Criteria for Selection of Well-Validated Atomic Data

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There are large number of papers on measurement and computation of

- **Oscillator strengths**
- **Radiative lifetimes**
- **Line shapes**
- **Line shift**
- **Energy levels**
- **Ionization energy for neutral and ionized atoms**

Also, adequate data is available on electron and photon impact of molecules leading to processes like

- **Excitation**
- **Dissociation**

CONTINUED

Ionization
Dissociative ionization
Electron attachment
Photoionization
Photodissociation…….

All these data are needed
***to give better insight regarding different phenomena**
***to help in putting forward better explanations and mechanisms.**

CONTINUED

***All these data need to be validated for accuracy.**

***But unfortunately, it is not being done systematically as the criteria for rejection of data followed in the process have not been used in a consistent manner.**

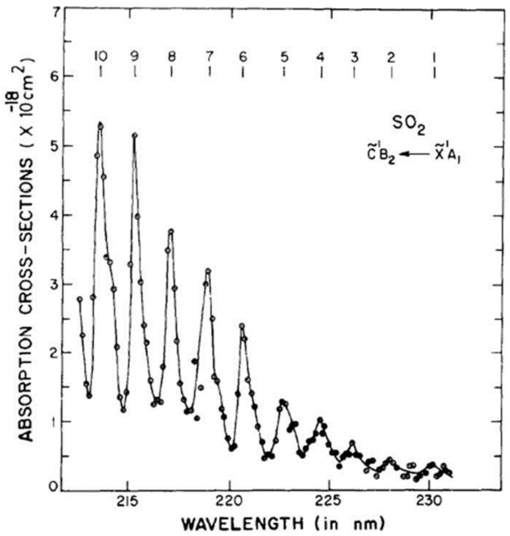
*** That is why we have to ascertain and fix these criteria once for all**

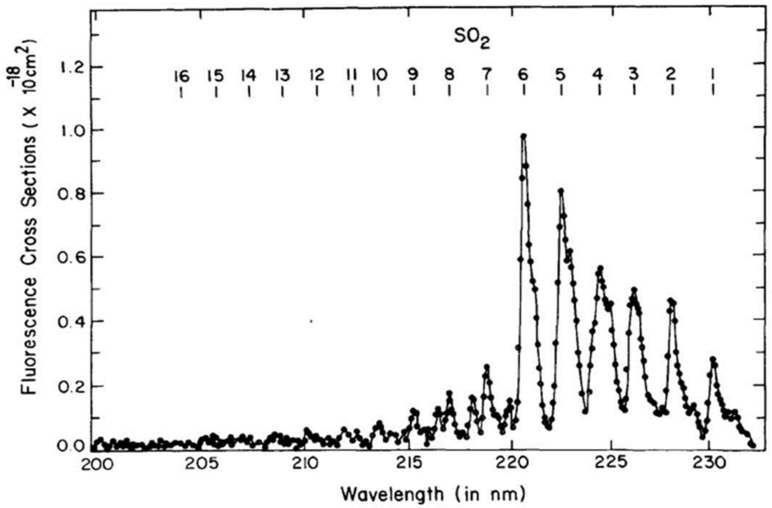
1. Absolute Cross Section versus Relative Measurement

- **Relative measurements normalized at one/two incident energies**
  - ⇒ Not to be considered for evaluation
  - ⇒ Reason is obvious
    - ⇒ Normalization factor at one energy may not be the same at other incident energies
    - ⇒ Would lead to wrong results

- **Absolute cross sections should only be considered for evaluation and validation.**

Top: Photoabsorption cross sections▸▸Absolute
Bottom: Fluorescence cross sections ▸▸Relative: Normalized at band 2 (228nm); Fluorescence quantum efficiency = 100% as reported by Hui and Rice (1972):Occurrence of Predissociation:Threshold wavelength 218.9-220.6nm





2. EXPERIMENTAL DATA VERSUS THEORETICAL COMPUTATION

- **It is strongly believed that experimental data should be preferred to one obtained by theoretical computation.**
- **Why???**
- **This is mostly true for polyatomic molecules where target wave functions cannot be represented unambiguously.**
- **Cross section calculations for diatomic molecules, both homo-nuclear and hetero-nuclear, can be obtained with higher accuracy as the target wave functions can be exclusively defined.**

