Evaluation of Cross Section Data

- a personal experience -

Y. Itikawa

Review and compilation of cross section data for electron collisions with molecules

N_2 JPCRD 35, 31 (2006)

O_2 JPCRD 38, 1 (2009)

H_2 JPCRD 37, 913 (2008)

CO_2 JPCRD 31, 749 (2002)

H_2O JPCRD 34, 1 (2005)

JPCRD=J. Phys. Chem. Ref. Data

Process of data compilation

- literature survey
- collection of numerical data
- evaluation of the collected data
- recommendation of the best values

“Data evaluation” is the most important but most difficult part. We have no standard method of it.

For data evaluation,
the following points should be taken into account:

(1) Quoted uncertainty
(2) Agreement among the data obtained by different authors / methods
(3) How the absolute values were determined
(4) Physics involved
(5) Consistency between related but different quantities

(1) Quoted uncertainty

Most of the experimental people estimate
and report the error (uncertainty) of their result.

Primarily we consider those quoted uncertainties.

But the cited error is the **statistical** one.
We should ask:

How much is the **systematic** error ?

To see **the systematic error**, we consider

(2) Agreement among the data obtained by different groups of authors

$e + O_2$

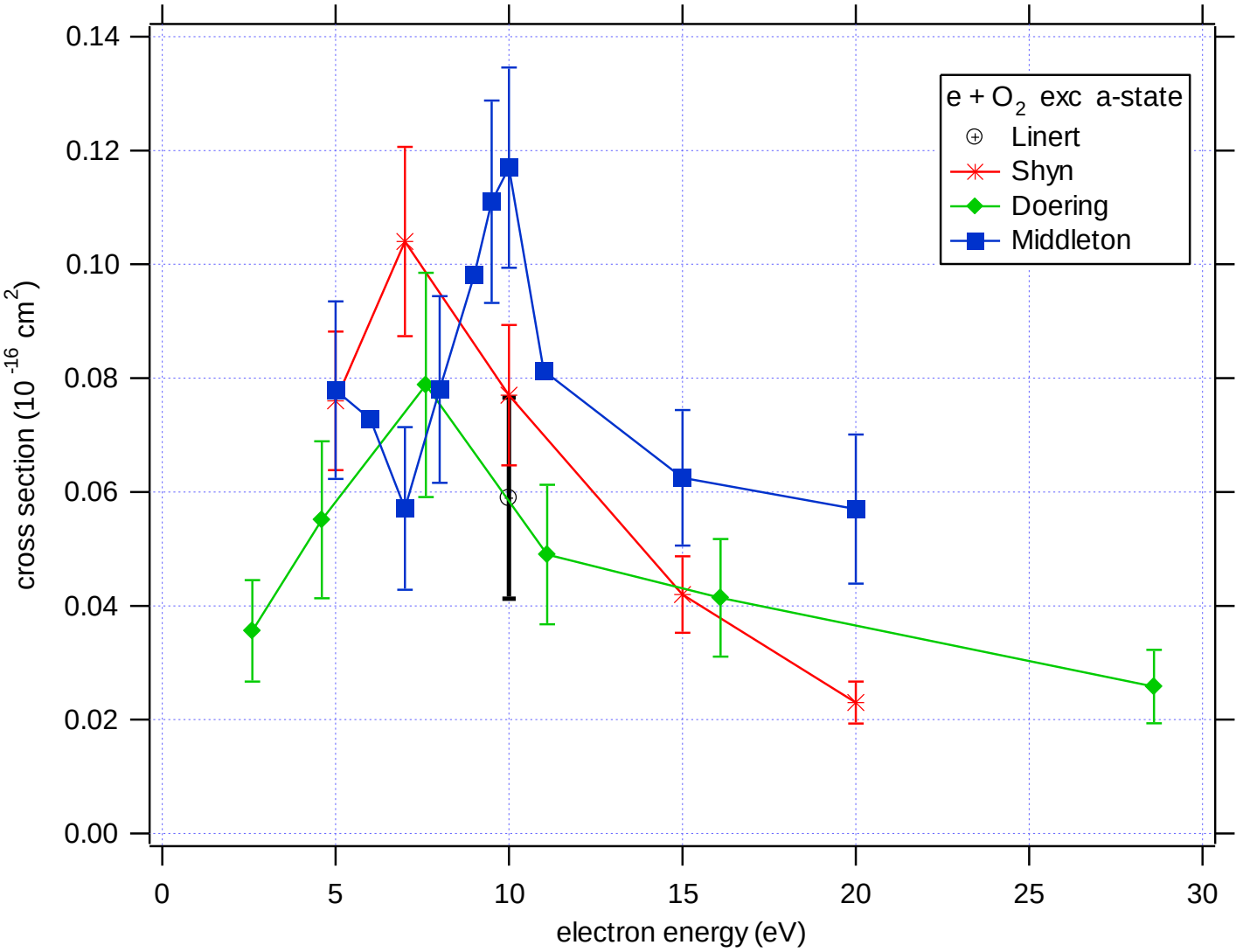
excitation of a $^1\Delta_g$ state

Middleton, Phys. Rev. Lett. 69, 2495 (1992)

Doering, J. Geophys. Res. A 97, 12267 (1992)

Shyn, Phys. Rev. A 47, 1006 (1993)

Linert, Chem. Phys. Lett. 429, 395 (2006)


e + O2 exc a-state
Linert
Shyn
Doering
Middleton
cross section (10-16 cm2)
electron energy (eV)
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0
5
10
15
20
25
30

