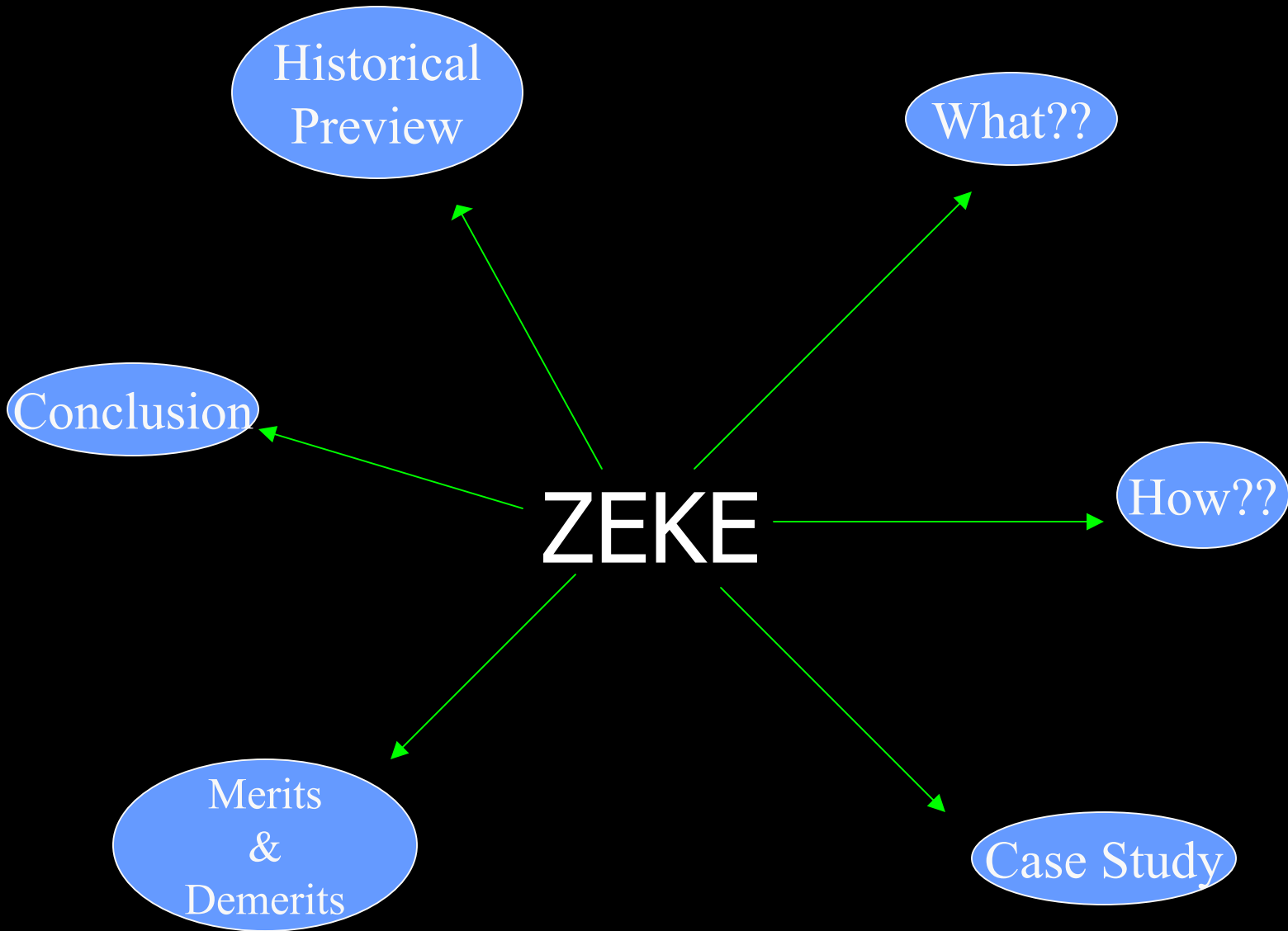


ZEKE

R.Devanathan
CY01C005



Not so long ago...



Dr. Klaus Müller-Dethlefs of TUM invented in 1984

The ZEKE Spectrometer

Now, what are these strange animals?

