Analytical Instrumentation

Analytical – of analysis
Analysis – *ana + lysis*, Greek
total, whole + separating, loosing
Separating the whole into parts, by examination

Analyst, analytical, analytic, analytics,…

Reductionism

Instrumentation concerned with analysis

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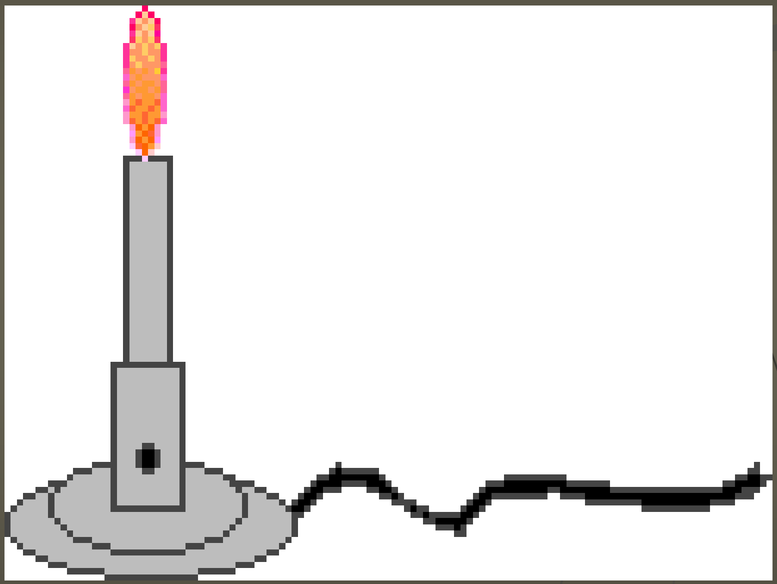
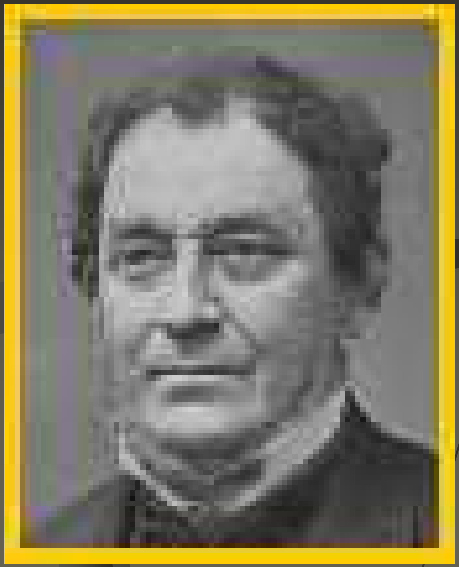
Accuracy – 10^{-6} g
Best balances – 10^{-9} g
Very best balances – single molecule

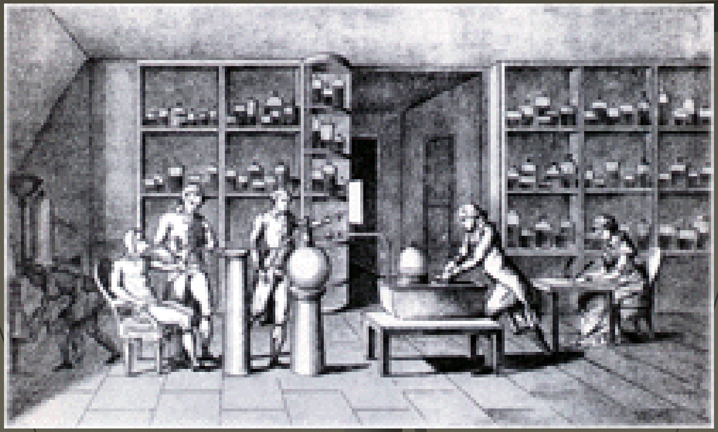
Instrumentation: a historical note





ROBERT WILHELM BUNSEN
(1811-1899)

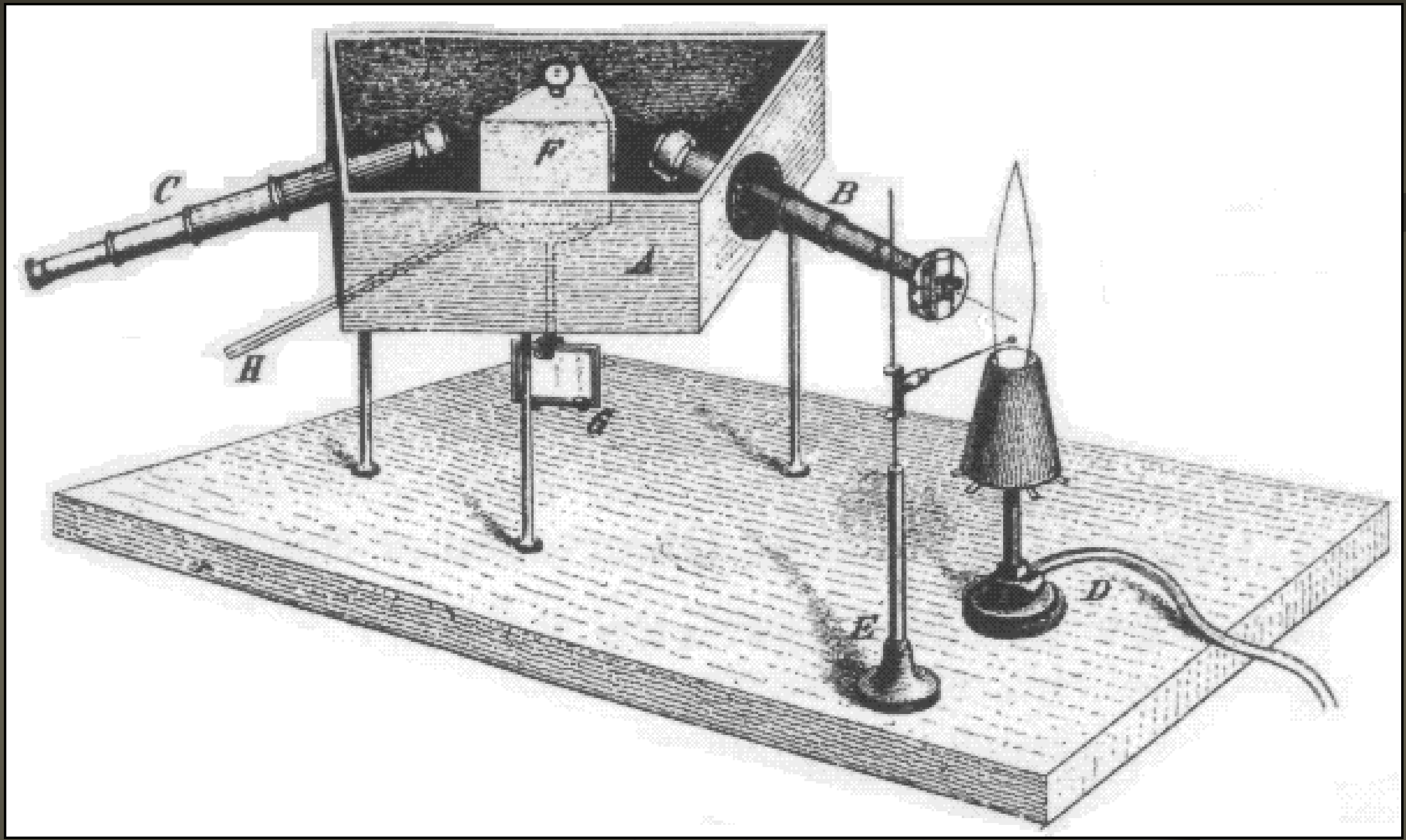
"Bunsen" burner was developed by Bunsen's laboratory assistant, Peter Desdega. Desdega himself likely borrowed from earlier designs by Aimé Argand and Michael Faraday.