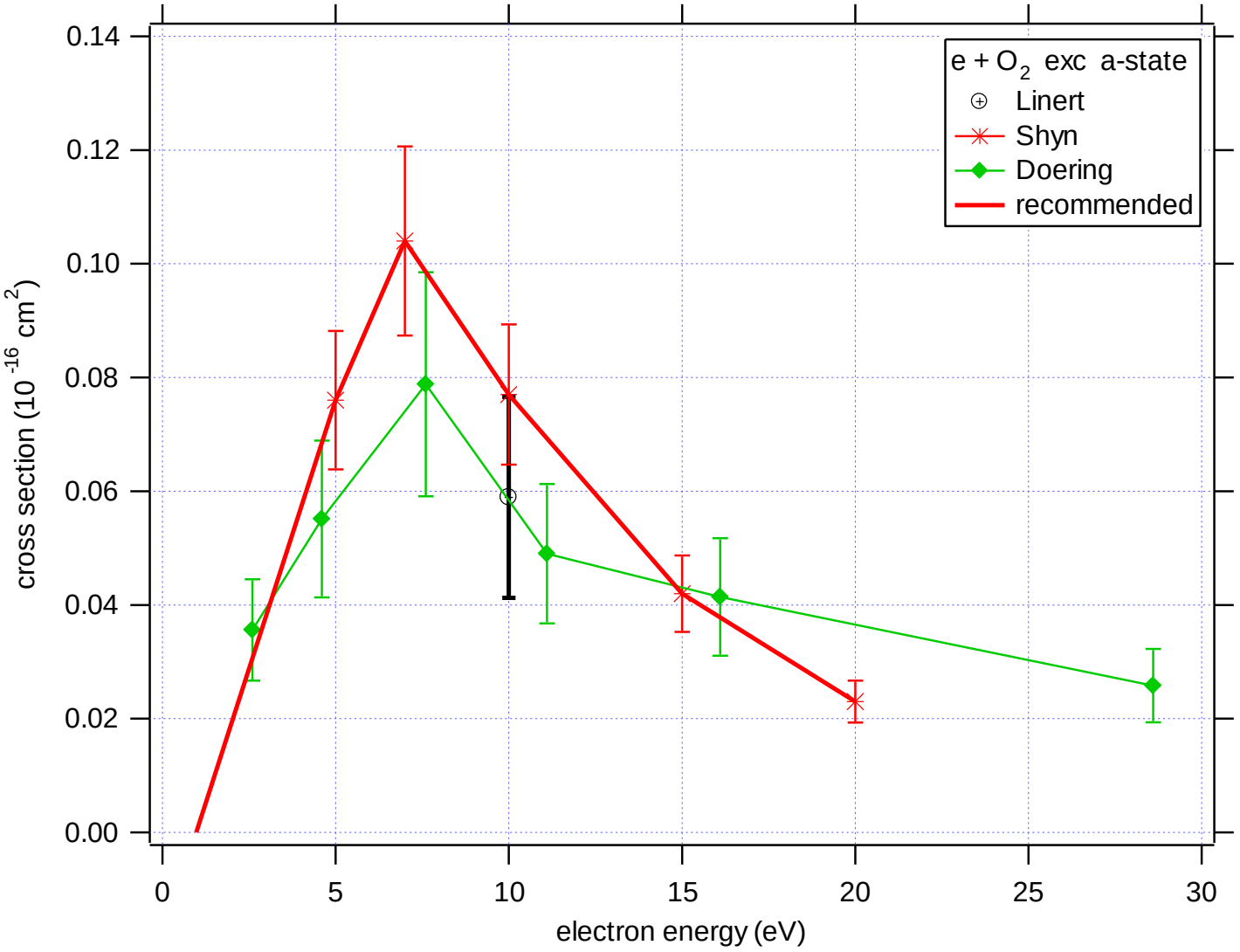
Middleton’s data have a different energy dependence.

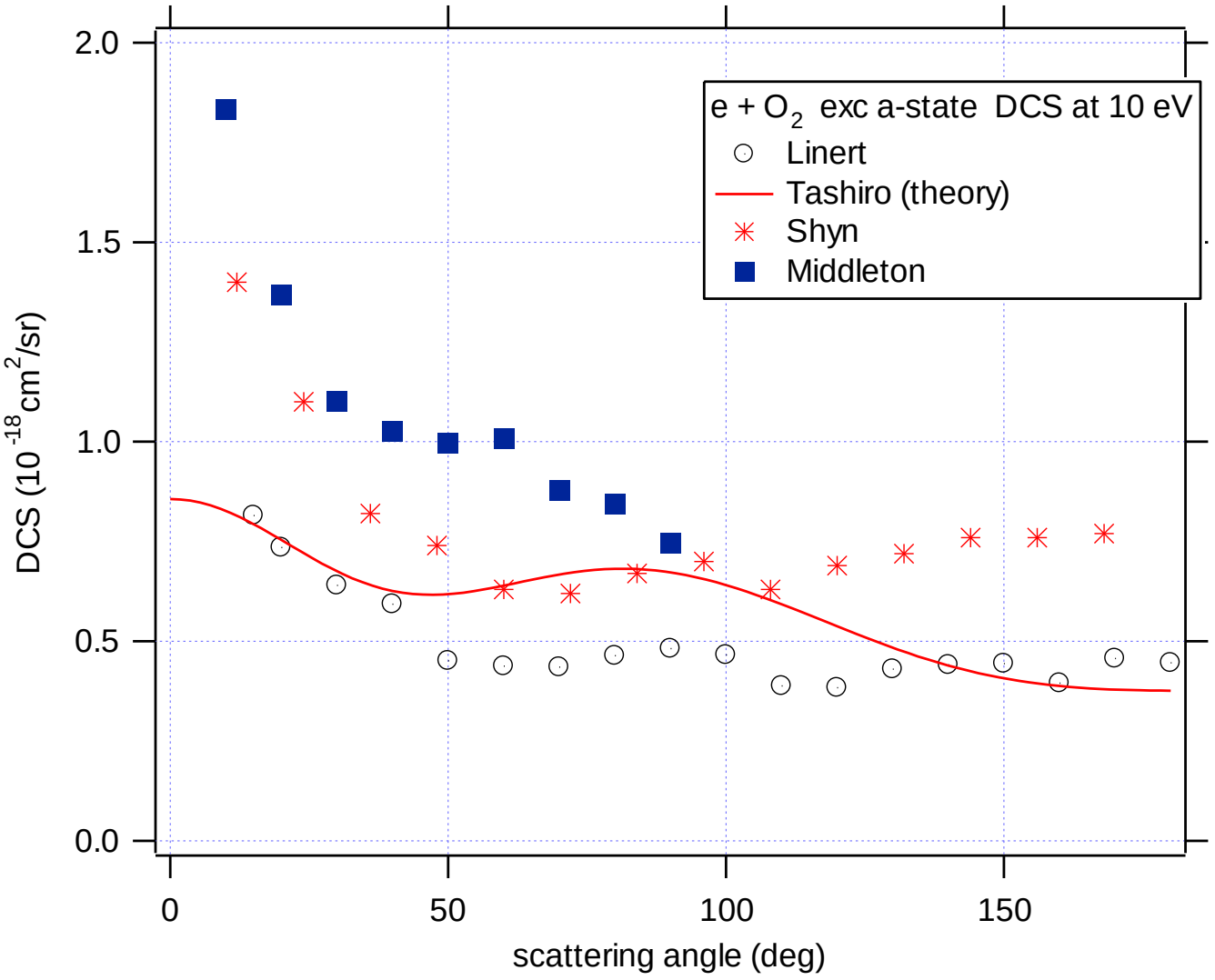
Others are in general agreement with each other.

Then Shyn’s values are recommended.

Linert data are the newest but only at 10 eV.

In JPCRD 2009




e + O2 exc a-state DCS at 10 eV
Linert
Tashiro (theory)
Shyn
Middleton
DCS (10-18cm2/sr)
scattering angle (deg)
2.0
1.5
1.0
0.5
0.0
0
50
100
150