Molecular Rydberg states

- one e^- excited to a high principal quantum number “ n ”
- n is very large compared to the left over ion core
- have novel properties like extreme reactivity, sensitivity to fields and collisions & high probability of interaction with radiation

rovibronic states



Frank Condon Factors (FCF's)

rate of e^- transfer is much shorter than atomic motion consequently no angular Momentum is transferred to and from transition state during e^- transfer.

What is ZEKE ?

ZEKE Spectroscopy is a new very high resolution spectroscopy for molecular ions, in particular for cations

Talking of resolution....

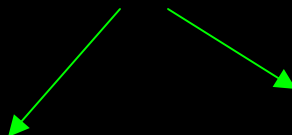
100 MHz (3 @ 10^{-4} cm⁻¹) which is about 1000 times that of conventional spectroscopic methods for molecular ions! May be attributed to the stabilization of molecular Rydberg states.

The Principle...

Monochromaticity of
Excitation source

ZEKE

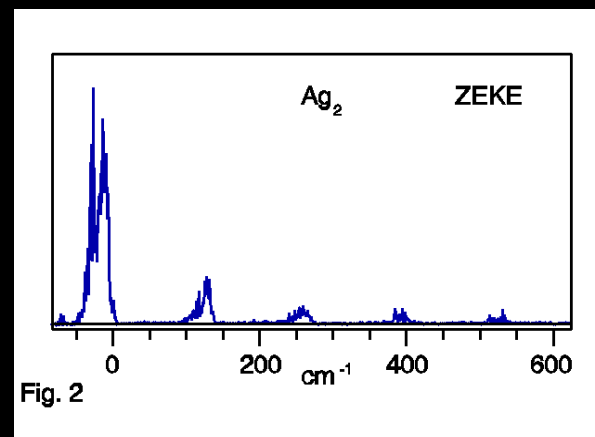
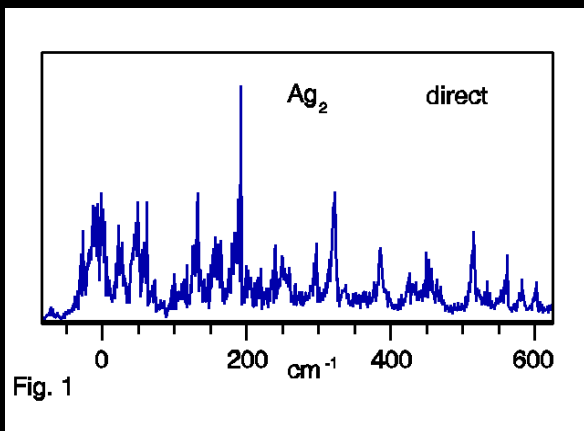
Energy of emitted
e⁻ at zero K.E



How is ZEKE different?

The Wigner Threshold law

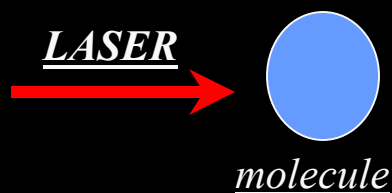
States that the threshold function for the absorption cross section to produce cations is a step function for each final state. The absorbed energy only defines a maximum energy for all states produced.



What Happens?

