RD51 eco gas meeting May 2023 S.F.Biagi

Aspects of atomic and molecular physics that impact the analysis of electron transport data.

A list of some useful references:

https://magboltz.web.cern.ch/magboltz	cf analysis notes of recent x-secs.
https://garfieldpp.web.cer/garfieldpp/examples/magboltzcs	plots
https://ccbdb.nist.gov	Computational chemistry now includes some calcs and data on hydro fluoro carbons..
https://us.lxcat.net	Contains swarm data, electron cross-sections and Brions digitised oscillator strength data for many atoms and molecules
Atomic and Molecular Photoabsorption	J.Berkowitz Academic Press 2002

The modelling of :

1) Rotation
2) Vibration
3) Excitation
4) Ionisation
5) Attachment

Can all be described by the use of functions based on physical models of each process. The functional forms allow the accurate description of the scattering processes without introducing very large arrays of data.

Rotation

Analytic born rotational models predict the rotation in most molecules accurately.
They are described by three parameters/variables:

1) Energy spacing of rotational levels Bo
2) Electric dipole moment of the ground state
3) Electric quadrupole moment of the ground state.

These 3 quantities are usually well measured and allow the calculation of the cross-sections if the geometrical structure of the molecule is known.

The geometry of the molecule is either:

1) Linear rotator examples in magboltz : H2,N2,O2,CO
2) Symmetric rotator : NH3
3) Asymmetric rotator : H20 and complex shaped molecules.

In the case of Symmetric and Asymmetric rotators the rotational energy spacing is changed from Bo to Bx, By Bz

The hydro fluorocarbons have very small values of Bo (~0.015 millivolts) in comparison the hydrocarbons have Bo ~ 0.15 millivolts.

The low value of Bo requires the use of over 1000 rotational levels which would increase the computation time . An approximate scheme can be applied where the rotational constant,Bo, is increased and the cross-section decreased proportionally.
The lowest Bo value, 0.015 mv, is close to elastic scattering x-section energy loss so another approximation would be to use an elastic scattering x-section which is the sum of the elastic and rotational x-sections .

The fluorine-carbon compounds generally have large electric dipole moments which lead to large cross-sections both for rotation and vibration.

The physical reason for this behaviour is that the chlorine atom attracts electrons very strongly and so the centroid of the bond charge is moved close to the chlorine atom and leaves an effective positive charge on the carbon.

Vibration

A consequence of the electronegativity of the fluorine is that the F—C—F structure in the molecule has a very large transition electric dipole moment for the stretch vibrations. The vibrational x-sections are typically a factor of 10 larger than they are for H—C—H stretch vibrations .

An excellent example of the electronegativity is in CF4 which gives this molecule its unique behaviour of high drift velocity and low diffusion.

An interesting case which shows the structure dependence of the dipole moments is r134a CF3CH2F and the isomer CF2HCF2H .

The r134a has a large dipole moment ,2.05 Debye , caused by the asymmetric structure of the molecule combined with the strong Fluorine electronegativity this dipole moment is larger than that of H20 1.86 Debye.

The CF2HCF2H can exist in two conformers where the Hydrogens are on opposite side of the molecule or on the same side The conformer with the hydrogens on opposite sides has almost zero dipole moment , the other conformer gives a dipole of about 1.3 Debye.

The vibrations in the all the Flouro -carbons have strong stretch vibrations driven by the large dipole moments. The result of this is that the born dipole formulae can also be applied to the x-sections of the fluoro-carbons (see C2F6 and C3F8)
The transition dipole moments for the transitions can be calculated from the infra-red transitions observed experimentally or those calculated (by NIST web site).
The relative amplitudes of the vibrational transitions are fixed to the ratios obtained from the infra red vibrational transition intensities.
The Argon-fluorocarbon mixture drift velocities can then be fitted by only varying one parameter the overall amplitude normalisation.
The born dipole approximation is very good in the fluorocarbons because of the large dipole moments. The direct interactions which compete with the dipole component are much smaller except where there are vibrational resonances.

The nomenclature in publications that describe the vibrations has two forms:

1) a linear array with indices describing the number of vibrations at each node

an example would be (0,2,0,0,1,0,0) for a 7 vibrational state molecule

This would describe a vibrational state where the second state had a an overtone of two units and the 5th state had one unit of vibration.

2) The alternative nomenclature would be (2V2,1V5)

Unfortunately there is no standard nomenclature for deciding the order of the vibrations in the array and it is often better to use bend, stretch etc in the description.

Generally there are 3*N-6 vibrations for a molecule , r134a has N=8 therefore the number of vibrational states 18

In HFO N=9 and there are 21 vibrational states.

Fortunately in these molecules not all vibrations are strongly dipole coupled . The 9 infra red strong dipole emitting states can be reduced to 4 effective levels by summing transitions close in energy.