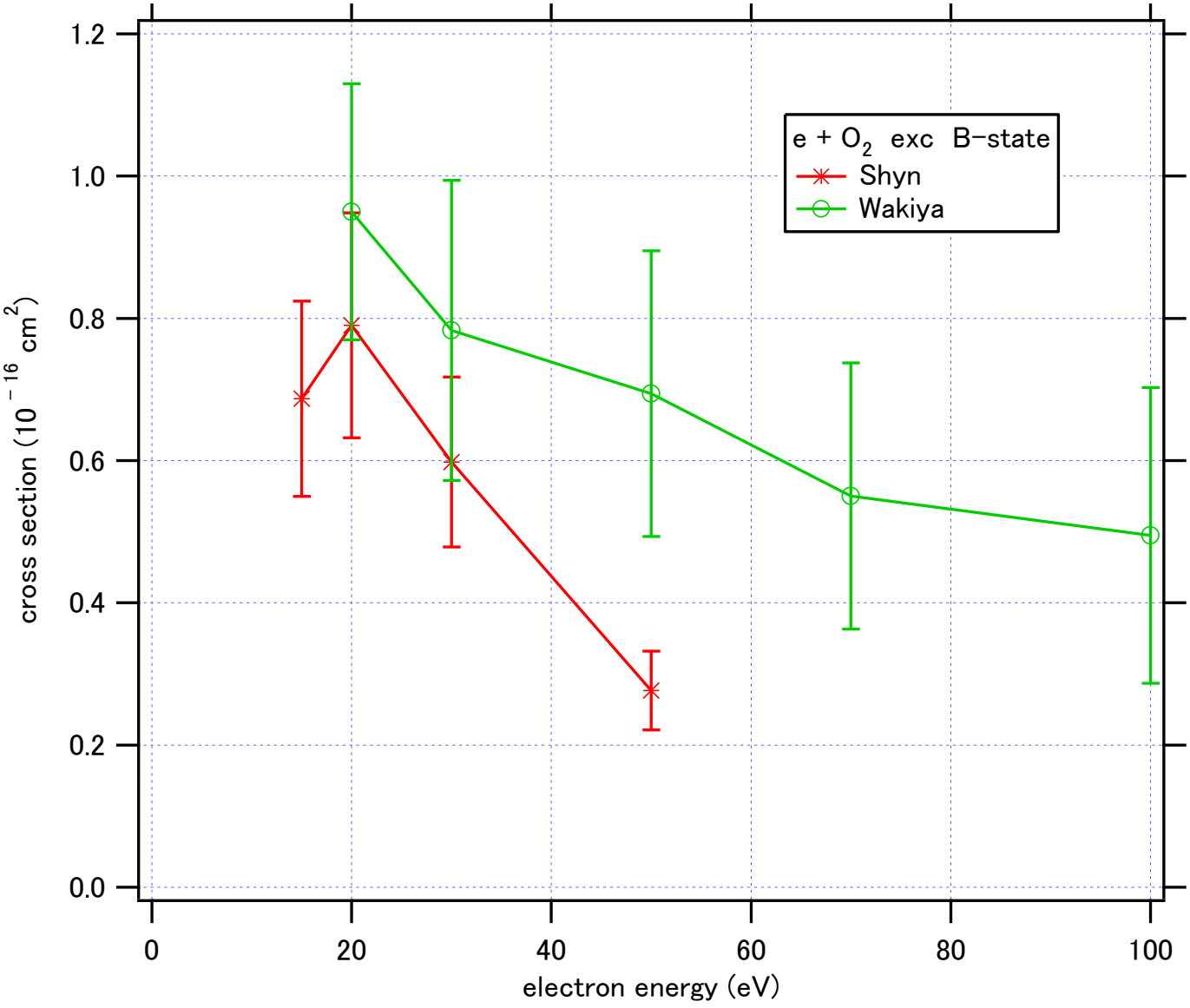
e + O_2

excitation of $B\ ^3\Sigma_u^-$ state

Before JPCRD 2009

Wakiya, J. Phys. B 11, 3913 (1978)

Shyn, Phys. Rev. A 50, 4794 (1994)

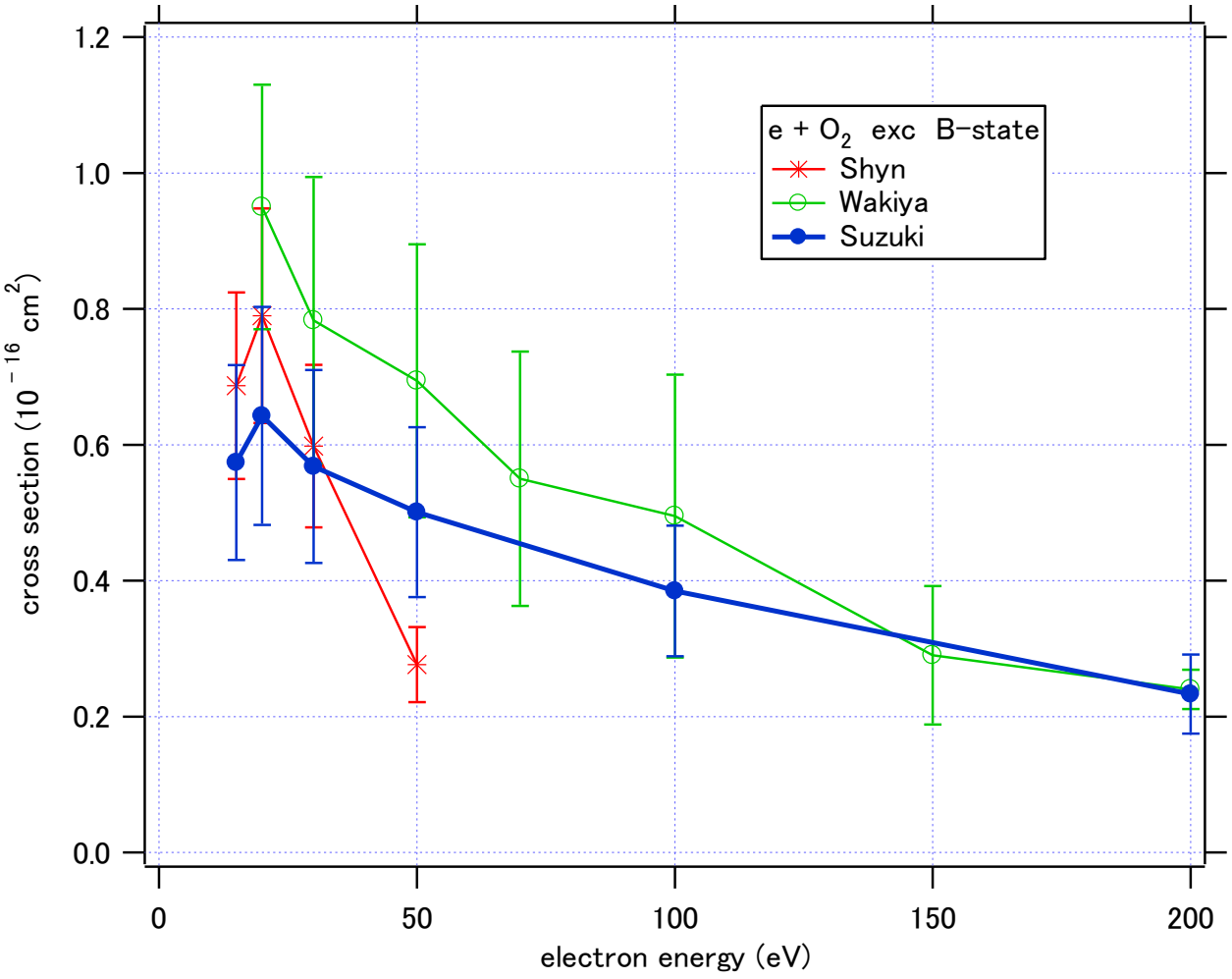

e + O2 exc B-state
Shyn
Wakiya
cross section (10 -16 cm 2)
electron energy (eV)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
20
40
60
80
100

In 2011

a new measurement reported

by Tanaka's group

Suzuki, J. Chem. Phys. 134, 064311 (2011)



Which is the best ?

