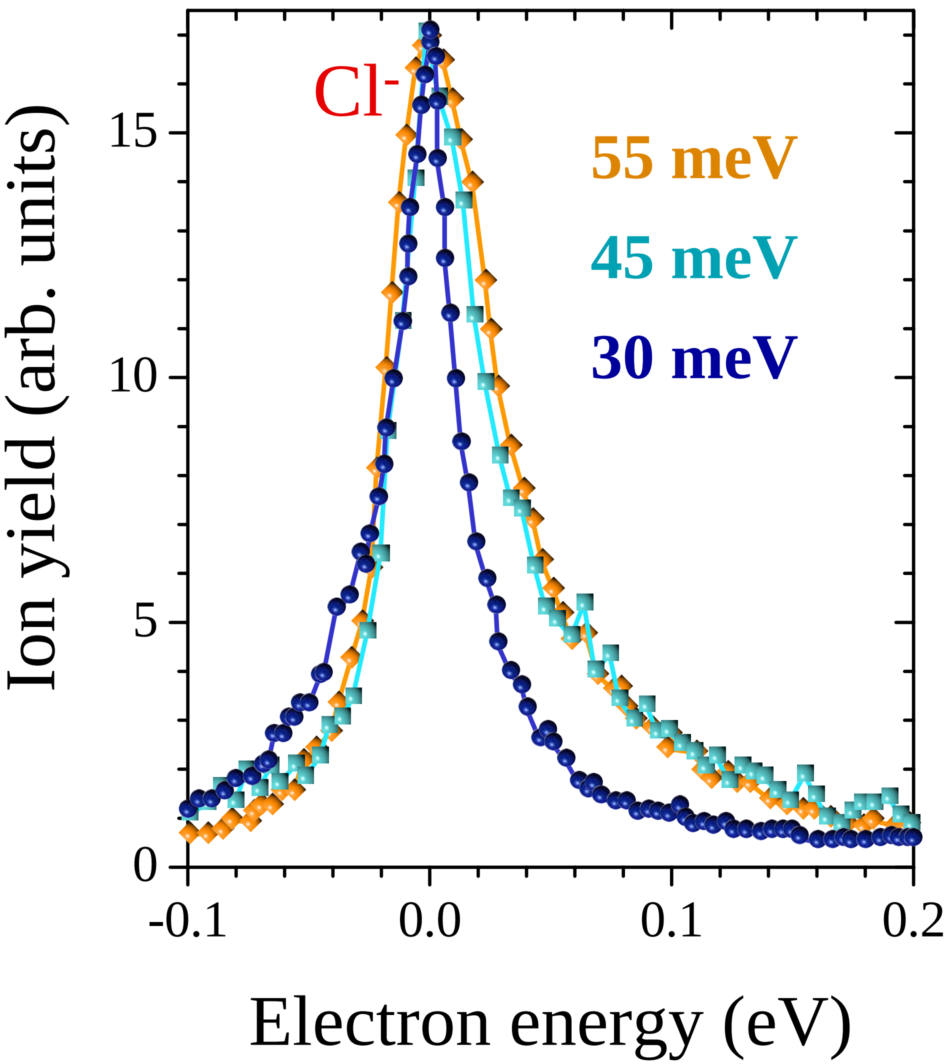
# Experiment



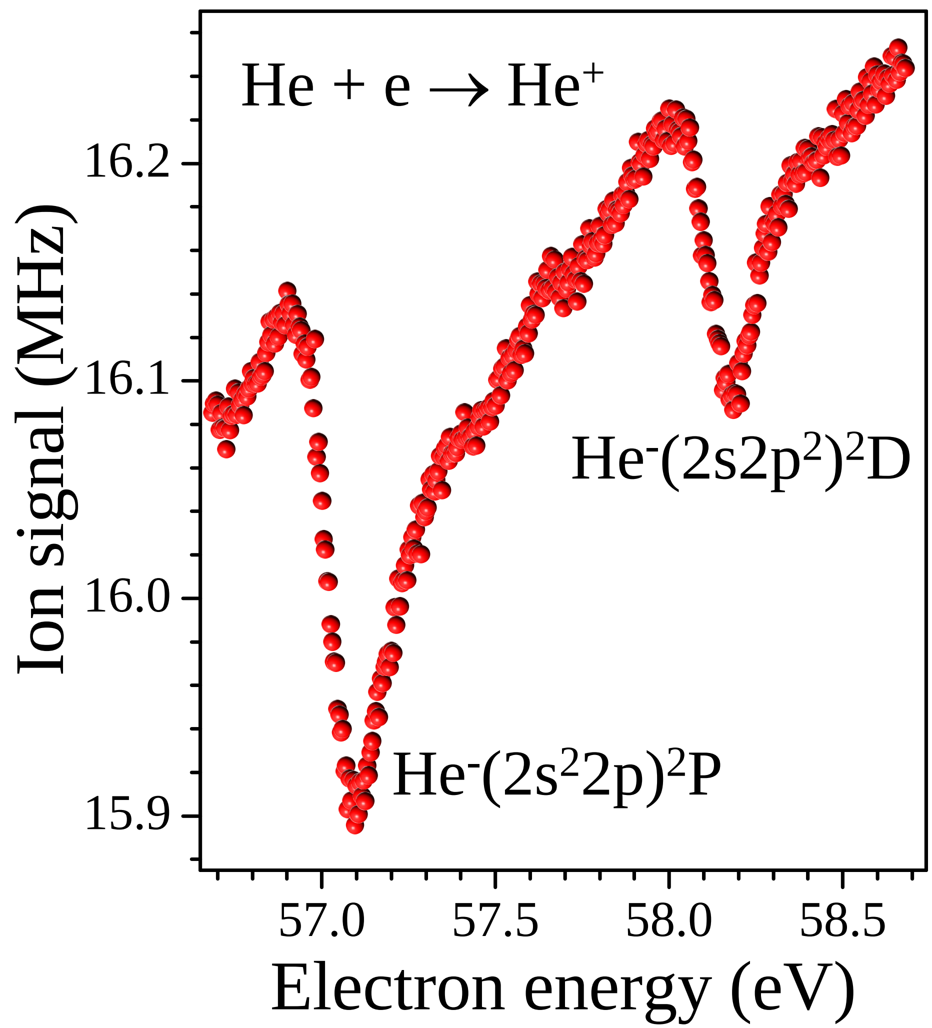

- Hemispherical electron monochromator
- Electron energy resolution: FWHM > 30 meV
- Maximum electron current: 5 nA
- Electron energy range: 0-1000 eV
- Mass range: 2000 Thomson