3. Single Data

- **What happens if only single set of data is available for a given parameter?**
- **Such data may only be considered if**

  ⇒ **repeatability is ensured in the measurement.**

  ⇒ **credibility of the researcher is well established.**

  ⇒ **measurements are obtained by using proven technique.**

4. CROSS CHECKING USING TWO DIFFERENT TECHNIQUES

- **Measurement/computation of cross section if made by two different techniques can be used as a cross check on one another and also on theory.**
  - **Example:**
    In DEA to vibrationally excited molecules: excited molecules can be produced by thermal excitation, laser excitation, electron beam excitation
  - **Example:**
    Total electron scattering CS at low electron energies: i)beam attenuation ii) electrons first momentum selected; then beam attenuation iii) momentum transfer: at least reproduction of shape of the cross section curve

5. Cross section measurement at discrete impact energies

- **Cross section measurements carried out at discrete electron/photon energies and not in a continuous range of energies should be avoided for evaluation and further validation even though innovative approach may have been used to obtain the required data.**
- **Why???**
- **There is a possibility that some finer structure in the cross section curve in between the two discrete incident energies may have been missed because of this inadequacy.**

5. CONTINUED

- **Example: Total electron scattering cross section measurement of atoms/molecules in gas phase at low electron energies using a photoelectron source**

  {Subramanian and Kumar, 1990}.

. **Line radiation {HeI: 58.4nm; NeI: 73.6 and 74.4nm}**

. $h\upsilon(58.4nm) + Ar \Rightarrow Ar^+ (^2P_{1/2}) + e(5.28eV)$

$$\Rightarrow Ar^+ (^2P_{3/2}) + e(5.46eV)$$

Ar, Kr, Xe and 73.6 and 74.4nm gives 18 electron energies.

. **And also**

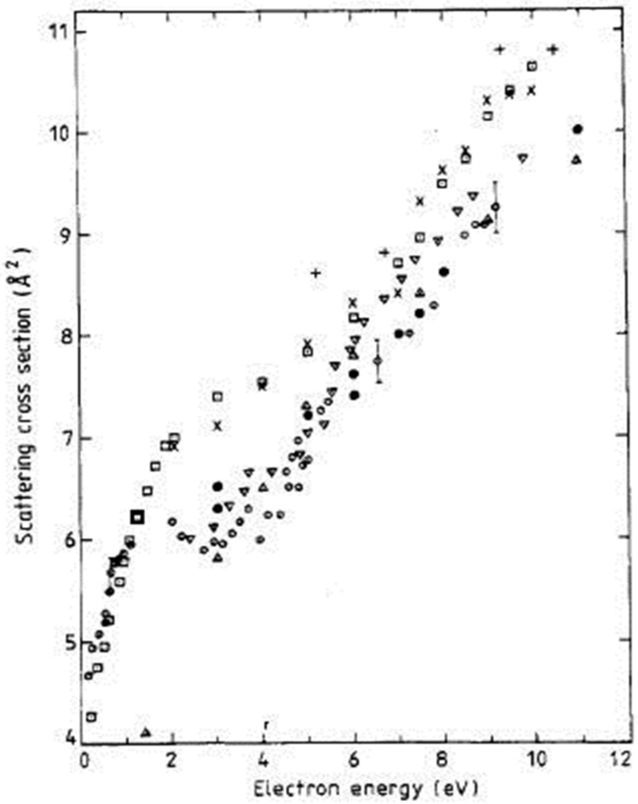
$h\upsilon(73.6nm) + O_2 \rightarrow O_2^+(a^4\Pi_u , \upsilon=2, 3, 4, 5)$

$$+ e\ (0.50, 0.38, 0.26.\ 0.15eV)$$

5. Continued

- **38 electron energies ranging from 0.15 to 9.14eV**
- **No energy points are available from 1.09 to 2eV.**
- **This technique of using photoelectrons have advantage over electrons produced by electron guns.**
- **But, we can't scan electron energies continuously and are liable to skip some important information, if any, between two discrete electron energies.**
- **Such measurements can't be included for validation of cross section data.**

5. CONTINUED



This technique can be revived using synchrotron radiation.