(3) How were the absolute values determined?

To obtain absolute values, data are often normalized to some other source.

In that case, the reliability of the source should be checked.

Emission cross section

It is difficult to determine the absolute values of radiation intensity.

→ Normalize to some standard cross section to obtain absolute values.

$e + H_2O \rightarrow O^*$

130.4 nm line emission from O*

Normalized to the same emission from

$e + O_2 \rightarrow O^*$

Original data for e + H_2O

Morgan, J. Chem. Phys. 60, 4734 (1974)

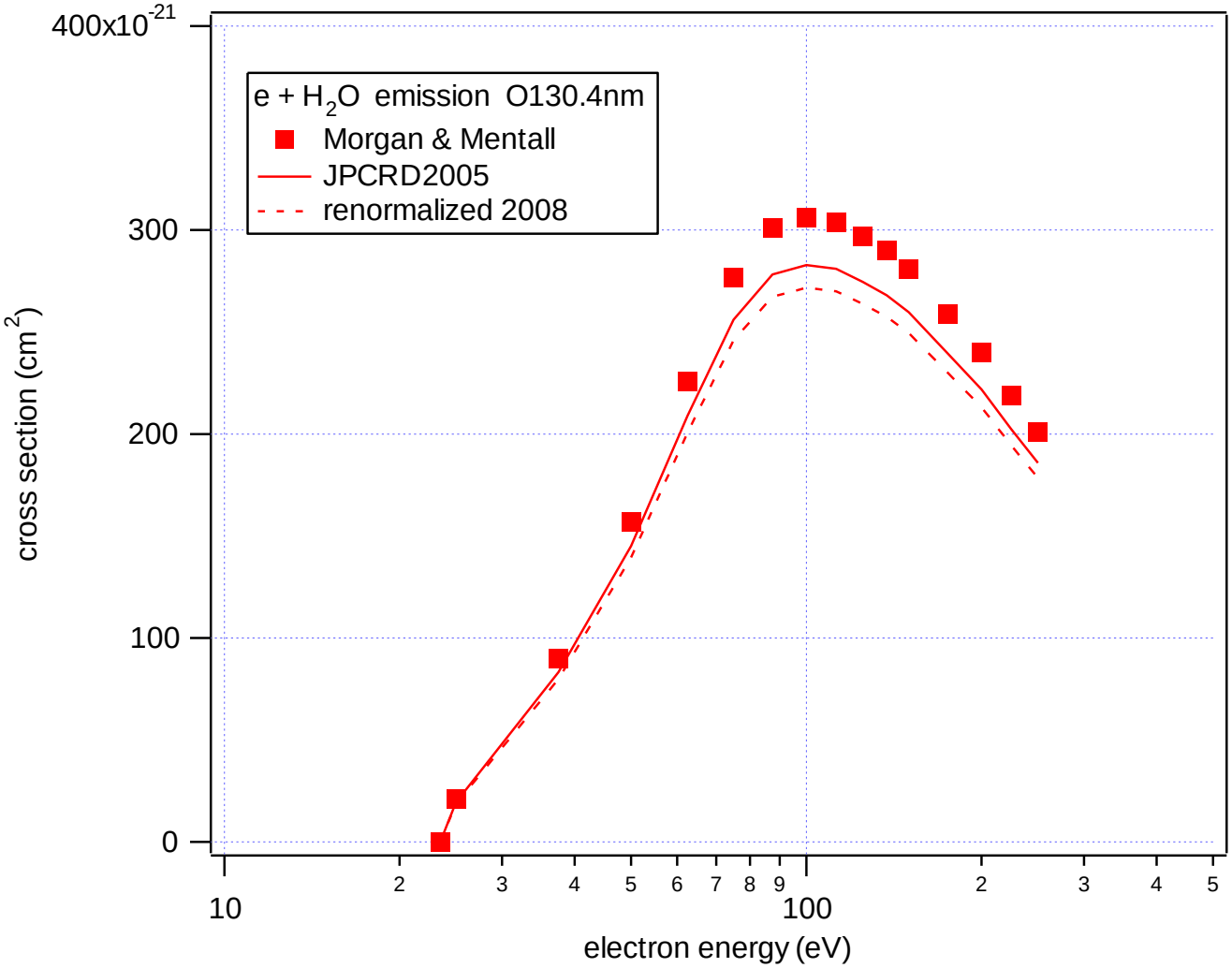
Normalized to

the emission C.S. for e + O_2 at 100 eV

Morgan (1974)	3.3×10^{-18} cm^2	
van der Burgt (1989)	3.05×10^{-18} cm^2	(adopted in JPCRD 2005)
McConkey (2008)	2.93×10^{-18} cm^2	

e + O_2 emission cross section

Morgan, J. Chem. Phys. 60, 4734 (1974)
Van der Burgt, JPCRD 18, 1757 (1989)
McConkey, Phys. Rep. 466, 1 (2008)



Difference is not much here. But, in principle we should take the most recent one.

(4) Physics involved

Consult theory !

When any structure appears in the plotted data, ask if theoretical foundations are available for that.

Test if known asymptotic feature or threshold law can be applied to the data.

!!! Based on the physics involved, sometimes a scaling law can be established.

BEf – scaling method

for the electron-impact excitation of dipole-allowed state

The Born method

For the dipole-allowed transition

like O_2 (X) → O_2 (B),

the Born approximation gives

a good result at high energies (say, > 100 eV).