# Electron resolution

**1:** $CCl_4 + e \rightarrow Cl^-$

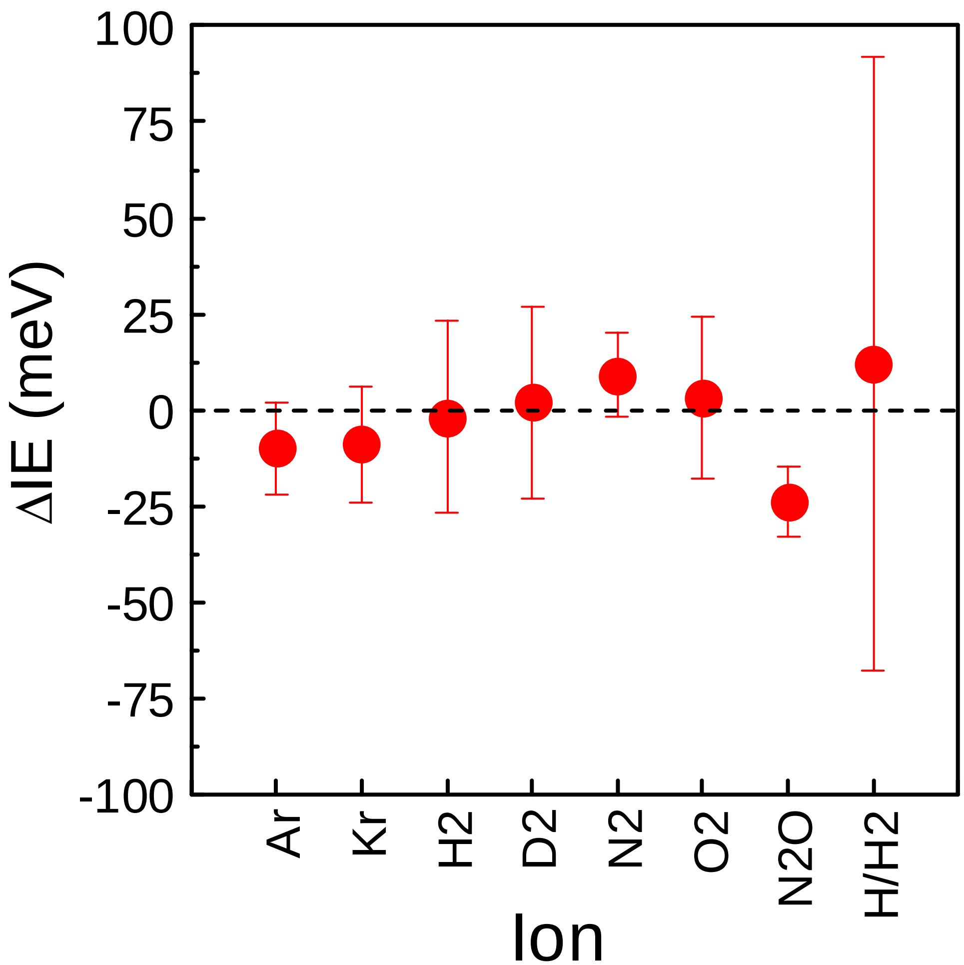



**2:** n = 2 intrashell He- resonances



# Accuracy of thresholds

**Comparison with NIST values. Calibration: IE(Xe) = 12.130 eV**

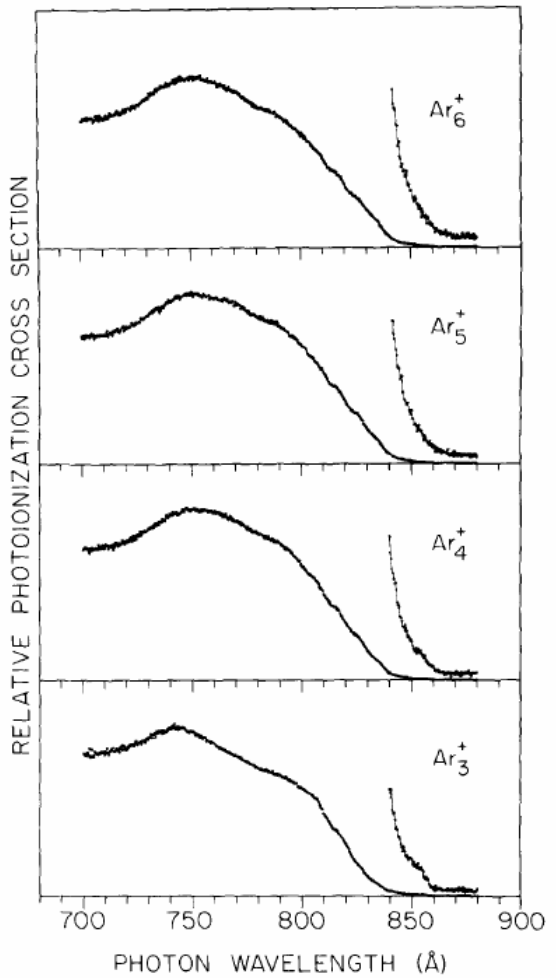



**Average deviation 12 meV**

# Data analysis: Eyeballing thresholds....

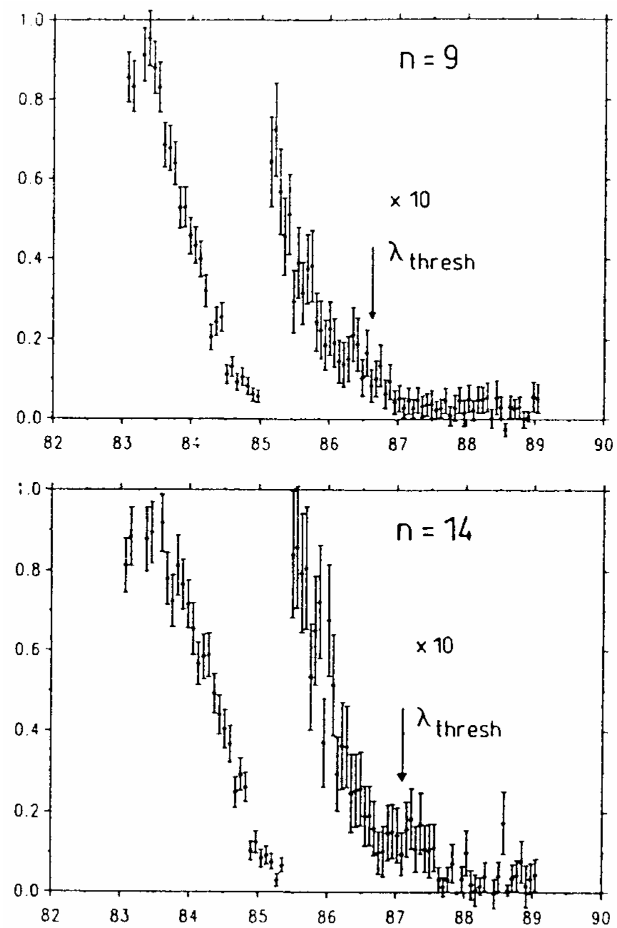
**photoionization**

Dehmer & Pratt, JCP 76 (1982)




**PEPICO**

Kamke et al., Z.Phys.D14 (1989)




**Eyeballing thresholds....**

Kamke et al.:

*We have resisted any temptation to fit these thresholds with an unmotivated analytical function. Rather, several experimentators have independently given their judgement and estimate for error bars.*

# Data analysis

PHYSICAL REVIEW VOLUME 90, NUMBER 5 JUNE 1, 1953

## The Threshold Law for Single Ionization of Atoms or Ions by Electrons

GREGORY H. WANNIER
*Bell Telephone Laboratories, Murray Hill, New Jersey*

(Received February 3, 1953)

When an electron hits an atom or ion, it may knock off an electron. This process is fundamental in almost all types of gas discharge. The reaction is endothermic; hence there is a threshold value in the electron energy below which it does not occur. In this paper, the dependence of the yield on the energy just above this threshold is derived. The derivation is not rigorous because it circumvents some of the difficulties of the three-body problem by applying ergodicity, albeit in a weakened form. The result is that, for atoms, the yield rises as the 1.127th power of the energy excess. For ions the exponent lies between this number and unity.