6. Effusive molecular beams versus supersonic beams in collision experiments

- **In most of the electron impact studies of molecules, cross sections have been obtained using effusive molecular beams.**
- **We get high resolution results but the cross sections include contribution from vibrationally excited states also.**
- **How???**
- **Effusive beams can be produced by**

  .. A single capillary tube

  .. A capillary array

Buckman et al.(1993) demonstrated superiority of capillary array whenever a spatially well defined molecular beam is required.

6. Continued

- **Let us take the example of PES of a molecule produced by a HeI(58.4nm) line. The observed resolution ΔE(FWHM) of a PE peak is given by**

$\Delta E = [\delta_{theory}{}^2 + \delta_{photon}{}^2 + \delta_{Doppler}{}^2 + \delta_{rotation}{}^2 + \ldots]^{1/2}$

where δ_{theory} is the theoretical spectrometer resolution and δ_{photon} , $\delta_{Doppler}$ and $\delta_{rotation}$ are the contributions to the peak width from the line broadening in the light source, from Doppler broadening and from rotational excitation (Dehmer and Dehmer, 1979) of the target gas. Broadening of the photon line is caused by self-absorption by He atoms.

6. Continued

- **Doppler broadening can be reduced by lowering the kinetic energy of the ejected photoelectron or by reducing the temperature of the target molecule.**
- **Doppler broadening at 300K ~ 7.7meV**
- **Doppler broadening at 15K ~ 1.7meV**
- **Rotational broadening is a complicated function of temperature, rotational constants, symmetries and angular momenta of the upper and lower states.**
- **Taking B as 10cm^{-1} for a molecule,**

  Rotational broadening at 300K ~ 27meV

  Rotational broadening at 15K < 4meV

So, both broadenings are greatly reduced by lowering the temperature.

6. Continued

- **Lowering of temperature**
  1. **By use of supersonic expansion**
  2. **By cryogenic cooling**

     ⇒ Results in condensation long before significant cooling occurs

Can work with a much higher resolution using a supersonic molecular beam.

Major factor:

At 300K, most of the target molecules are in υ=0 state but population of higher vibrational state is not negligible.

6. CONTINUED

- **But electron impact cross sections for υ >0 are extremely large.**
- **DEA cross sections (in cm^2)**

υ	H_2	D_2
0	$1.6x10^{-21}$	$3.0x10^{-24}$
1	$5.5x10^{-20}$	$1.5x10^{-22}$
2	$8.0x10^{-19}$	$3.3x10^{-21}$
3	$6.3x10^{-18}$	$4.2x10^{-20}$
4	$3.2x10^{-17}$	$3.6x10^{-19}$

So, all electron impact cross section measurements made using effusive molecular beams have contributions from both υ=0 and υ >0 excited levels.

So, measurements should be made at lower temperatures using supersonic molecular beams where the contribution is only from υ=0 level.

6. CONTINUED

Cross sections obtained by supersonic molecular beams cannot be made absolute using the traditional relative flow method as is done while using effusive molecular beams.

Alternative method for normalization of electron collision cross sections using SS jet beams has now been suggested by Hargreaves et al. (2007).

7. Example of High Temperature Plasma Spectroscopy

- High temp. plasma spectrum from Tokamak extends from X-rays to Infrared.
- A typical spectrum is very complex as line radiation from so many radiating species is present.
- Each impurity atom is distributed throughout the tokamak plasma from the hot core ($T_e \geq 100$eV) to the cooler edge ($T_e \geq 10$eV).
- All ionization stages of a given impurity atom (C, O, N, and metals from the wall and PFCs) are present in the core.
- Plasma edge is the origin of contamination.
- But, plasma temp. and density at the edge are poorly known.