Scaling by Yong-Ki Kim

To extend the Born c.s. toward lower energies,

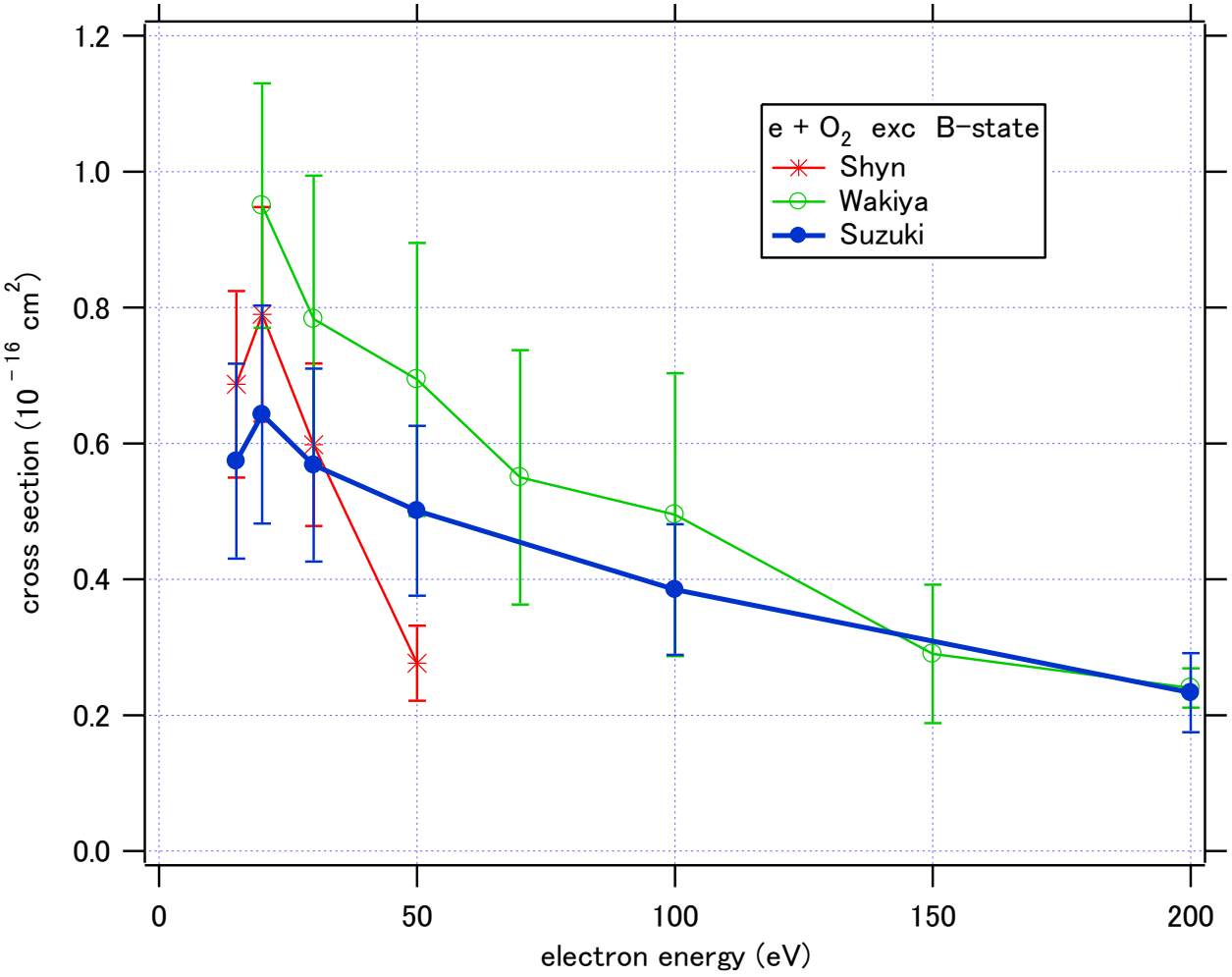
Kim proposed a scaling method

$$Q = \frac{T}{T + B + E} Q_{Born}$$

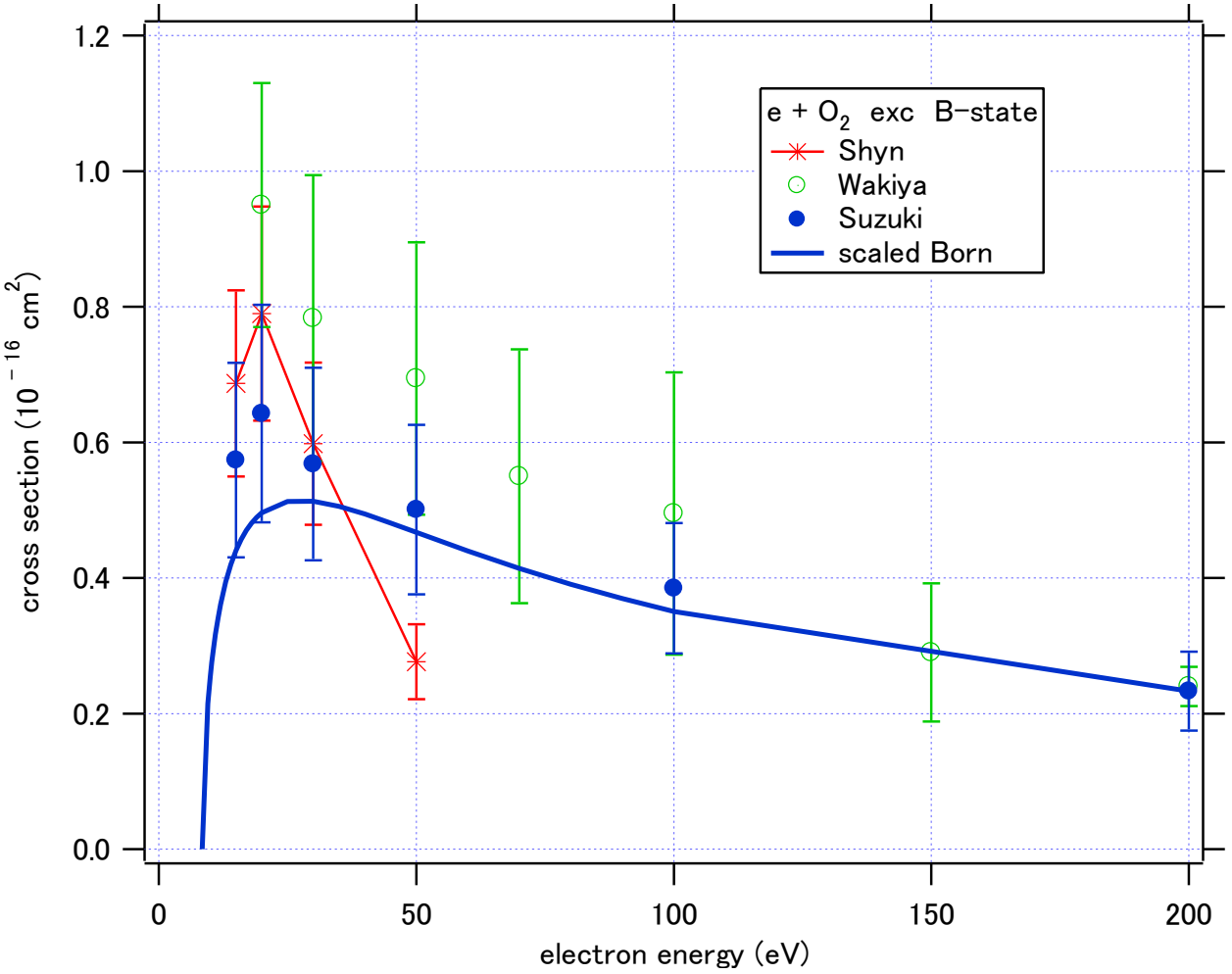
T: energy of incident electron
B: binding energy of the excited electron
E: excitation energy

Y.-K.Kim, J. Chem. Phys. 126, 064305 (2007)