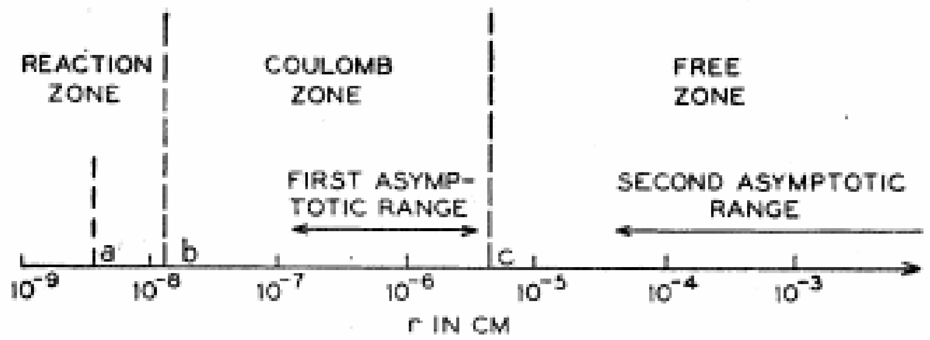
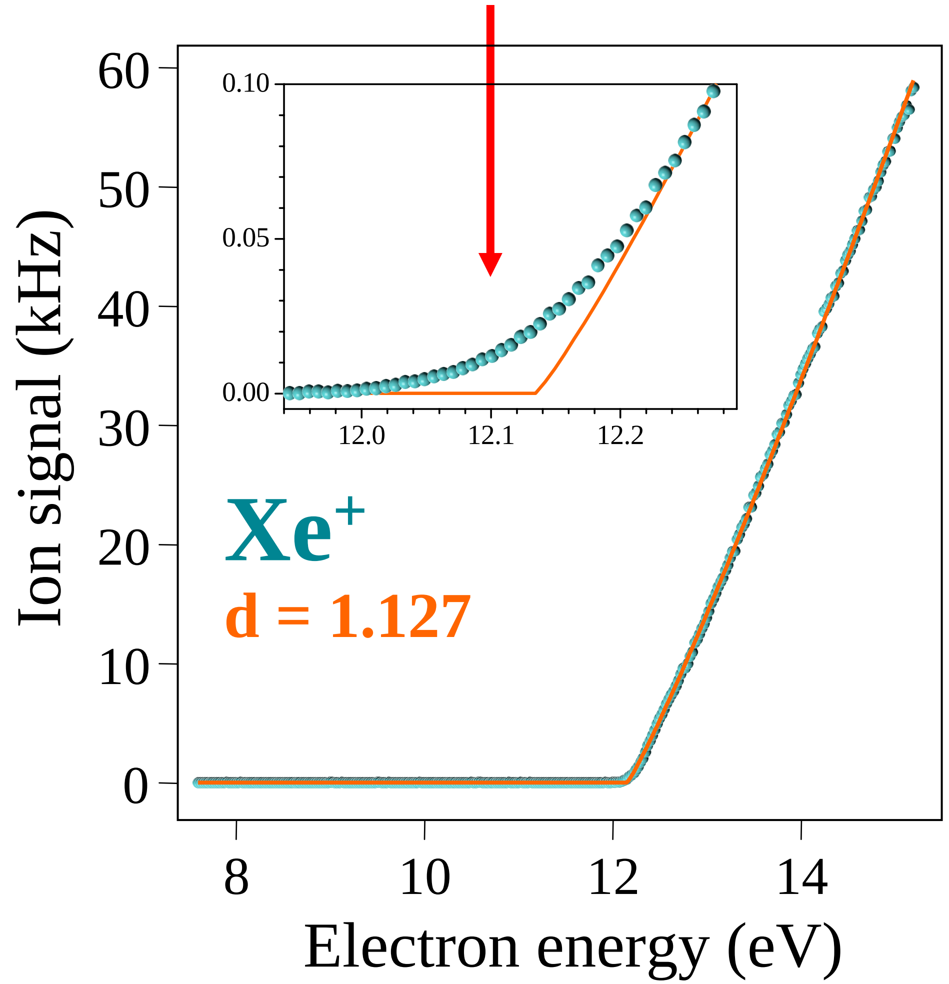



FIG. 1. Qualitative picture of the zones of behavior of $r$; $r=(r_1^2+r_2^2)^{\frac{1}{2}}$.