CASE 1

Cation 1 + ZEKE e⁻

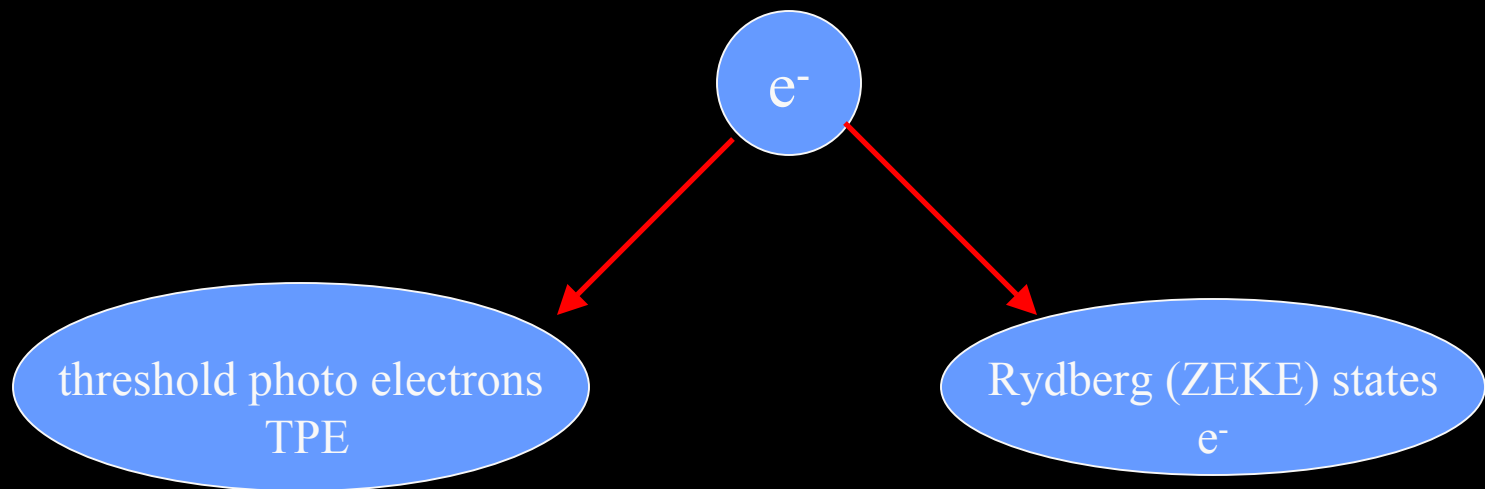


- According to Law Of Conservation Of Energy
Cation 1 > Cation 2 energy
- Probability of the the two cations being produced is given by FCF
- Case 1 leads to ZEKE spectroscopy while Case 2 is the principle behind fundamental PES spectroscopic techniques.

CASE 2

Cation 2 + Kinetic e⁻

ZEKE electrons.... a closer look !



Detection Techniques

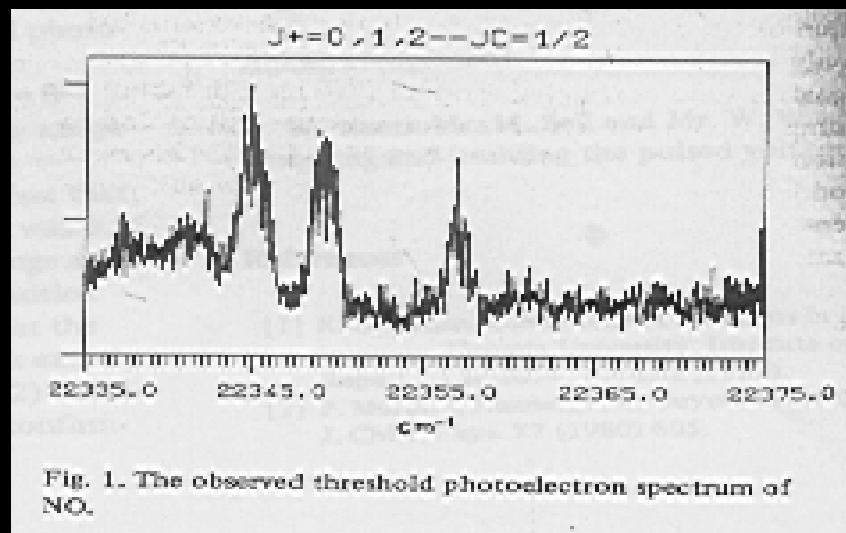
MATI or TOF

Case Studies

Our Protagonist

NO

- An important intermediate in biological as well as interstellar events.