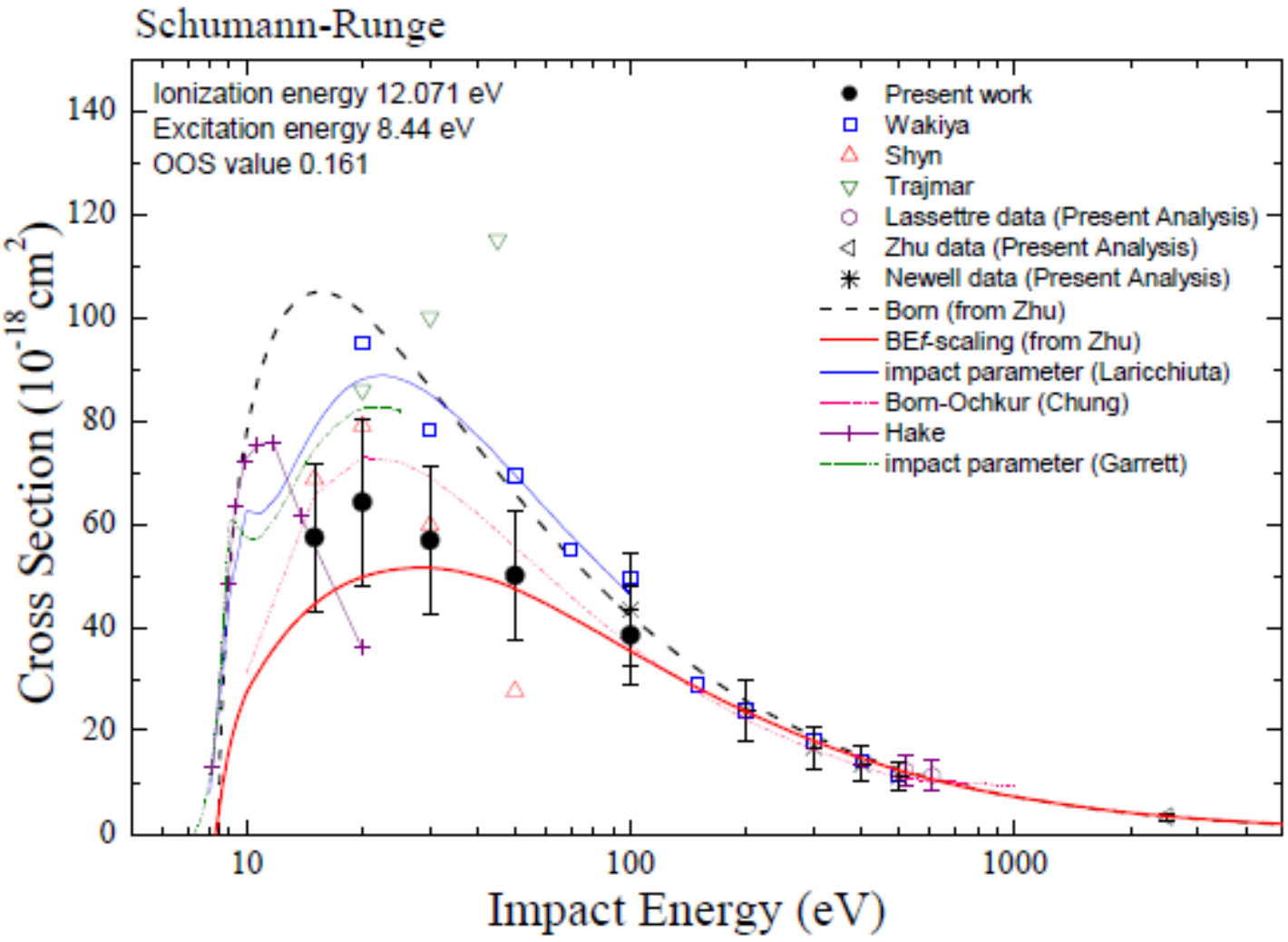
Let’s apply the BEf scaling to the example presented before



Then we have


e + O2 exc B-state
Shyn
Wakiya
Suzuki
scaled Born
cross section (10^-16 cm^2)
electron energy (eV)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
0
50
100
150
200

From Suzuki (2011)



Conclusion:

Based on the BEf-scaling,
the new measurement of Suzuki should be recommended .

More practically the resulting values of the scaled Born cross section can be used for application.

Tanaka's group has applied the BEf-scaling method to

H_2, O_2, CO, CO_2, N_2O, H_2O

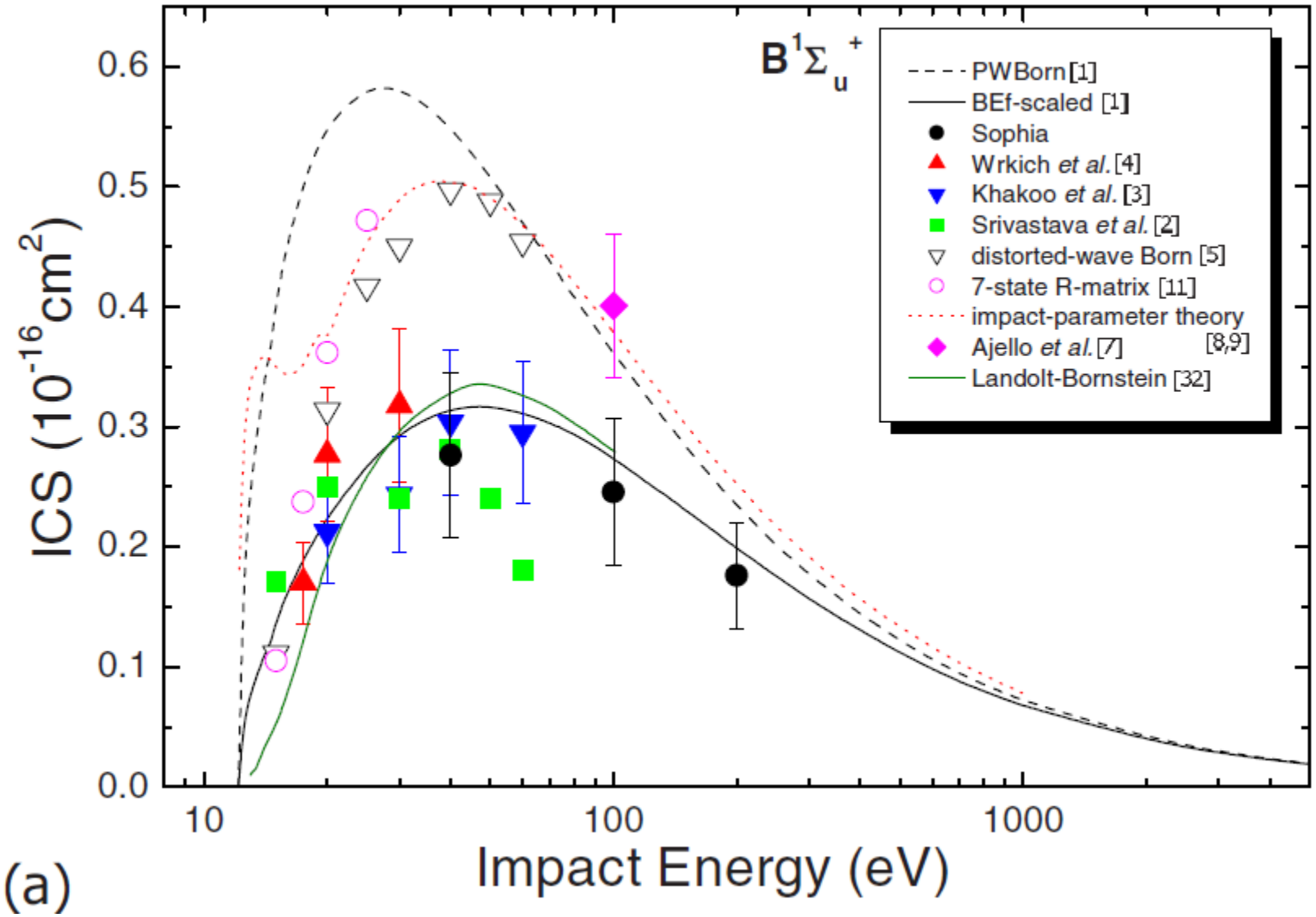
and obtained reliable cross sections for the excitation of electronic states.