**yield = const $(E\text{-}I_o)^{1.127}$**
**for EI of atoms,**
**single quantum state**

# Data analysis

**Effect of finite electron resolution**




**Fit function**

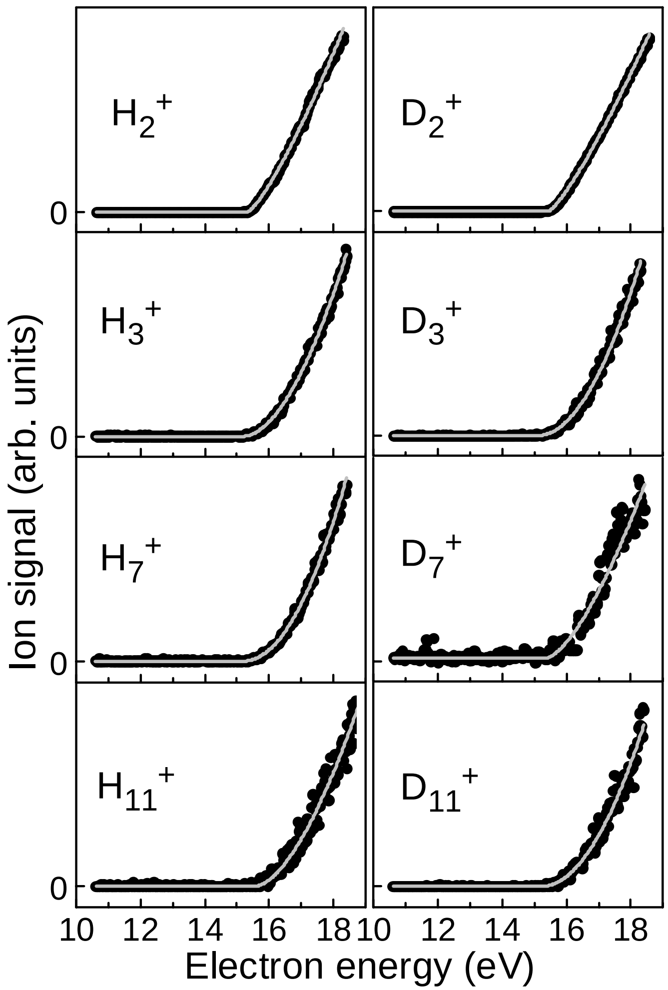
$$f(E) = b + c(E - I)^p$$

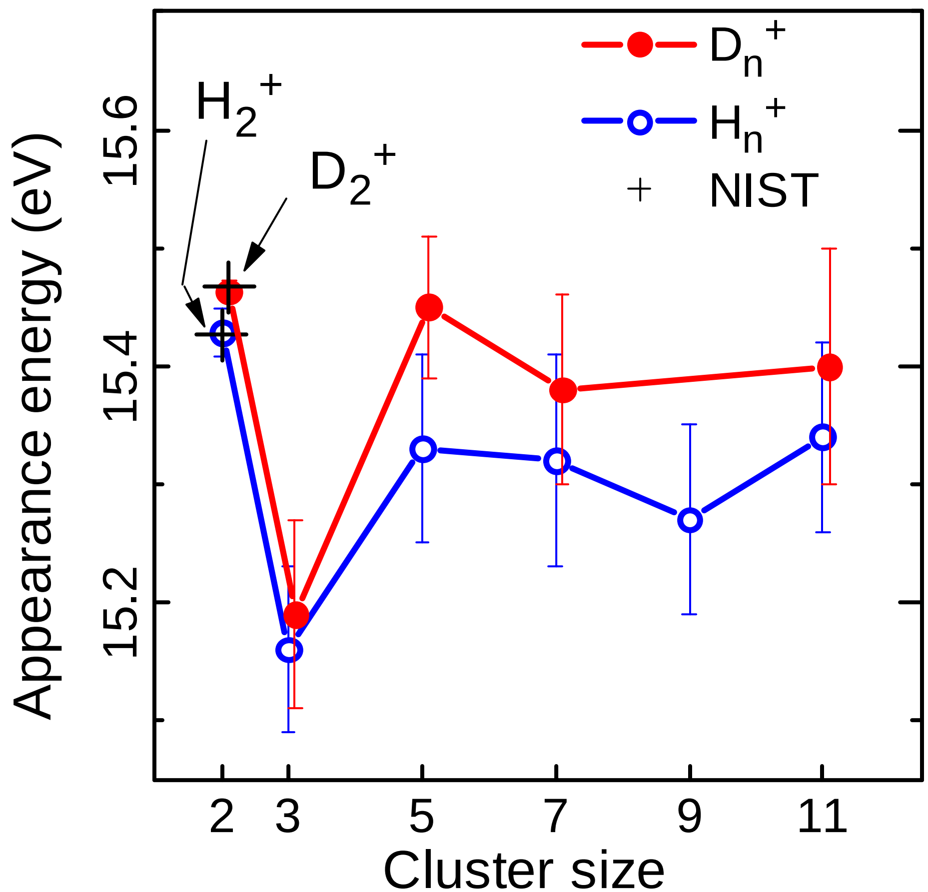
$$= b \qquad \text{if } E \leq I$$

**May fold with energy distr. of electron beam**

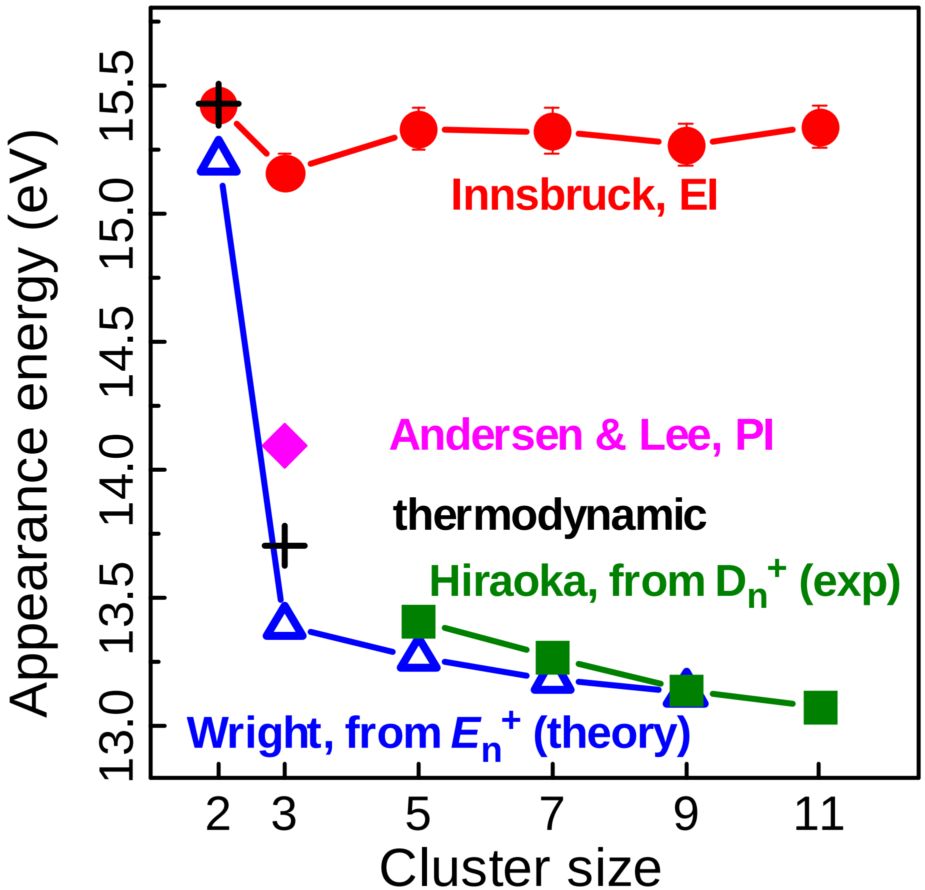