Antoine-Laurent Lavoisier (1743–1794)

“Analysis and Synthesis of Air--Composition of Oxides and Acids--Composition of Water--Theory of Combustion--Respiration and Animal Heat--Permanence of Weight of Matter and Simple Substances- -Imponderable Nature of Heat and Its Role in Chemistry. “

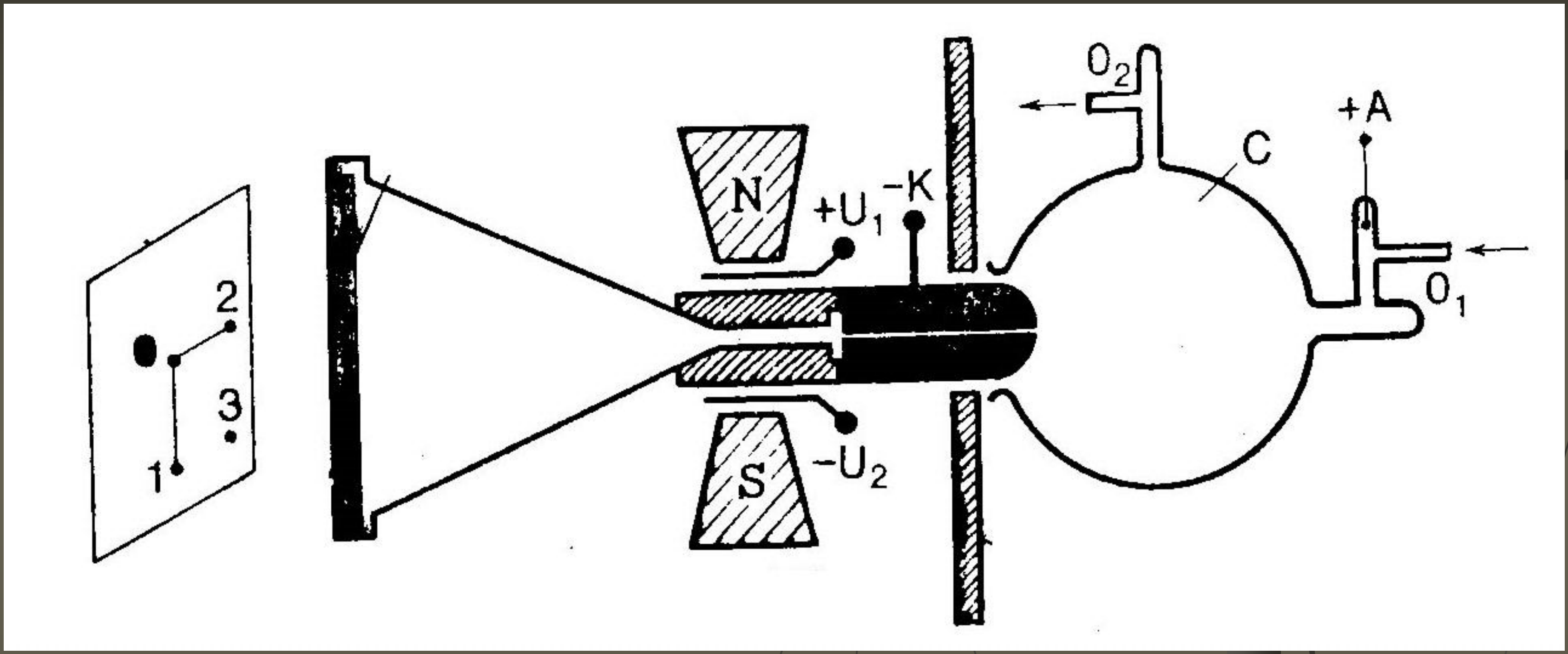
First, to assure myself that precipitated mercury per se was a genuine metallic calx, that it gave the same results, the same species of air on reduction according to the ordinary method (that is, to use the customary expression, with the addition of phlogiston), I mixed an *once* of this calx with 48 *grains* of powdered charcoal and introduced the mixture into a little glass retort of 2 cubic *pouces* or more capacity. This I placed in a reverberatory furnace of proportionate size. The neck of this retort was about a *pied* and 3 to 4 *lignes* in diameter and was bent in various places by means of an enameler's lamp in such a manner that its end was disposed beneath an ample glass bell filled with water **and inverted in a tub of the same. The apparatus which is here before the eyes of the Academy will suffice to illustrate its operation**. This apparatus, simple as it is, is even more accurate in that it has neither joints nor lute nor any passage through which the air may escape…..