The relative amplitude ratios of the 4 states can be fixed to the dipole /infra red amplitudes at the summed energies of 0.374, 0.155,0.139 and 0.1125 ev (r134a).

The vibrations typically have a resonance enhancement at energies above 2 ev

From systematics we assume that the resonance structure is similar to that in C2F6 which has two resonances. The lower energy resonance is a vibrational attachment resonance which allows the dissociative attachment of electrons by 2 or 3 body effects. The higher resonance is not a vibrational attachment resonance.

Excitation

The excitation in molecules can be split into states that couple directly to the ground state by dipole transition and are referred to here as singlet states.

States that are not dipole coupled to the ground state by dipole are termed triplet states.

Singlet states

The cross-section for singlet states are accurately described by the oscillator strength of the transition . In the literature there are many measurements of the oscillator strength using either a photon beam (typically from a SRS source) or by measuring the cross-section of electron scattering at 0 degrees . The cross-sections are usually normalised by assuming the integral of the oscillator strength is equal to Z the total charge of the molecule. (TRK sum rule)

The accuracy of the oscillator strengths is typically better than 2% and when combined with the born correction formula , called BEF scaling in the literature ,this leads to cross-sections of similar accuracy +- 2%.

I have introduced the tables of oscillator strength produced by Brion on the LXCAT web site which is freely available (thanks to Chris Brion).

Triplet states

The triplet states pose a problem in the analysis of transport data since only a few molecules have accurate triplet cross-section measurements.

The behaviour of triplet scattering as a function of energy is completely different from that given by singlet scattering. The cross-section rises to a peak at about twice the threshold energy and then falls as 1/ energy**2.

The amplitude of the triplet cross-sections can be derived by fitting to the Townsend gain coefficient. Note this is the only degree of freedom involved in fitting the Townsend coefficient. The energy of the triplet cross-sections is generally 0.3 ev below the corresponding singlet cross-section (quantum mechanics).

Combined analysis of triplet and singlets.

The singlet cross-sections are obtained by integrating the oscillator strength over the structures (levels) in the spectrum. It is important to include levels above the ionisation energy in the analysis. These are levels that decay by neutral dissociation above the ionisation threshold. The oscillator strength for these above ionisation levels are obtained by integrating the oscillator strength multiplied by the quantum ionisation efficiency .

The triplet cross-sections are taken from measurements where available or are assumed to be split over the region from the lowest level up to 1.5 times the ionisation energy. Typically 3 or 4 triplet levels are taken and the amplitudes adjusted to fit the Townsend coefficient.

Ionisation

Ionisation cross-sections generally are accurately measured in experiments and typically have less than 3% errors .
Theoretically there are a some accurate models typically called BEB models (Binary Encounter Bethe). These give good results for the counting ionisation if no experimental data are available. The energy range of the models is typically valid to 3000 ev . Above this energy the cross-section is described well by the ionisation matrix element which can be calculated from the Oscillator strength data times the ionisation efficiency.

There are many experimental measurements of the dissociative ionisation and in Magboltz it is assumed that above 1kev the relative dissociative ionisation branching fractions are constant. The total sum of the dissociative ionisation and ionisation are taken to be the total counting ionisation.

The BEB model in some forms does not include multiple ionisation so 2+ ions and larger are not included and the counting ionisation is no longer the same as the gross ionisation. The Fluoro-carbons have typically 10% multiple ionisation yields and should be accounted for in the BEB calculation.

Attachment

The 2 and 3 body attachment in large molecules is generally associated with a vibrational resonance. There are some exceptions such as Oxygen where a 3 body stabilisation of a negative ion can occur for vibrational levels below the Oxygen ground state.

The attachment in C2F6 is shown in the following plots of the cross-section and occurs at exactly the vibrational excitation energy of 3 ev

The attachment in C3F6 is both a two and three body process the main two body attachment occurs at the vibrational resonance energy 2 ev and the 3-body attachment is on the low energy tail of the 2-body process.

The physics of the attachment process in C3F6 can be understood by assuming the attachment resonance is not a single resonance but contains contributions from rotation and vibration. In a 3 body collision the energy transfer can be above 0.05 ev and the energy within the negative ion vibrational resonance is moved to a point where the attachment will stabilise .

From these arguments is is expected that r134a should not have a 3body attachment but HFO which is closer in vibrational structure to C3F6 should have a 3 body attachment.

Experiment ,Basile et al , indicates that there is a weak 3-body attachment in r134a (shown in the Magboltz2010 x-section) this is likely due to attachment by real dimers and trimers which are formed due to the large ground state dipole moment.