# Result: Hydrogen clusters

Innsbruck, electron impact

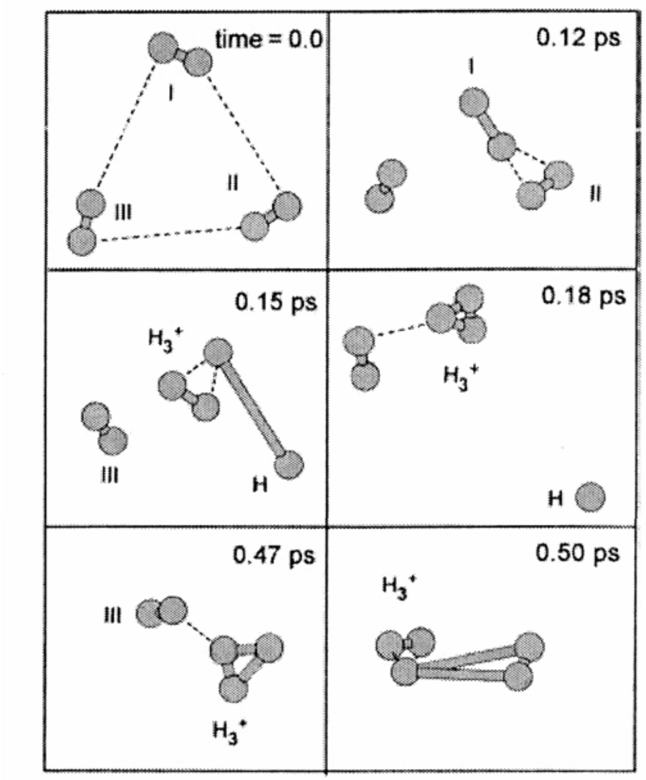


# Hydrogen clusters: The whole picture

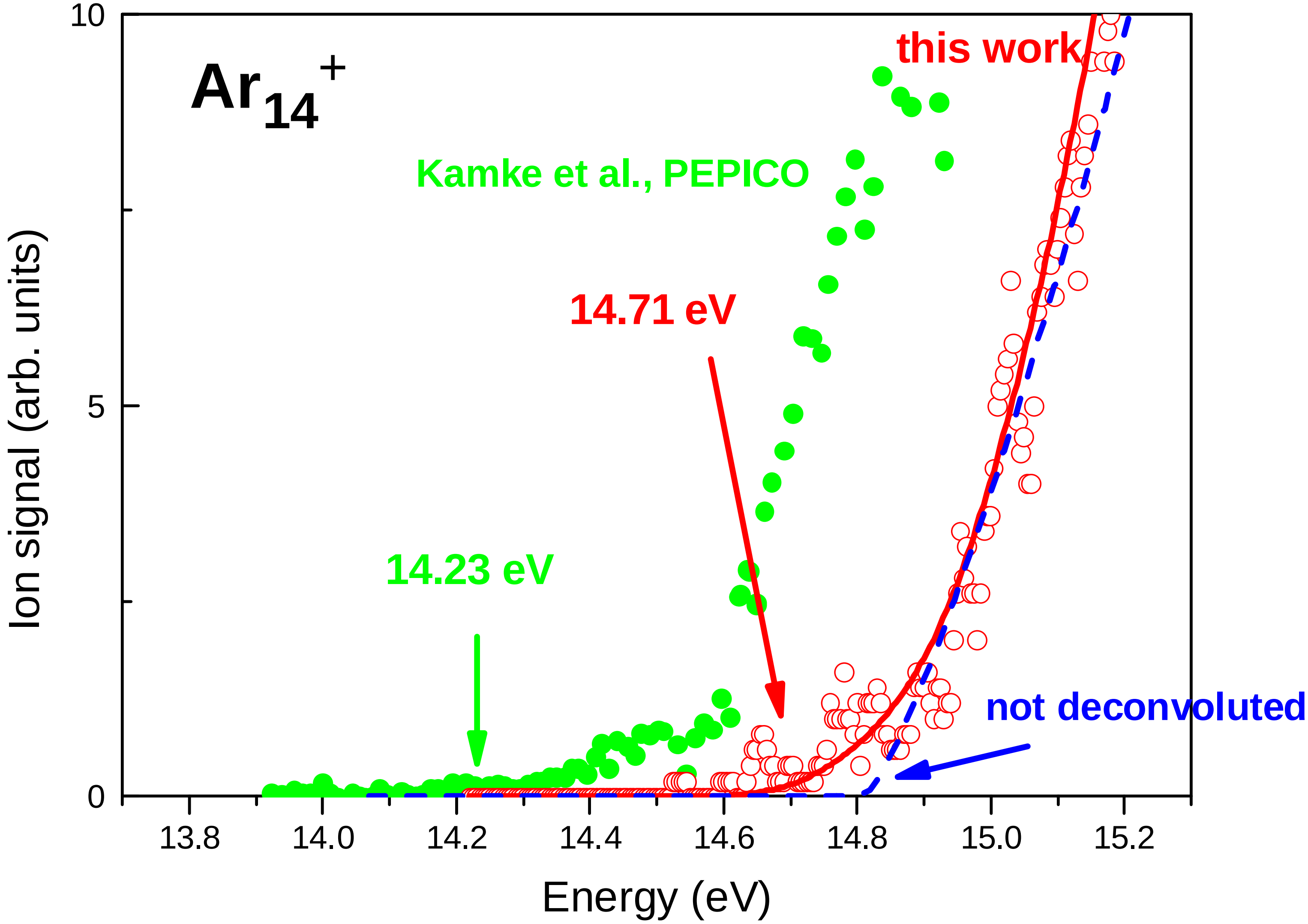



Vertical ionization of $(H_2)_3$
ab-initio MD, Tachikawa, PCCP 2, 2000

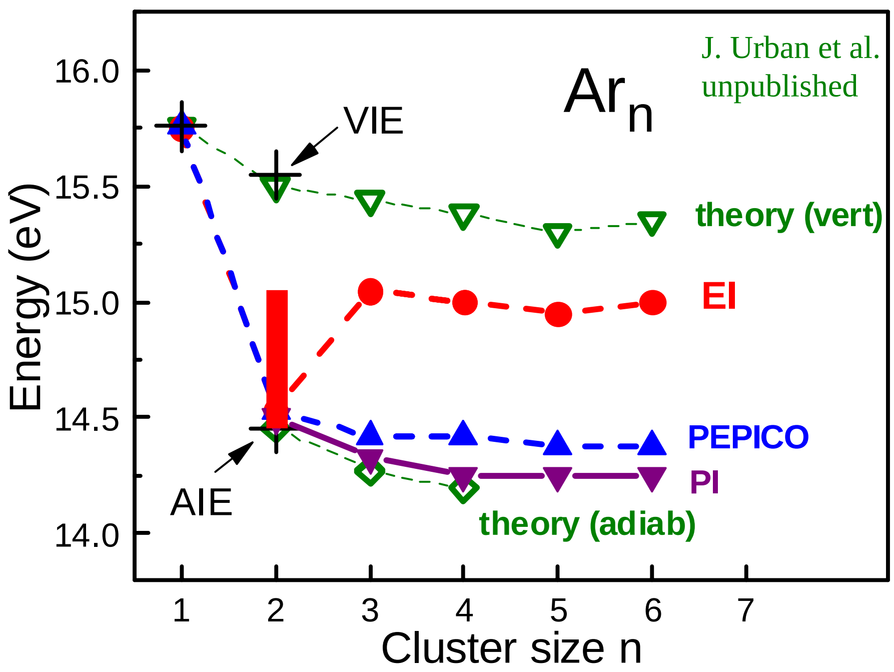



**Conclusion: Neither PI nor EI reach adiabatic threshold for $(H_2)_2$ + e $\rightarrow$ $H_3^+$ + H**

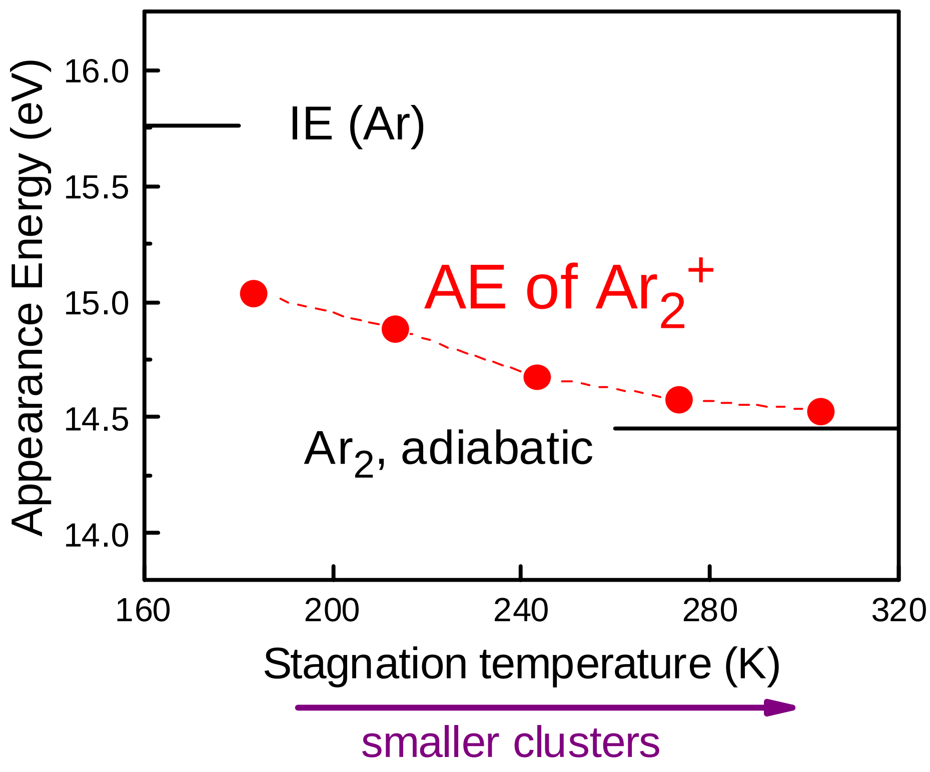