Bunsen & Kircchoff spectrograph

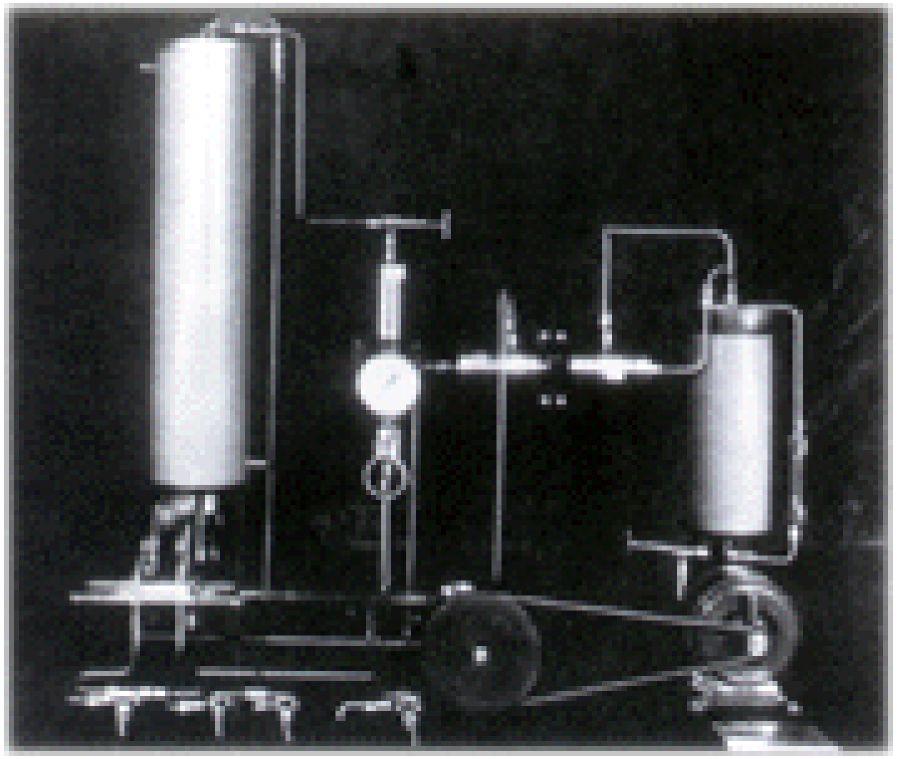
Discovered Rubidium and Cesium

Figure 3-1 shows the apparatus we used for the observation of spectra. A is an internally blackened box with a trapezoidal bottom resting on three legs; the two oblique side walls, which form an angle of about 58° with each other, carry the two small telescopes B and C. The eyepiece of the first is removed and replaced by a plate in which a slit formed by two brass edges is adjusted at the focus of the objective lens. The lamp D is arranged before the slit so that the rim of the flame is on the axis of tube B. Somewhat below the spot where the axis meets the rim, there is the end of the loop formed in a fine platinum wire, which is held by arm E. The little pearl of the dry chlorine compound to be investigated is melted to this loop. Between the objective lenses of telescopes B and C is the hollow prism F of 60° refractive angle; it is filled with carbon disulphide. The prism rests on a brass plate that can be rotated on a vertical axis.