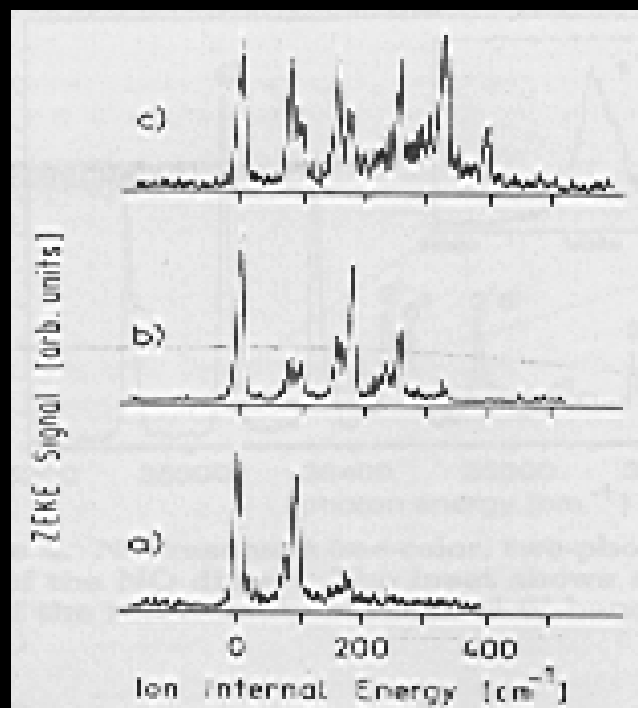


Courtesy: Klaus Müller-Dethlefs et al. *Chemical Physics Letters* Vol 112 page 292

Experimental Setup

- Temperature below 10 K.
- Pressure of 4.5 bar was employed.
- Excimer pump LASER with 2 synchronously pumped dye LASERS employed. Dye system used was coumarin 450.
- 2 LASERS are focused into the molecular beam region from opposite sides by a $f = 200$ nm lens each.

And now for the Ar- NO complex...

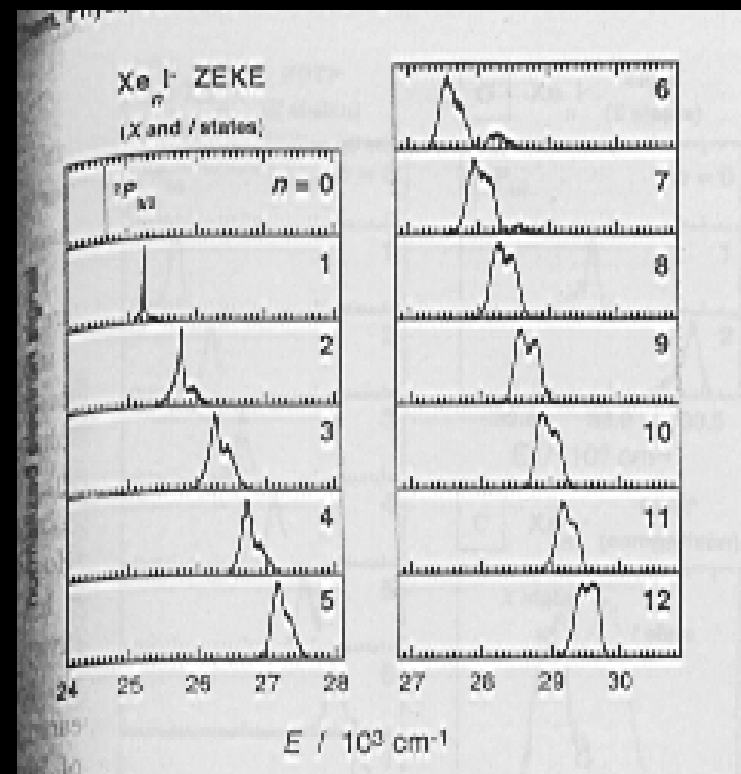
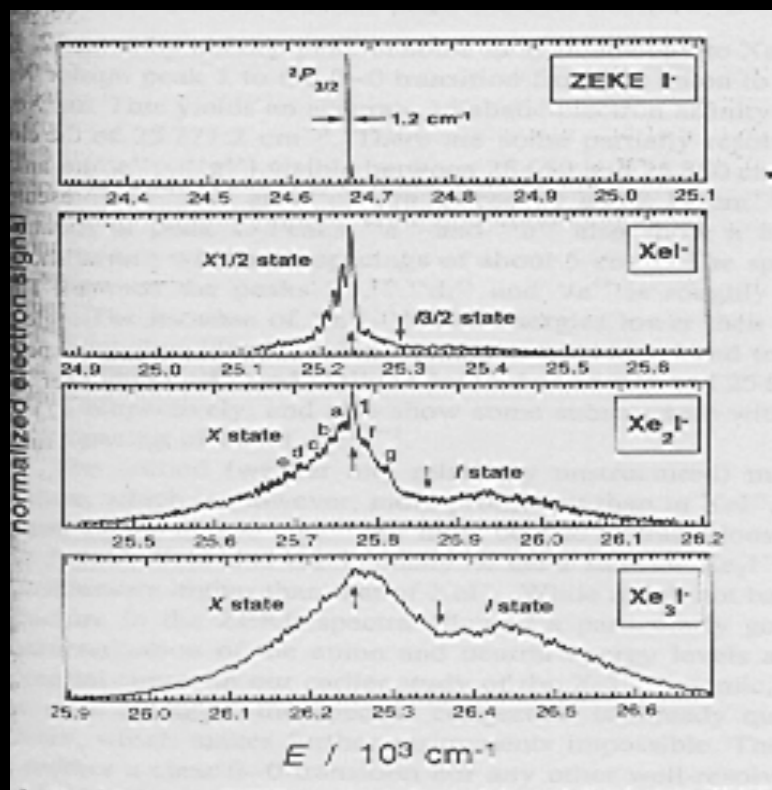