# Results: Argon clusters



# Small argon clusters



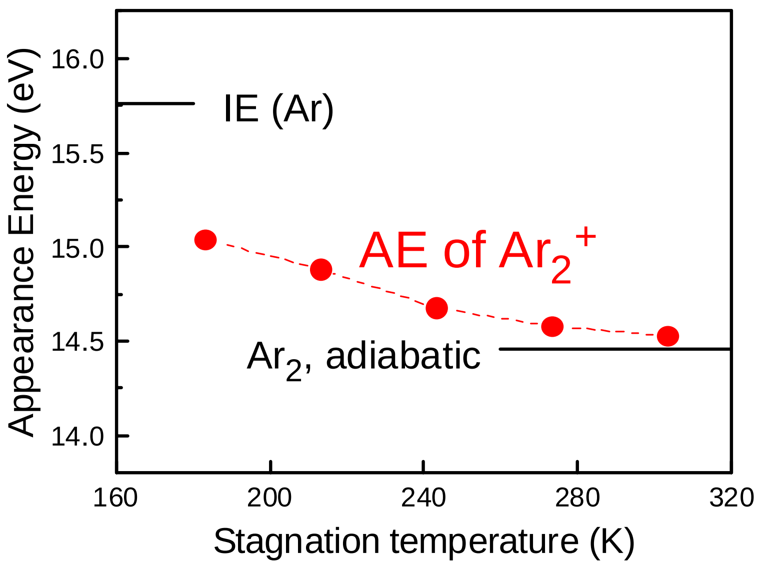

**AE($Ar_2$) depends on cluster expansion**



# Effect of expansion conditions

**Electron impact**

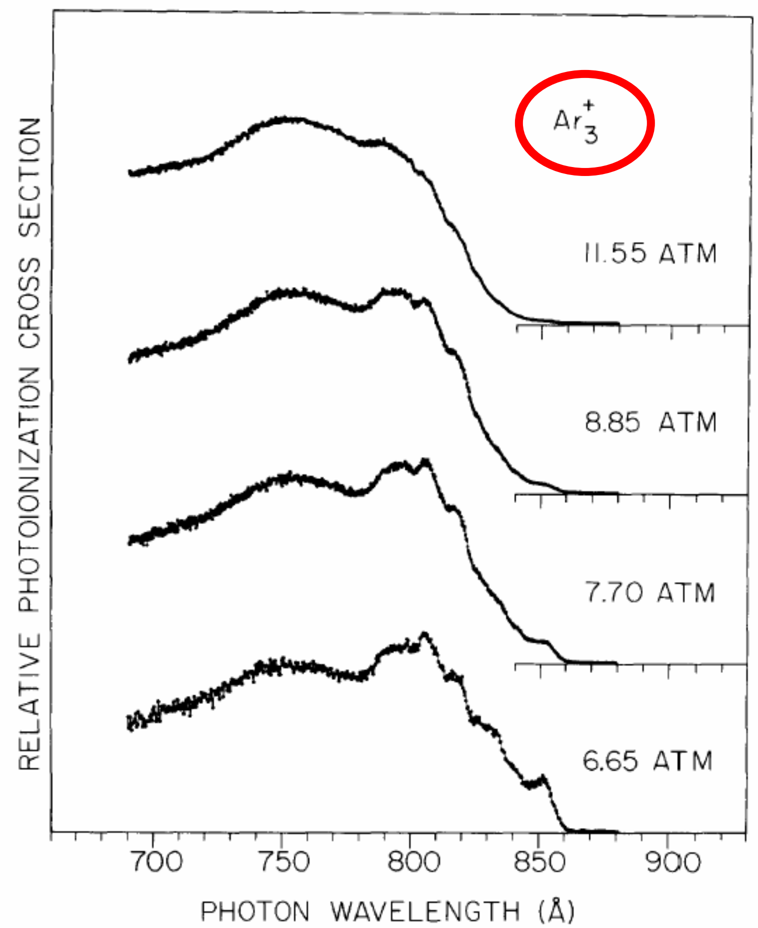
Innsbruck




smaller clusters

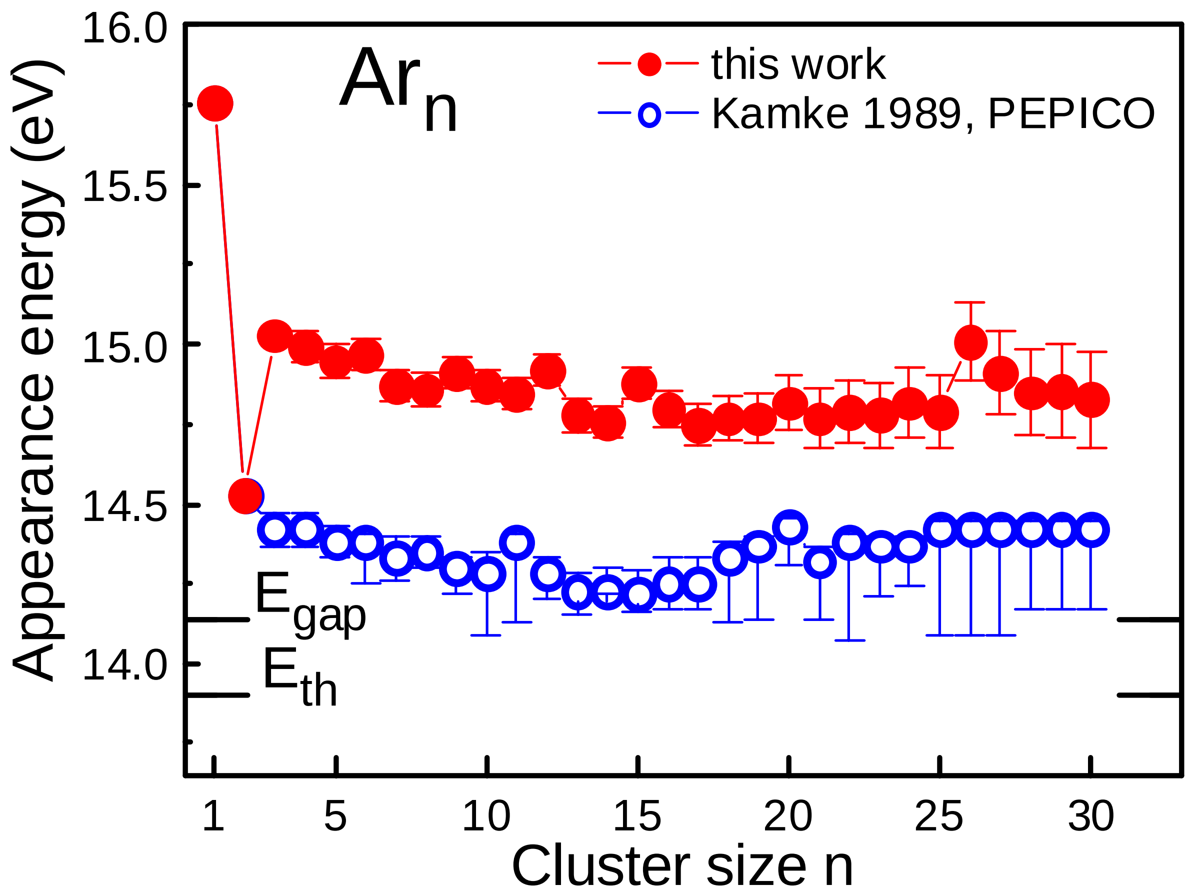
**Photoionzation**

Pratt & Dehmer, JCP 76 (1982)