Fano Factors and derived cross-sections

The Fano factors are conventionally defined as F0 F1 F2 F3 ----Fn

The Fano factors describe the ionisation charge distribution released by radiation either charged particles or photons released in the target.

The distribution has a peak and a width which tends towards a gaussian shape at large energies.

F0 is the mean charge release per event and is sometimes called W0 in the literature and is measured in electron/volts per ion pair

F1 is defined as the width of the distribution

F2 is defined as the Skew width of the distribution

F3 is defined as the Kurtosis width of the distribution

The electron scattering cross-sections are used in Degrad to calculate the Fano factors and very accurate values can be obtained.

The experimental Fano factors can be used to constrain the ratio of the ionisation to the excitation cross-section above typically 3 times the ionisation energy in molecules.

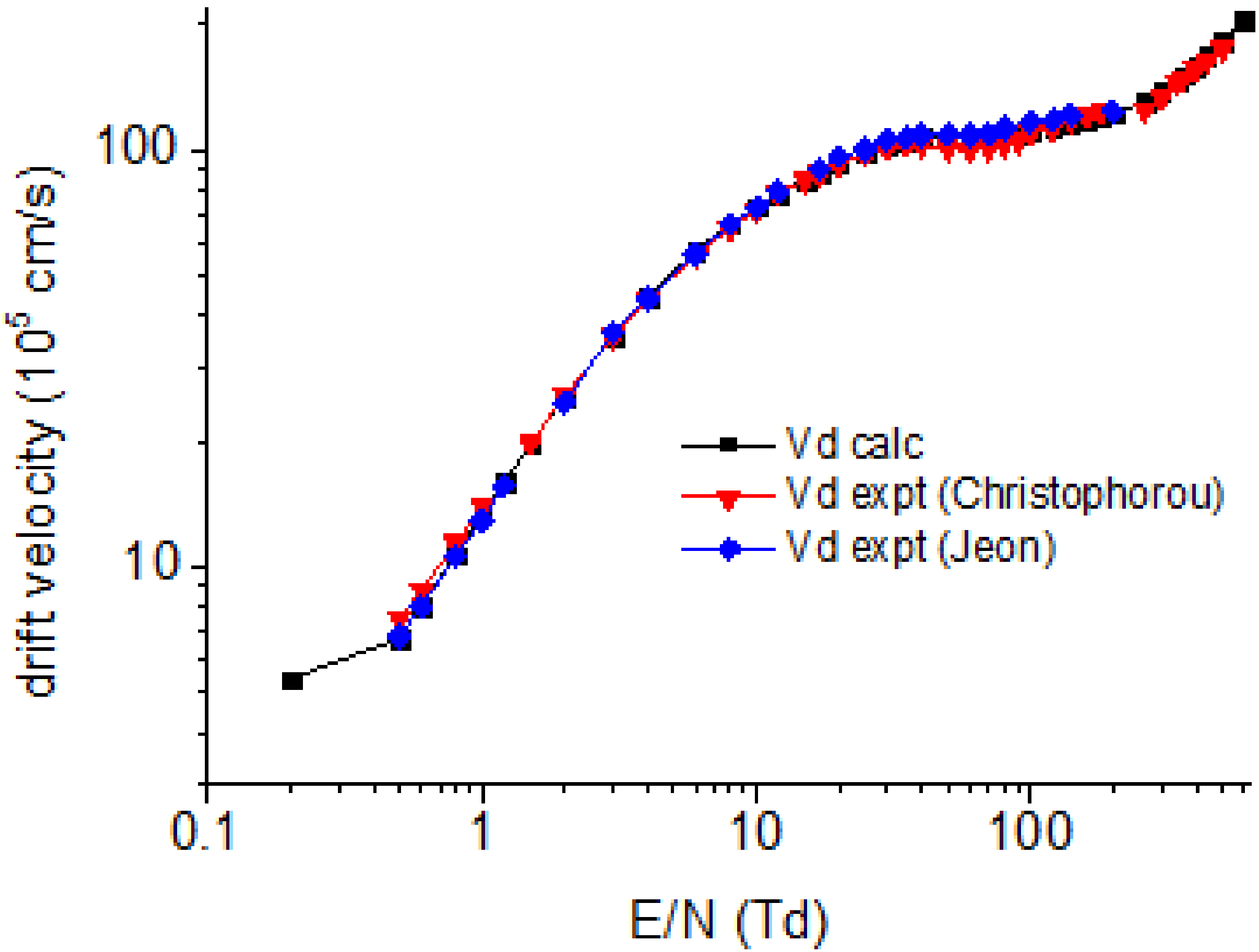
The Fano factors and the Townsend operate in a complimentary fashion in the analysis

The Townsend coefficient is sensitive to the ratio from threshold to 3 times the ionisation energy and the Fano factor F0 is sensitive to the ratio above 3times the ionisation energy.