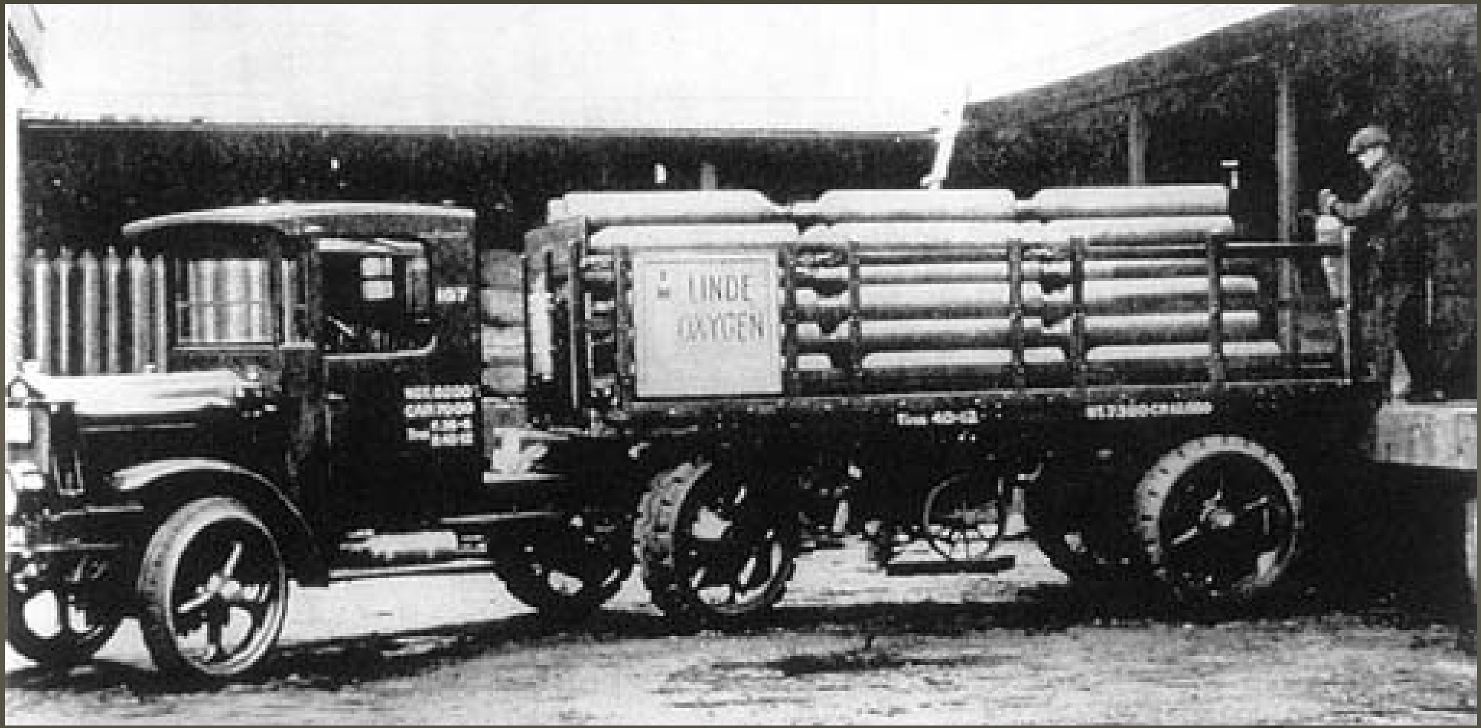


Thomson's mass spectrometer

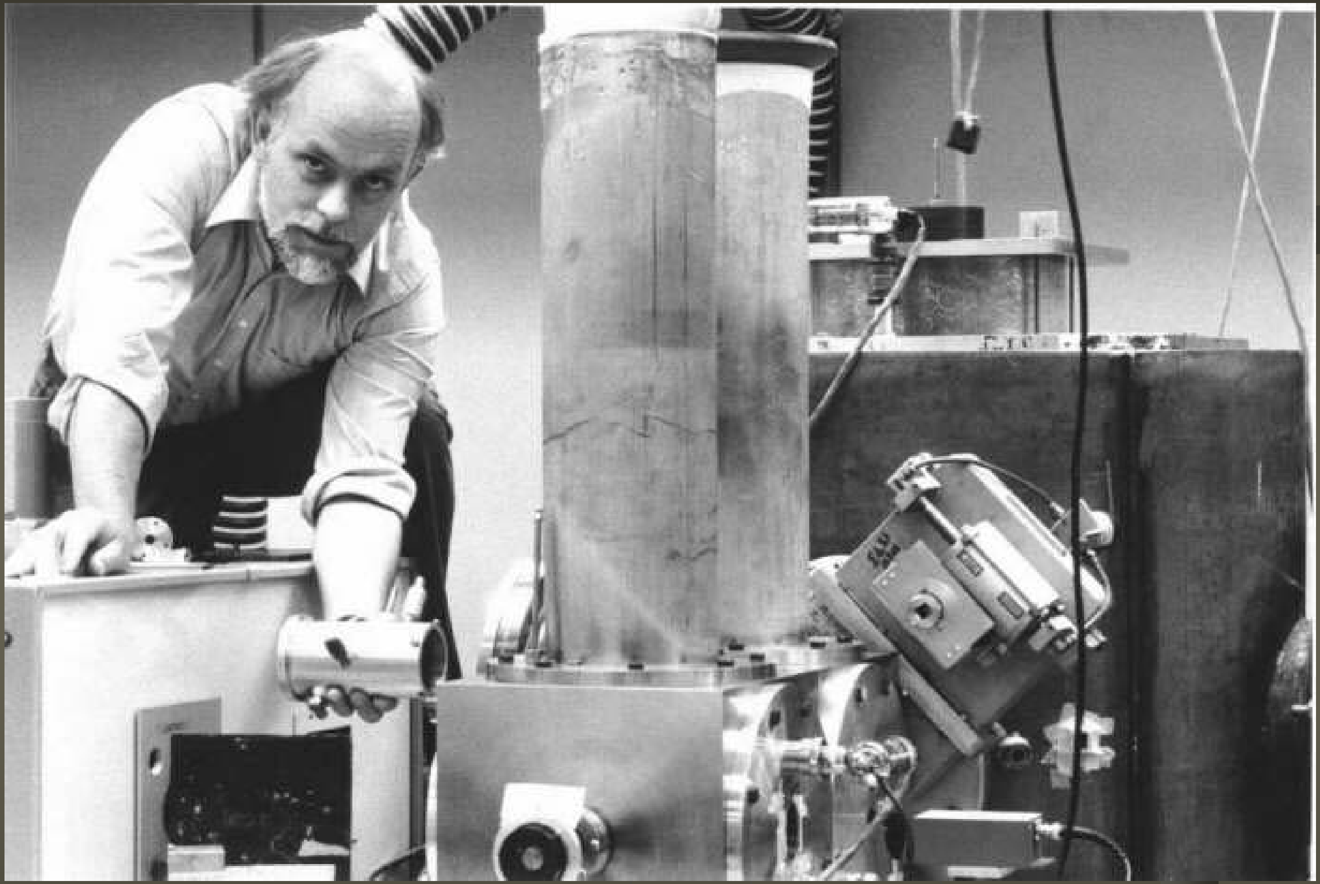
Today's machine

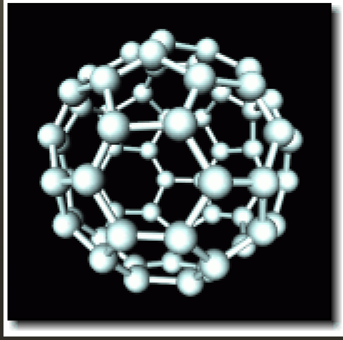


Haber's ammonia production apparatus.