See a review in

Anzai et al., Eur. Phys. J. D (2012)

$e + H_2$

Kato et al., Phys. Rev. A 77, 062708 (2008)



(5) Consistency between related, but different, quantities

Examples:

(1) Total ionization cross section

vs partial ones

(2) Total scattering cross section

vs cross sections for individual processes

Electron impact ionization of H_2O

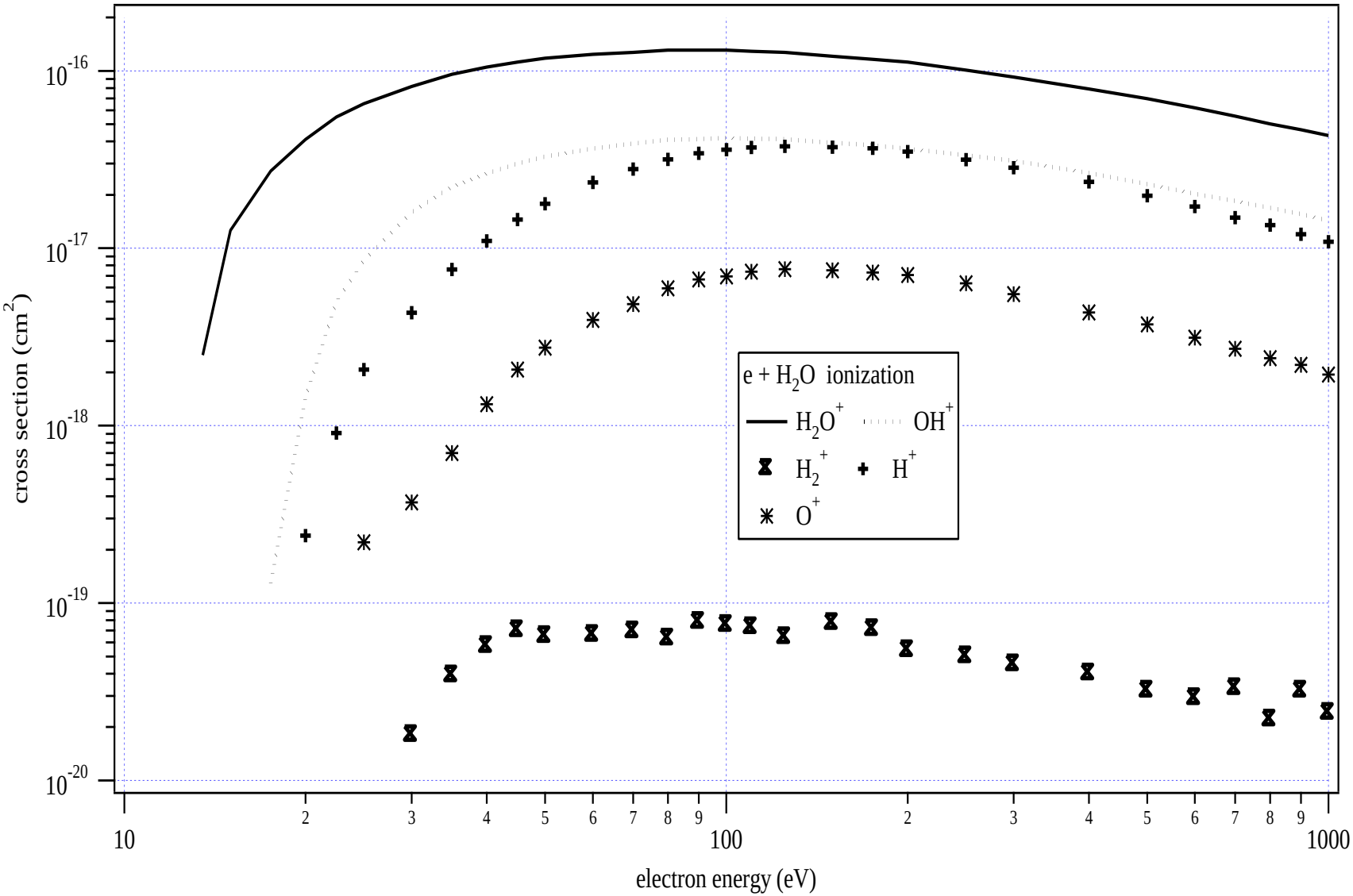
Produces

H_2O^+, OH^+, H_2^+, H^+, O^+

Cross section for each product

→ Partial ionization cross section

$e + H_2O$ Partial ionization cross sections recommended in JPCRD 2005



Electron impact ionization of H_2O

Total ionization cross section

= Sum of all the partial cross sections

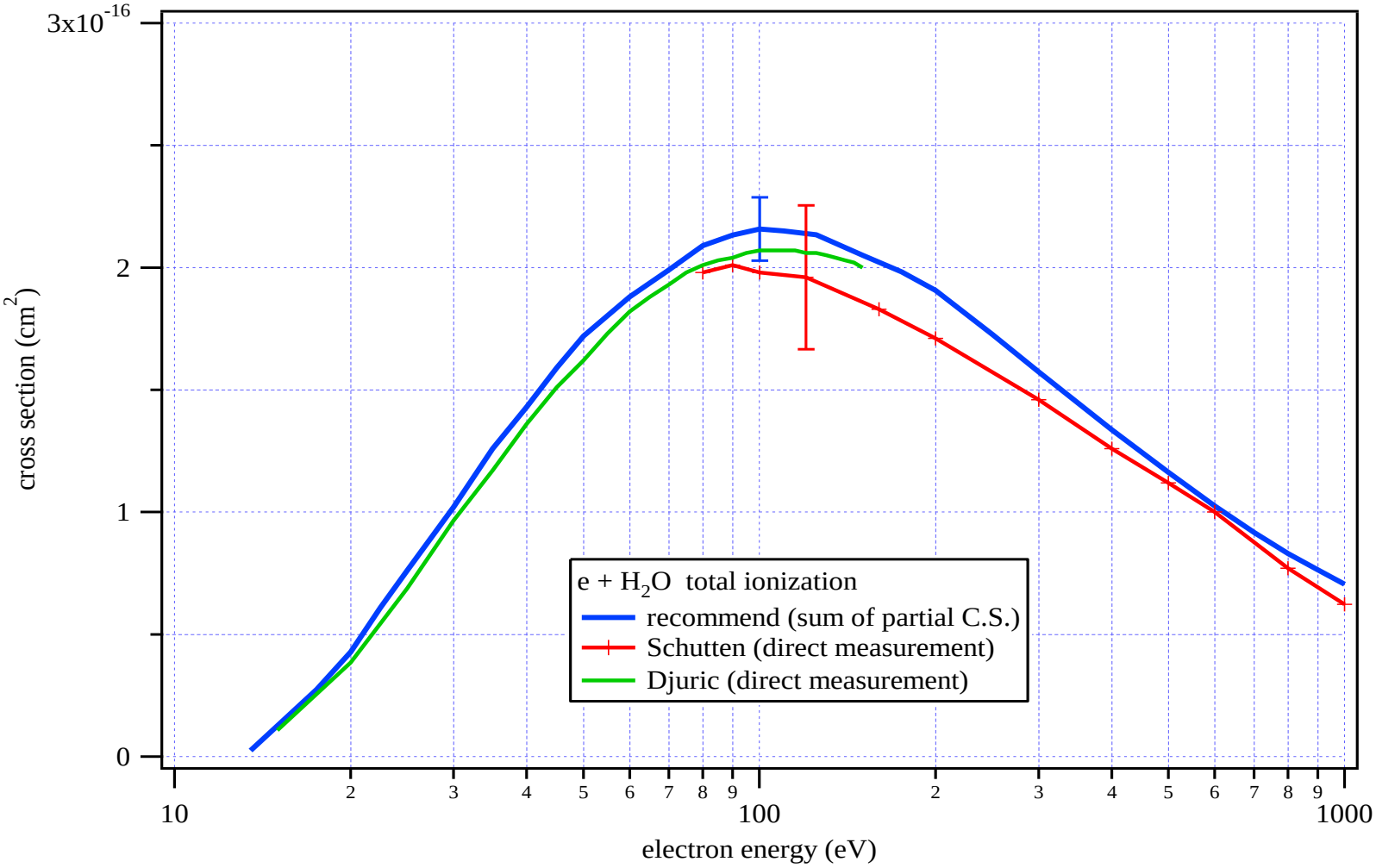
Total ionization cross section

can be also obtained with a direct

measurement of the total ion current

Both the values should agree with each other.

e + H_2O Total ionization cross sections



Sum of partial c.s. = total ion current measurement

e + H_2O total ionization cross section

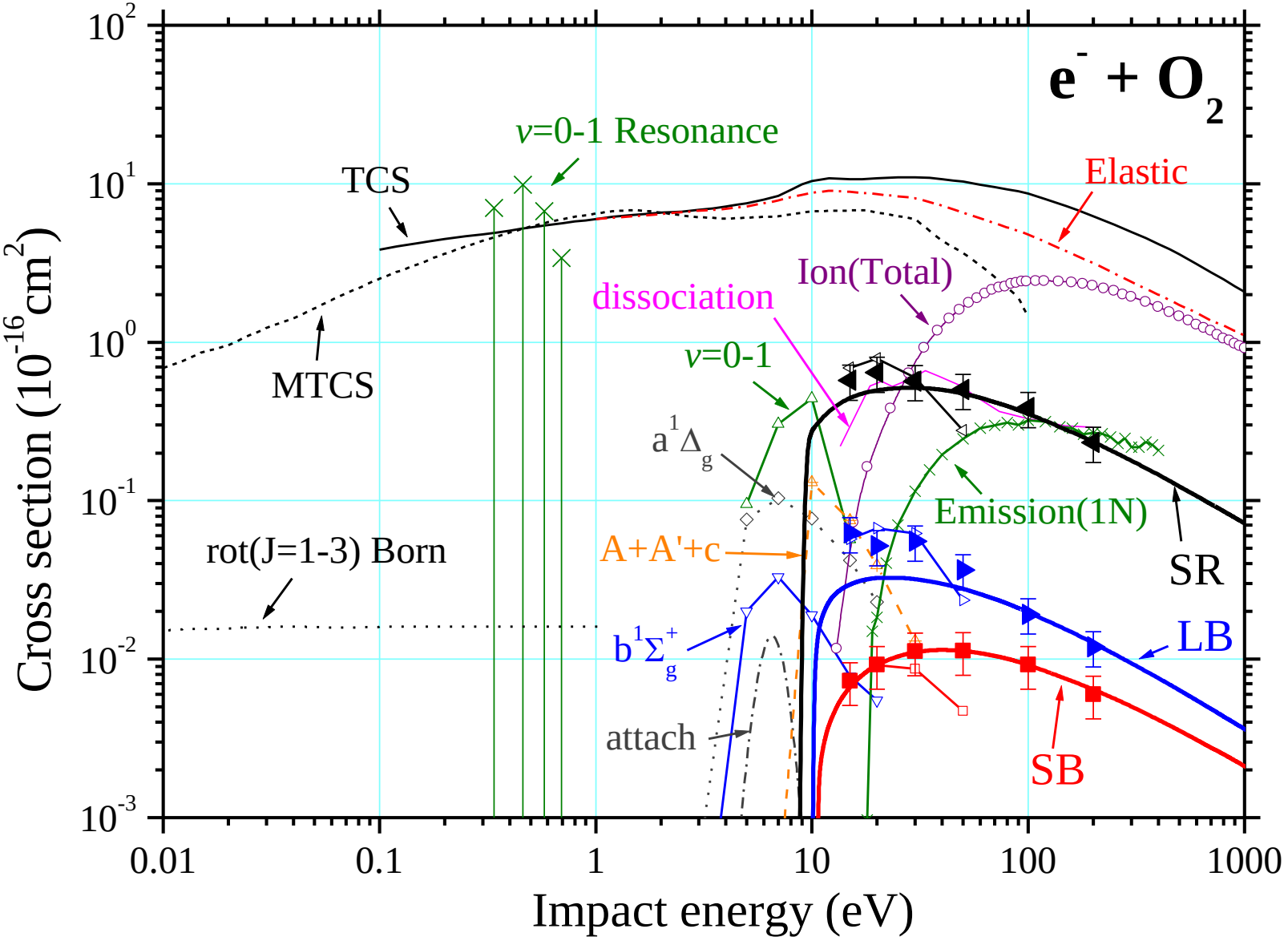
Schutten, J. Chem. Phys. 44, 3924 (1966)
Djuric, J. Mass Spec. Ion Proc. 83, R7 (1988)

Total scattering cross section

$$Q_T = \sum_s Q_s$$

s: all the processes