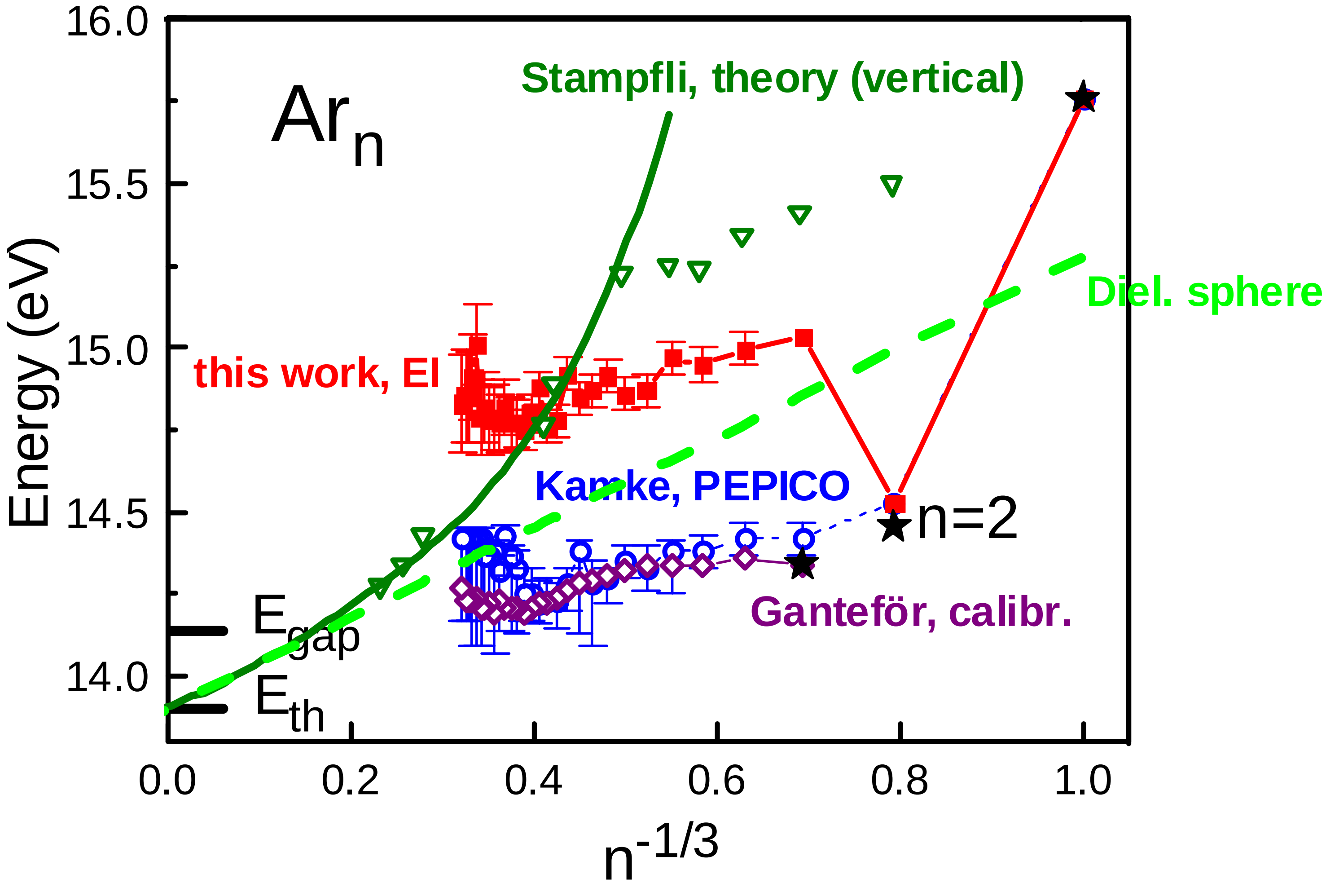



smaller clusters

# Large argon clusters

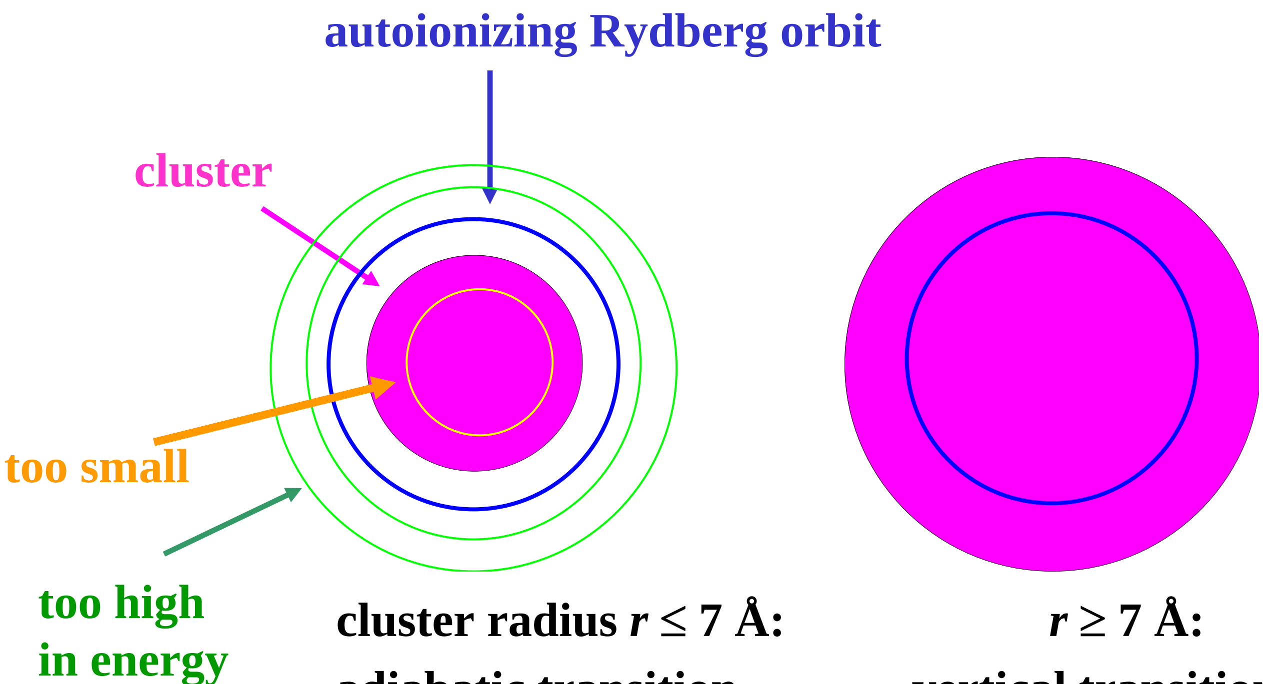


# Large argon clusters: Experiment and theory



# Predicted transition from adiabatic to vertical ionization

Stampfli & Bennemann, Ber. Bunsenges. Phys. Chem. 96 (1992) 1243



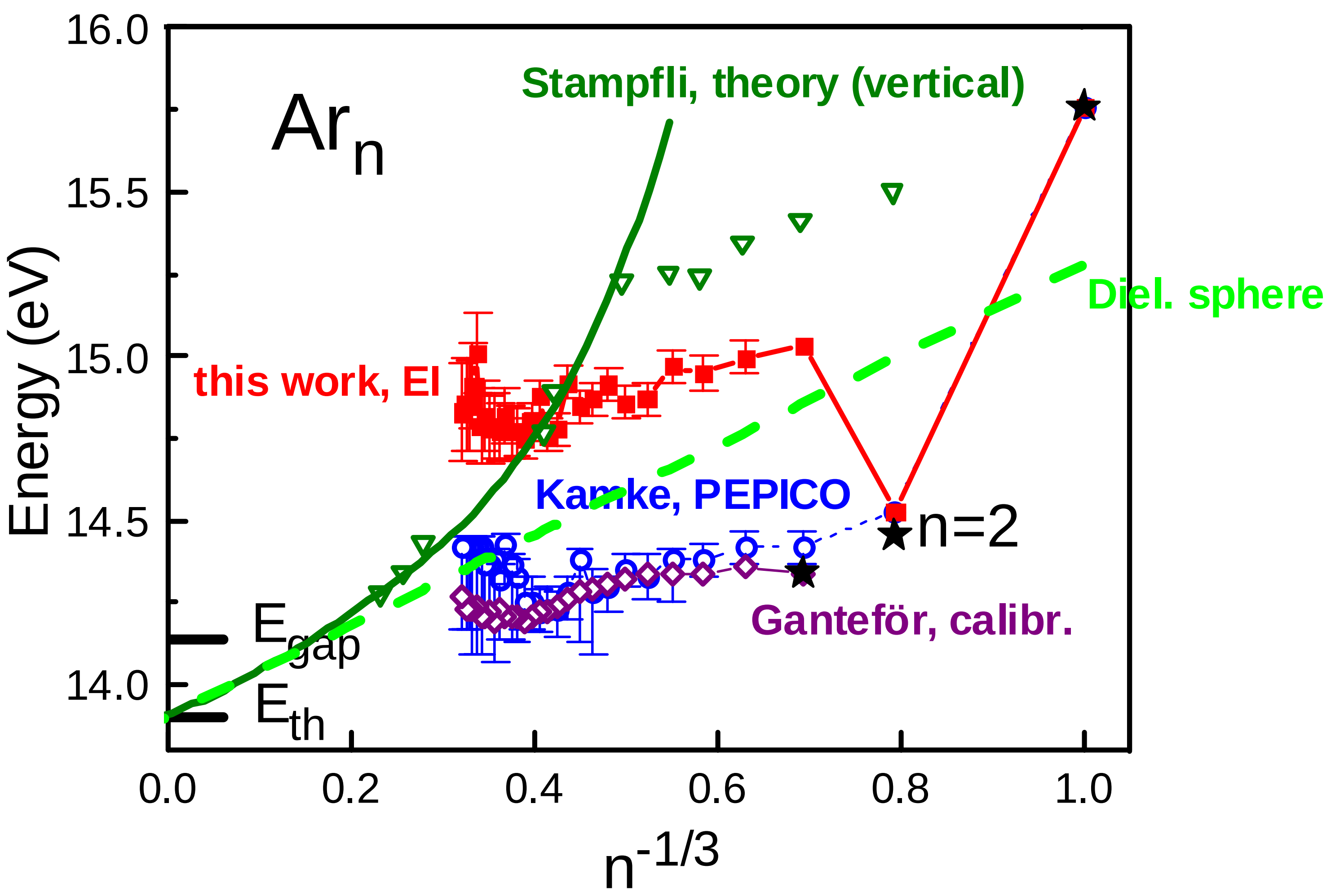

**cluster radius *r* ≤ 7 Å:**
**adiabatic transition**

***r* ≥ 7 Å:**
**vertical transition**

**Adiabatic transition via autoionizing Rydberg orbit requires:**

- **Orbit large (outside of cluster)**
- **Orbit small (at least ≈ 1 eV below vertical transition)**

# Any experimental evidence for transition?

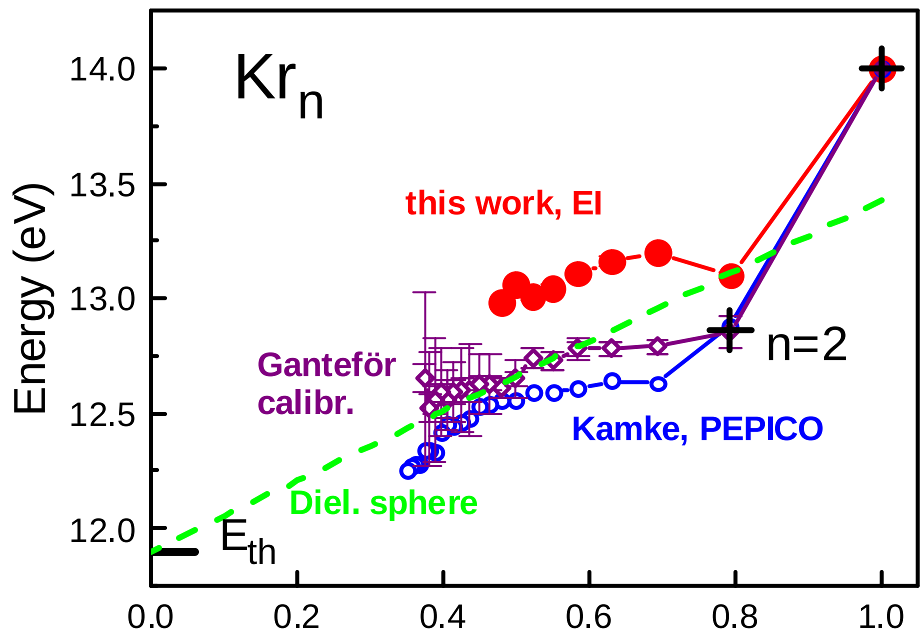


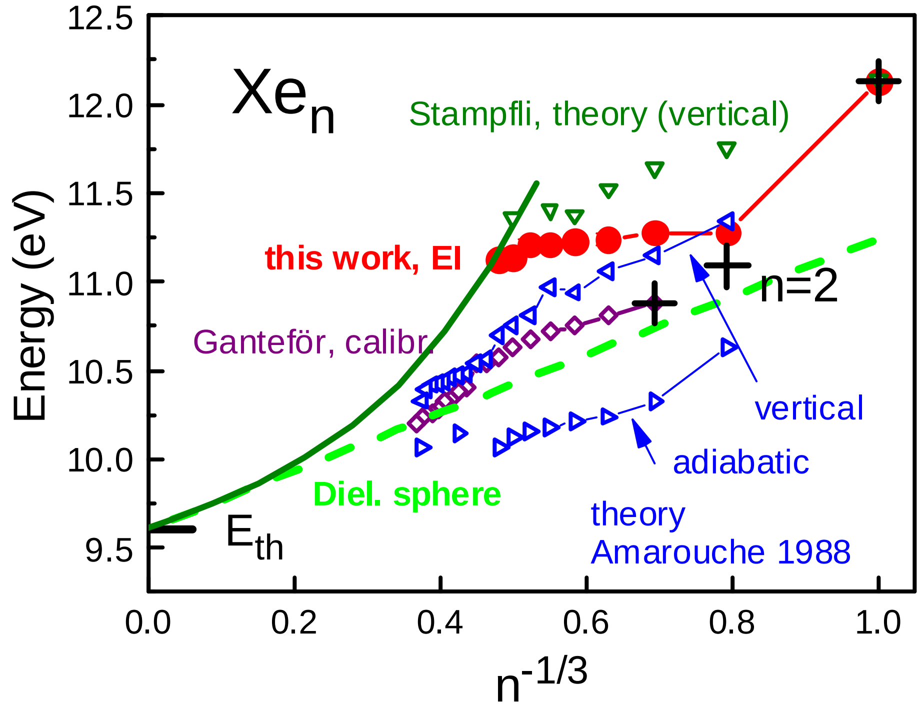
# Possible problem with concept of autoionizing states

Last and George, JCP 98 (1993) 6406, diatomics-in-ionic-systems calculations

1. The interaction in $Ar_n^*$ is very different from that in $Ar_n^+$, for $n > 2$.
2. For nearly all low-lying states, and for all cluster sizes except $Ar_3^*$, the interaction with neutral atoms is repulsive.
3. In the excited $Ar_{13}^*$ clusters, all 12 outer Ar atoms in all excited states asymptotic to the $Ar^*$ (4s) atomic states are subjected to repulsive forces...

# Krypton & xenon clusters



# Summary

1. Resolution of EI (< 100 meV) comes close to PI (30 meV)
2. For $Ar_2^+$, EI reaches adiabatic threshold even though the adiabatic IE lies 1.1 eV below the vertical IE
3. We do not quite reach adiabatic IE for $Kr_2^+$ and $Xe_2^+$
4. Hydrogen dimer $(H_2)_2 + e \rightarrow H_3^+ + H$: Neither EI nor PI reach adiabatic IE
5. Rare gas clusters Ar, Kr, Xe: No clear evidence for postulated transition from adiabatic IE for small cluster size to vertical IE for large size.
6. True adiabatic IE of rare gas clusters, $n > 4$, still unknown