Linde’s oxygen cylinders





Smalley’s machine

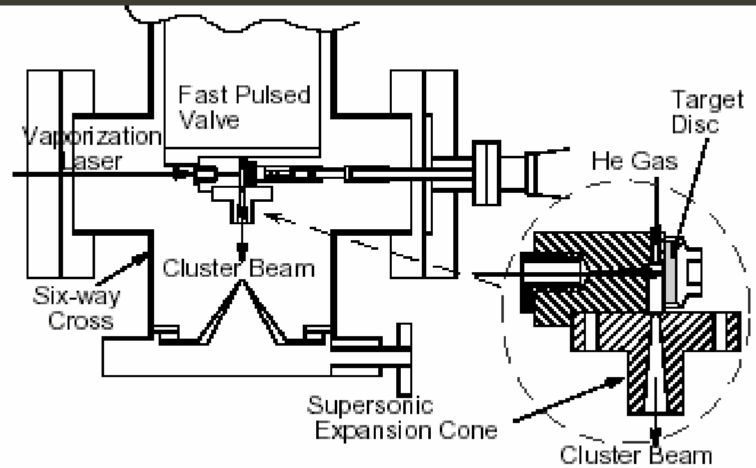


Fig. 1 Schematics of cluster beam source apparatus

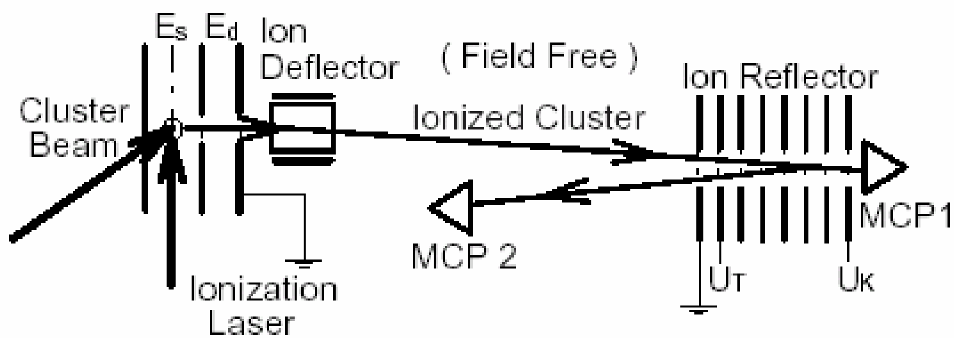
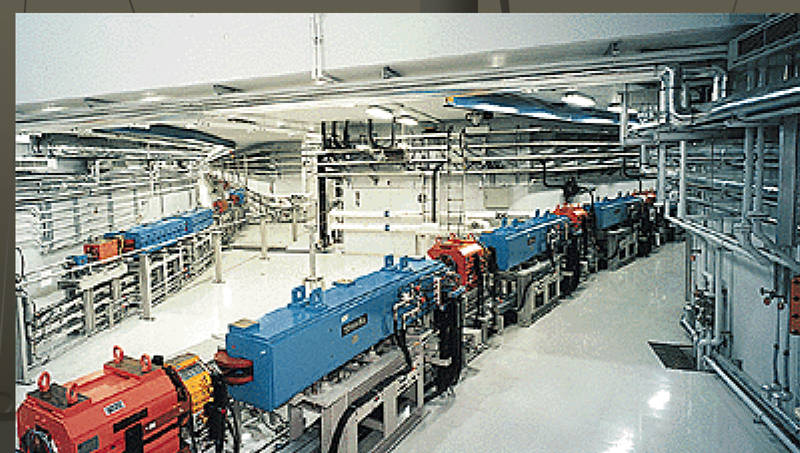


Fig. 2 Schematics of reflectron TOF mass spectrometer

A typical modern day TOF-MS lab

CERN Geneva



Real-Time Observation of the Vibration of a Single Adsorbed Molecule

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IBM Research Division, Almaden Research Center, San Jose, CA 95120

The newly developed femtosecond field emission camera was used to observe the time dependence of field emission through a single copper phthalocyanine molecule adsorbed on a tungsten tip. In many of the individual 212-picosecond-long recordings, the field emission was found to oscillate with a frequency between 5 x 10^{10} and 20 x 10^{10} hertz. The oscillations, which were not observed from a bare tip, are believed to arise from the vibration of a single molecule with respect to the surface. Numerical simulations confirmed the statistical significance of the data. SCIENCE VOL. 262 PP.1244-1247 19 NOVEMBER 1993

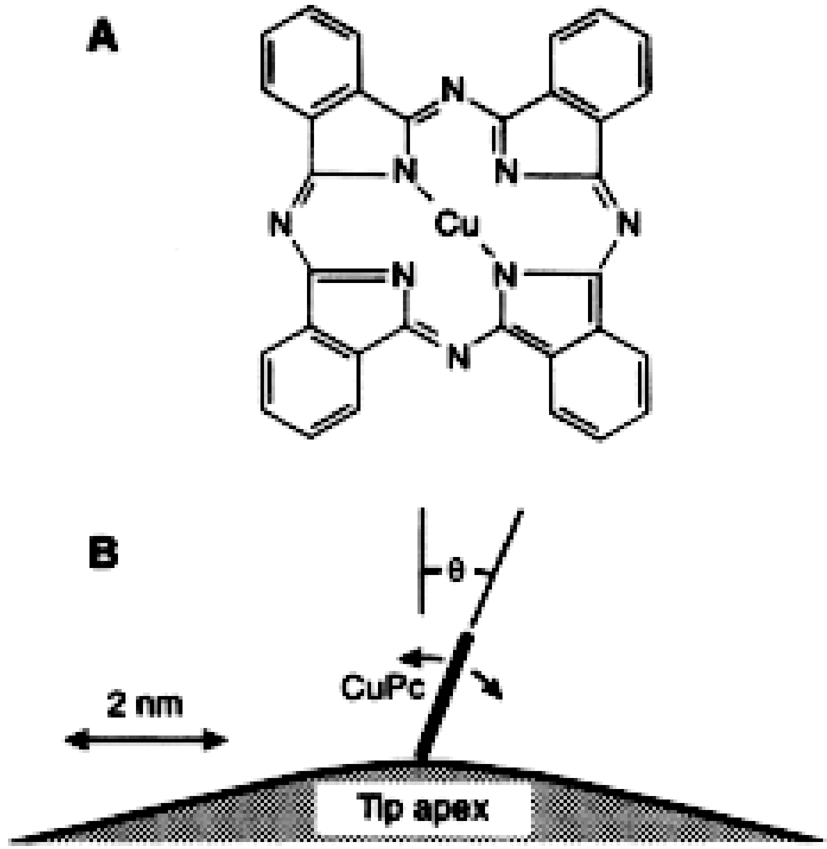


Fig. 3. (**A**) The CuPc molecule. (**B**) Schematic of a CuPc molecule (viewed edgewise) adsorbed on the end of a tungsten tip, showing a possible observed vibrational motion. The perpendicular orientation is energetically favored by high electric fields.

Summary

Science at the frontiers of discovery requires new instrumentation and experimental brilliance makes breakthgroughs. Adaptation of instrumentation to new objectives has always been central to science. The process of discovery is even more difficult today.

Instrumentation for analysis

Physical properties

- Density
- Viscosity
- Boiling point
- Melting point
- Conductivity
- Resistance
- Magnetic properties
- Thermodynamic properties

Only tools prior to 1950s

Spectroscopy

- Light based
- Electron based
- Neutron based
- Atom based

Scattering

- X-rays
- Neutrons
- Electrons

Spectroscopy

Photon based

Optical absorption spectroscopy
Fluorescence spectroscopy
X-ray absorption spectroscopy
X-Ray emission spectroscopy
Gamma ray spectroscopy
Infrared spectroscopy
Microwave spectroscopy
Electron paramagnetic resonance spectroscopy
Nuclear magnetic resonance spectroscopy NMR

Photoemission spectroscopy
X-ray fluorescence spectroscopy

Photoacoustic spectroscopy…..