7. Continued

- **To measure number density of the impurity atom, one needs to measure the intensity of the line radiation absolutely. Line radiance due to the transition (pq) defined as number of photons cm^{-2} $s^{-1}sr^{-1}$ is given by**

$$^{z}B_{p,q}=\frac{\Gamma_{p,q}}{4\pi}(n_e)_{av}\,{}^{z}Q_{1,p}\int_0^a n_z\,dr$$

Here, $^{z}Q_{1,p}$ is the excitation rate coefficient from the ground state to the upper level p, $\Gamma_{p,q}$ is the branching ratio of this upper level for the transition considered and $(n_e)_{av}$ is the average electron density. Here, $^{z}Q_{1,p}$ is considered to be independent of electron temperature. This way, n_z, the number density of the zth ionization state can be determined.

7. Continued
How do we measure absolute intensity of line radiation accurately?

Standard primary source

⇒Blackbody radiators (Spectral coverage as per temp. of the BBR)

⇒Continuum emission from a hydrogen plasma (53-92nm; 124-360nm)

⇒Synchrotron radiation

Standard primary detector

⇒ Photoionization chamber (25-102.2nm)

⇒ High Accuracy Cryogenic Radiometer (HACR)(X-rays to Infrared)

[Gentile et al., 1996)].

7. CONTINUED

- **Out of the primary and transfer source standards, synchrotron radiation is the only one which covers the spectral range from X-rays to Infrared.**
- **But this primary source can't be transported to the place of experiment.**

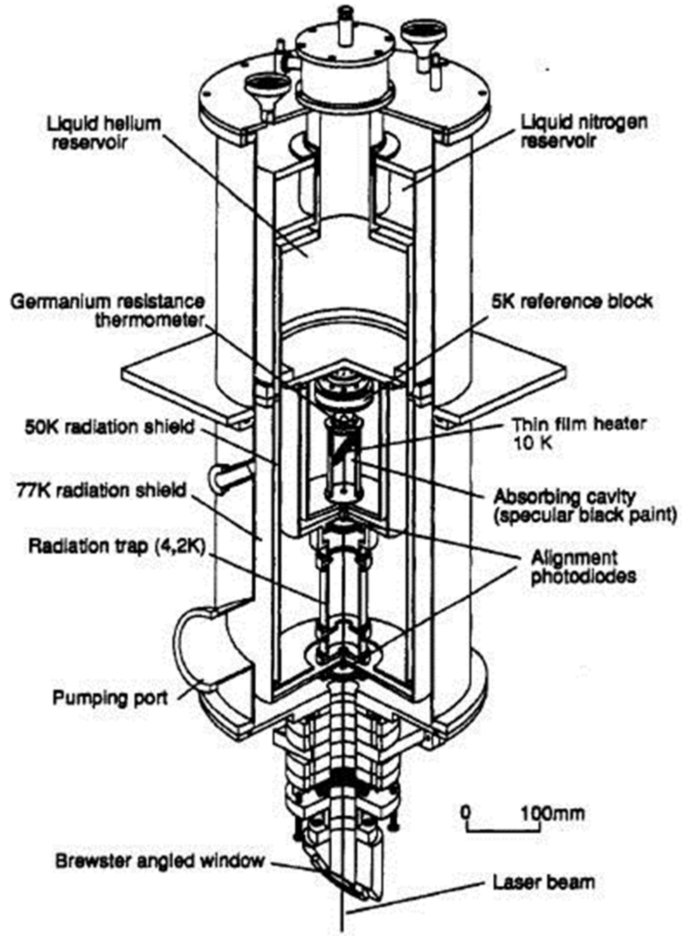
- **Out of the primary and transfer detector standards, HACR covers from X-rays to Infrared and is easily transportable.**
- **HACR can be safely used for optical power measurements.**

7. CONTINUED HACR

- Large copper cavity
  ⇒ Heat capacity of copper is reduced by a factor of 1000 from 300 to 5K.
  ⇒ Gives smaller time constant at 5K.

Heating is first performed with the optical power i.e. from the incident line radiation.

Magnitude of this power is determined by finding the electrical power, which yields the same temperature.



7.CONTINUED

- **Conclusion**

1. Seeing the utility of measurement of absolute intensity of line radiation in tokamak discharge, it is definitely required to attach a radiometry laboratory to the tokamak research centre.

2. HACR or an improved radiometer, the Primary Optical Watt Radiometer (POWR), again made