We should test this relation.


e- + O2
ν=0-1 Resonance
TCS
Elastic
Ion(Total)
dissociation
ν=0-1
MTCS
a1Δg
Emission(1N)
A+A'+c
rot(J=1-3) Born
SR
LB
b1Σg+
attach
SB
Cross section (10-16cm2)
Impact energy (eV)
10^2
10^1
10^0
10^-1
10^-2
10^-3
0.01
0.1
1
10
100
1000

e + O_2

energy	100 eV	500 ev	1000 eV	uncertainty
total(T)	8.68	3.58	2.08	5 %
elastic(E)	4.78	1.72	1.10	20 %
ionization(I)	2.43	1.46	0.922	5 %
T-(E+I)	**1.47**	**0.40**	**0.06**	
exc	0.41	0.13	0.08	25 %
dissociation	0.33			

cross section in 10^{-16} cm^2

$$T - (E + I) = exc + diss \quad ?$$

Within uncertainties of each cross section, we have

$$Q_T = \sum_s Q_s$$

To summarize,
the following points should be taken into account:

(1) Quoted uncertainty
(2) Agreement among the data obtained by different authors / methods
(3) How the absolute values were determined
(4) Physics involved
(5) Consistency between related but different quantities

But one more !

(6) Reliability of authors

Judged from their previous works.

Further suggestions

1. Evaluate the “evaluated data set”

Select model experiments to test the evaluated data

2. Find and train “evaluators” (scientists who are engaged in data evaluation)

→ Organize network of evaluators