Infrared spectroscopy

- Dispersive infrared
- Fourier transform infrared
  - Gas phase spectroscopy
  - Liquids
  - Long path length infrared spectroscopy
  - Atmospheric monitoring
  - Low temperature infrared
- Diffused reflectance
- Attenuated total reflectance
- Grazing incidence
- Reflection absorption infrared
- **Infrared microscopy**
- Sum frequency spectroscopy

Electron spectroscopy

Acronym	Technique
AEAPS	Auger Electron Appearance Potential Spectroscopy
AES	Auger Electron Spectroscopy
AFM	Atomic Force Microscopy
APECS	Auger Photoelectron Coincidence Spectroscopy
APFIM	Atom Probe Field Ion Microscopy
APS	Appearance Potential Spectroscopy
ARPES	Angle Resolved Photoelectron Spectroscopy
ARUPS	Angle Resolved Ultraviolet Photoelectron Spectroscopy
BEEM	Ballistic Electron Emission Microscopy
BIS	Bremsstrahlung Isochromat Spectroscopy
CFM	Chemical Force Microscopy
DAPS	Disappearance Potential Spectroscopy
DRIFT	Diffuse Reflectance Infra-Red Fourier Transform
EAPFS	Extended Appearance Potential Fine Structure
EDX	Energy Dispersive X-ray Analysis
EELS	Electron Energy Loss Spectroscopy
	Ellipsometry, see RDS
EMS	Electron Momentum Spectroscopy
EPMA	Electron Probe Micro-Analysis
ESCA	Electron Spectroscopy for Chemical Analysis
ESD	Electron Stimulated Desorption
ESDIAD	Electron Stimulated Desorption Ion Angle Distributions
EXAFS	Extended X-ray Absorption Fine Structure
FEM	Field Emission Microscopy
FIM	Field Ion Microscopy
FTIR	Fourier Transform Infra Red
FT RA-IR	Fourier Transform Reflectance-Absorbtion Infra Red

HAS	Helium Atom Scattering
HEIS	High Energy Ion Scattering
HREELS	High Resolution Electron Energy Loss Spectroscopy
IETS	Inelastic electron tunneling spectroscopy
KRIPES	k-Resolved Inverse Photoemission Spectroscopy
ILS	Ionisation Loss Spectroscopy
INS	Ion Neutralisation Spectroscopy
IPES	Inverse Photoemission Spectroscopy
IRAS	Infra-Red Absorbtion Spectroscopy
ISS	Ion Scattering Spectroscopy
LEED	Low Energy Electron Diffraction
LEEM	Low Energy Electron Microscopy
LEIS	Low Energy Ion Scattering
LFM	Lateral Force Microscopy
MBE	Molecular Beam Epitaxy
MBS	Molecular Beam Scattering
MCXD	Magnetic Circular X-ray Dichroism
MEIS	Medium Energy Ion Scattering
MFM	Magnetic Force Microscopy
MIES	Metastable Impact Electron Spectroscopy
NEXAFS	Near-Edge X-ray Absorption Fine Structure
NSOM	Near Field Scanning Optical Microscopy
PAES	Positron annihilation Auger Electron Spectroscopy
PEEM	Photo Emission Electron Microscopy
Ph.D.	Photoelectron Diffraction
PIXE	Proton Induced X-ray Emission
PSD	Photon Stimulated Desorption

RAIRS	Reflection Absorbtion Infra-Red Spectroscopy
RAS	Reflectance Anisotropy Spectroscopy
RBS	Rutherford Back Scattering
RDS	Reflectance Difference Spectroscopy
REFLEXAFS	Reflection Extended X-ray Absorption Fine Structure
RHEED	Reflection High Energy Electron Diffraction
RIfS	Reflectometric Interference Spectroscopy
SAM	Scanning Auger Microscopy
SEM	Scanning Electron Microscopy
SEMPA	Scanning Electron Microscopy with Polarisation Analysis
SERS	Surface Enhanced Raman Scattering
SEXAFS	Surface Extended X-ray Absorption Spectroscopy
SHG	Second Harmonic Generation
SH-MOKE	Second Harmonic Magneto-Optic Kerr Effect
SIMS	Secondary Ion Mass Spectrometry
SKS	Scanning Kinetic Spectroscopy
SMOKE	Surface Magneto-Optic Kerr Effect
SNMS	Sputtered Neutral Mass Spectrometry
SNOM	Scanning Near Field Optical Microscopy
SPIPES	Spin Polarised Inverse Photoemission Spectroscopy
SPEELS	Spin Polarised Electron Energy Loss Spectroscopy
SPLEED	Spin Polarised Low Energy Electron Diffraction
SPM	Scanning Probe Microscopy
SPR	Surface Plasmon Resonance
SPUPS	Spin Polarised Ultraviolet Photoelectron Spectroscopy
SPXPS	Spin Polarised X-ray Photoelectron Spectroscopy
STM	Scanning Tunnelling Microscopy
SXAPS	Soft X-ray Appearance Potential Spectroscopy
SXRD	Surface X-ray Diffraction
TDS	Thermal Desorption Spectroscopy
TEAS	Thermal Energy Atom Scattering
TIRF	Total Internal Reflectance Fluorescence
TPD	Temperature Programmed Desorption
TPRS	Temperature Programmed Reaction Spectroscopy
TXRF	Total Reflection X-ray Fluorescence
UPS	Ultraviolet Photoemission Spectroscopy
XANES	X-ray Absorption Near-Edge Structure
XPD	X-ray Photoelectron Diffraction
XPS	X-ray Photoemission Spectroscopy
XRR	X-ray Reflectometry

Instrumentation for what analysis

Molecular properties

Surface properties

Chemical composition
Adsorption
Reactivity
Magnetism

Thermal properties

Stability
Heat changes
Dimensional changes
Property changes….

Separation

Chromatography
GC
HPLC
GPC
Electrophoresis
Ion chromatography

Identification

Properties

Electronic absorption
Emission
Chemical bonds
Nuclear spin
Electron spin
Magnetic moment
….