Ar

95.2° 3.711Å



And finally the anionic ZEKE study of Xe_nI^- clusters where $n = 2 - 14$



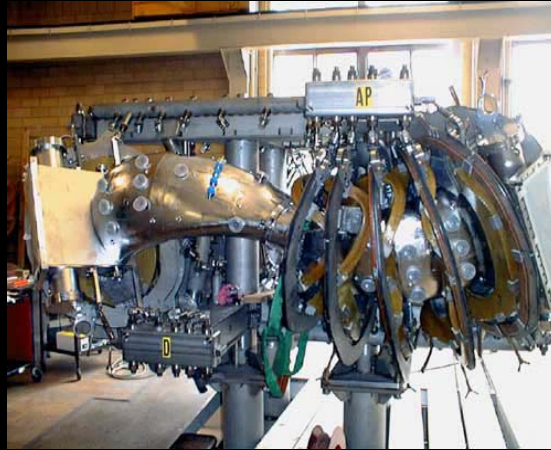
Experimental Setup

Production Of Xe_n^- anion clusters

Pass a mixture of 10 - 20 % Xe in Ar over CH_3I at 0 degrees and expand it into vacuum through a 0.5 mm aperture in a pulsed valve.

- Pressure applied 10 – 30 psi
- Anions are formed by the dissociative attachment of low energy secondary e^-
- Weak D.C field of -15 mV/cm applied across e^- detachment region at all times.
- After a delay of 200 – 500 nano seconds , the electrons are extracted co axially to the ion beam by applying a pulsed extraction field of 4 V/cm across the extraction region.

The Magnetic Bottle...



Colorful term used to describe a closed field structure for magnetic confinement of an electron perpendicular to the local field direction.

Key concepts and principles

Movement of charged particles in magnetic field , tokomak , stellarator , plasma physics.

Conclusion

- Though Xenon Iodide clusters were quoted as an example the study of anions pose a significant problem.
- Owing to high resolution and sensitivity ZEKE can be used as a probe technique for monitoring dynamical effects.
- ZEKE spectra of neutral and cationic species provide accurate data on ionizational energy and vibrational structure.

The References

- Klauss Muller Dethlefs ,Schlag W. and Michael Sander
Chemical Physics Letters, Vol **112** (1984) 291
- Klauss Muller Dethlefs & Otto Dopfer
Chemical Reviews, Vol **94** (1994)1845
- W.Schlag et al. *Journal of Chemical Physics* ,Vol **107** (1997)
- Neumark et al. *Journal of Chemical Physics* ,Vol **110**(1999)

An ode to ZEKE

.....he thought he was a ZEKE state that lined up in the sky and every time the world went by he hung his head to cry ! that one so far and far away was never meant to die.....

.....he thought he was a ZEKE state that cruised in outer space He looked again and found it was a molecular disgrace..... & then he saw it show up again and said.....everything's in place!

(Anonymity preferred!)