Separation-identification

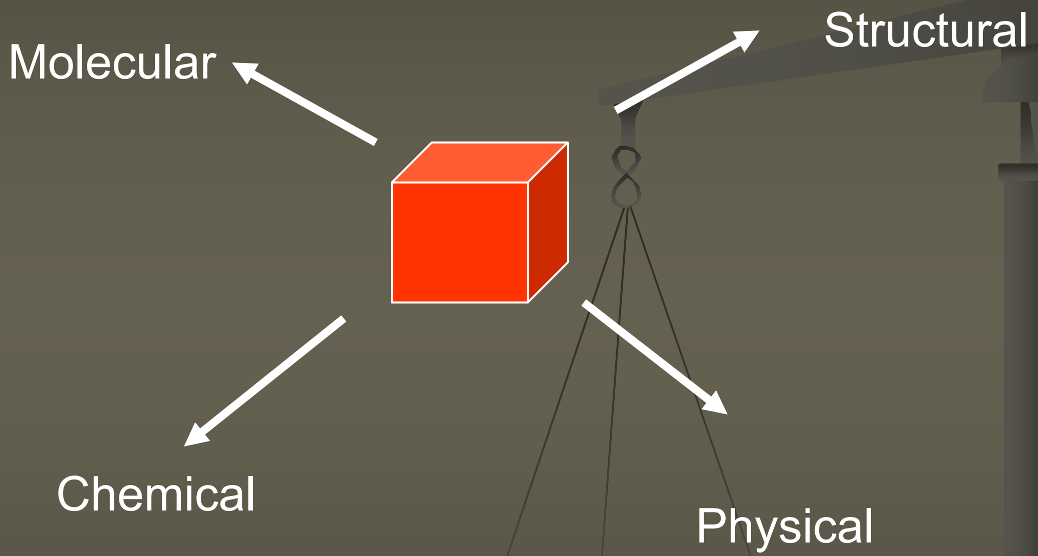
Hyphenated techniques

GC-MS
LC-MS
ICP-MS
TGA-MS
TGA-IR
....

What species you want to analyse?

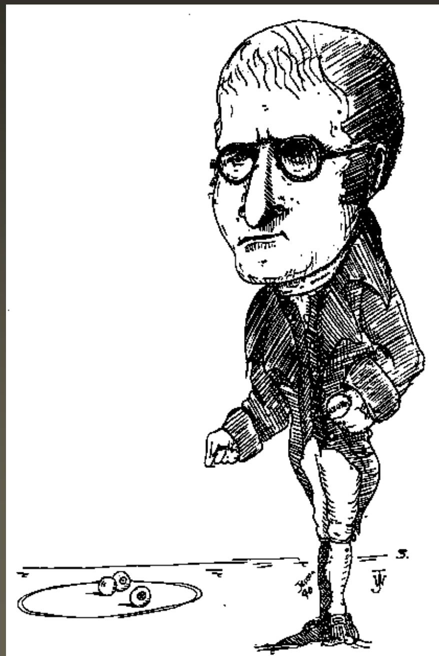
Atomic	Ionic	Molecular	Solids
AAS	Electrochemistry	Spectroscopies	XRD
AES			Spectroscopies
XRF			SIMS
XPS			Property measurements
EDAX			
WDX			

Materials possess properties



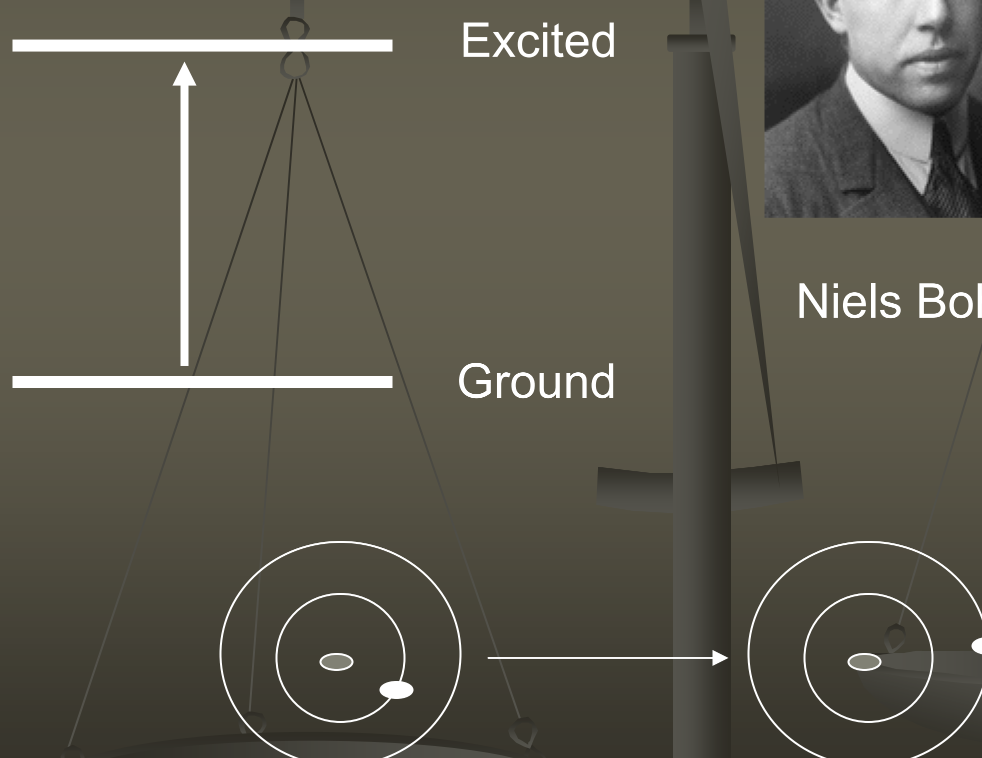
Properties can be probed

Atomic nature of matter
Quantum theory



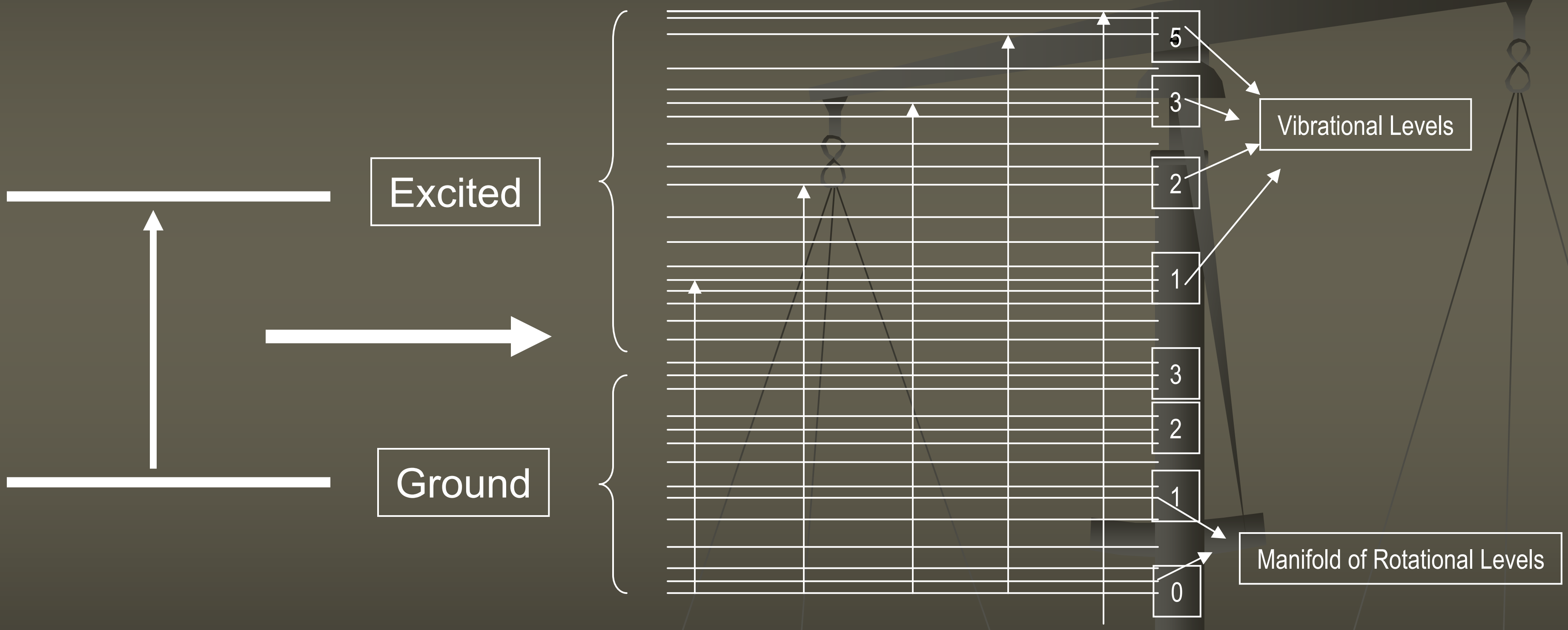
John Dalton

Johann Jakob Balmer



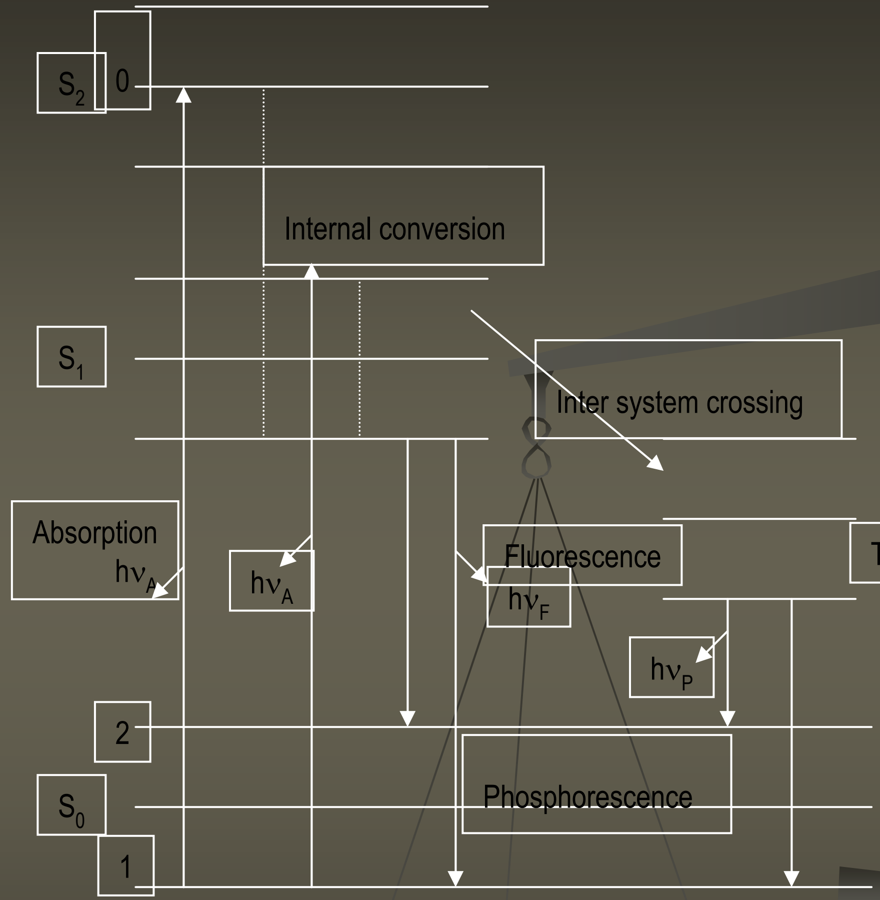
Niels Bohr

What are these energy levels?



There is a spectroscopy for every excitation

Excitation does not stay for long!



The simplified Jablonski diagram. S_o, S_1 and S_2 refer to various singlet states and T_1 represents the first triplet state.

Decay becomes another spectroscopy

Every process has chemical specificity

$C{=}O$

CO_2 CO OCS $HCHO$ CH_3CHO CH_3COOH CH_3CONH_2 CH_3COCH_3

But...not enough!

Phase specific

Conformation specific

Structure specific

Medium specific

....

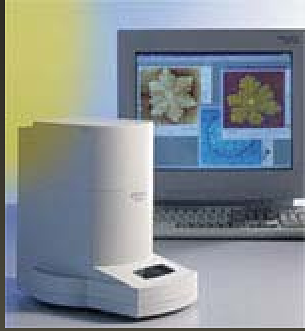
....

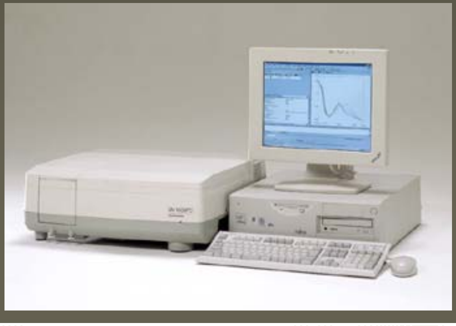
Look….

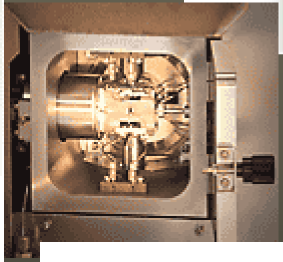
What has happened to

The balance of Laoiviser!


LAB CENTER

RF-1501




GC-17A