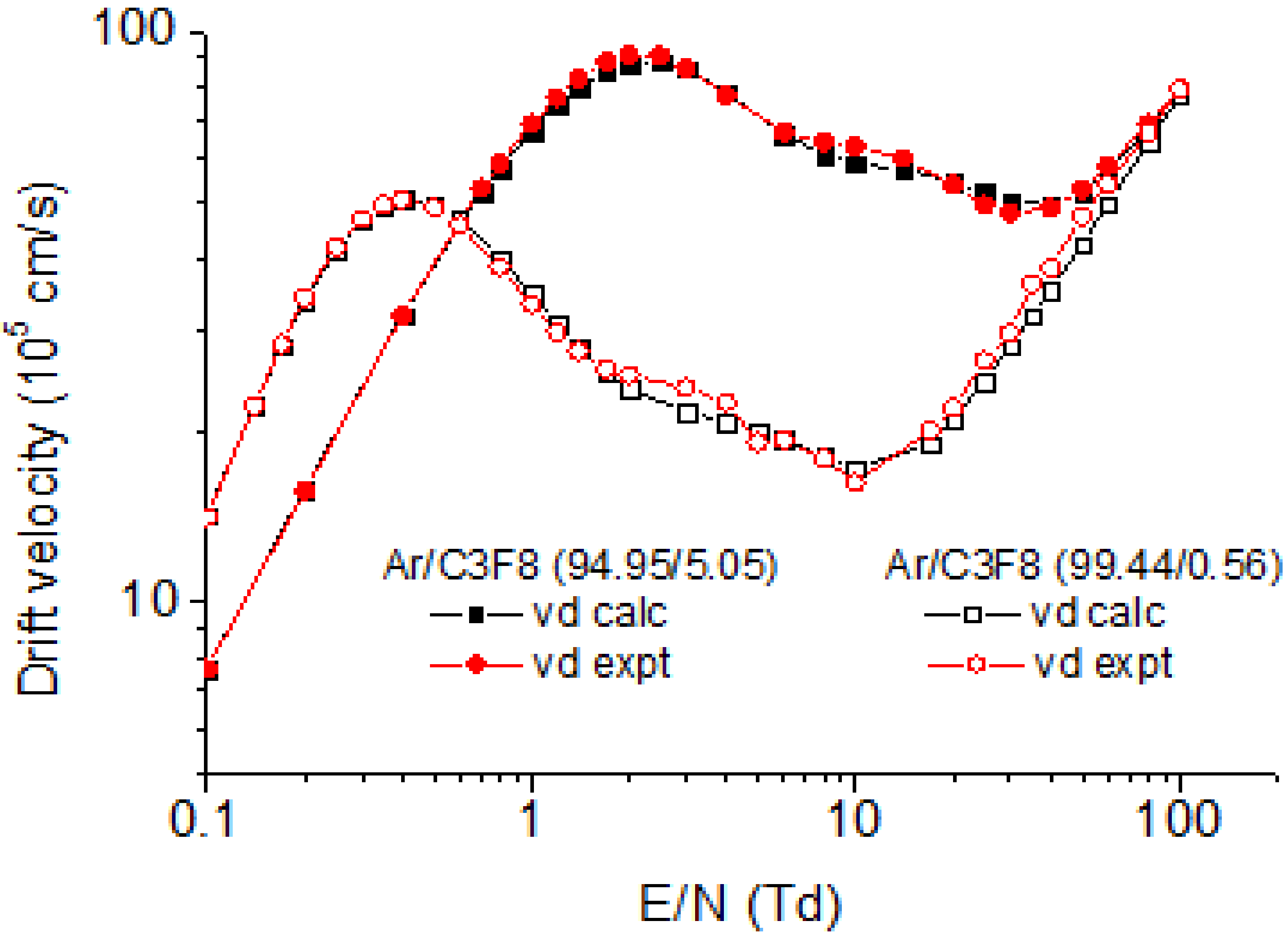
The fluoro carbons tend to have large dipole moments leading to an enhancement of the singlet dipole excitations compared to the triplet excitations.
A consequence of this enhancement is that more energy is lost to dipole excitations And the Fano factor W0 of the Fluorocarbons are over 31 ev/ion/pair
In comparison the hydrocarbons tend to have lower W0 values around 25 ev/ion pair.
The derivation of the C2F6 and C3F8 cross-section for dipole excitation relied on the experimental W0 values since no accurate data was available for the dipole excitation.

The analysis of r134a and HFO will assume a value of W0 above 31ev/ion pair .
However, it would help the analysis if an experimental measurement of the W value in these gases was made. The measurements can be made with 5 Mev alpha sources or 1.3Mev gamma rays.

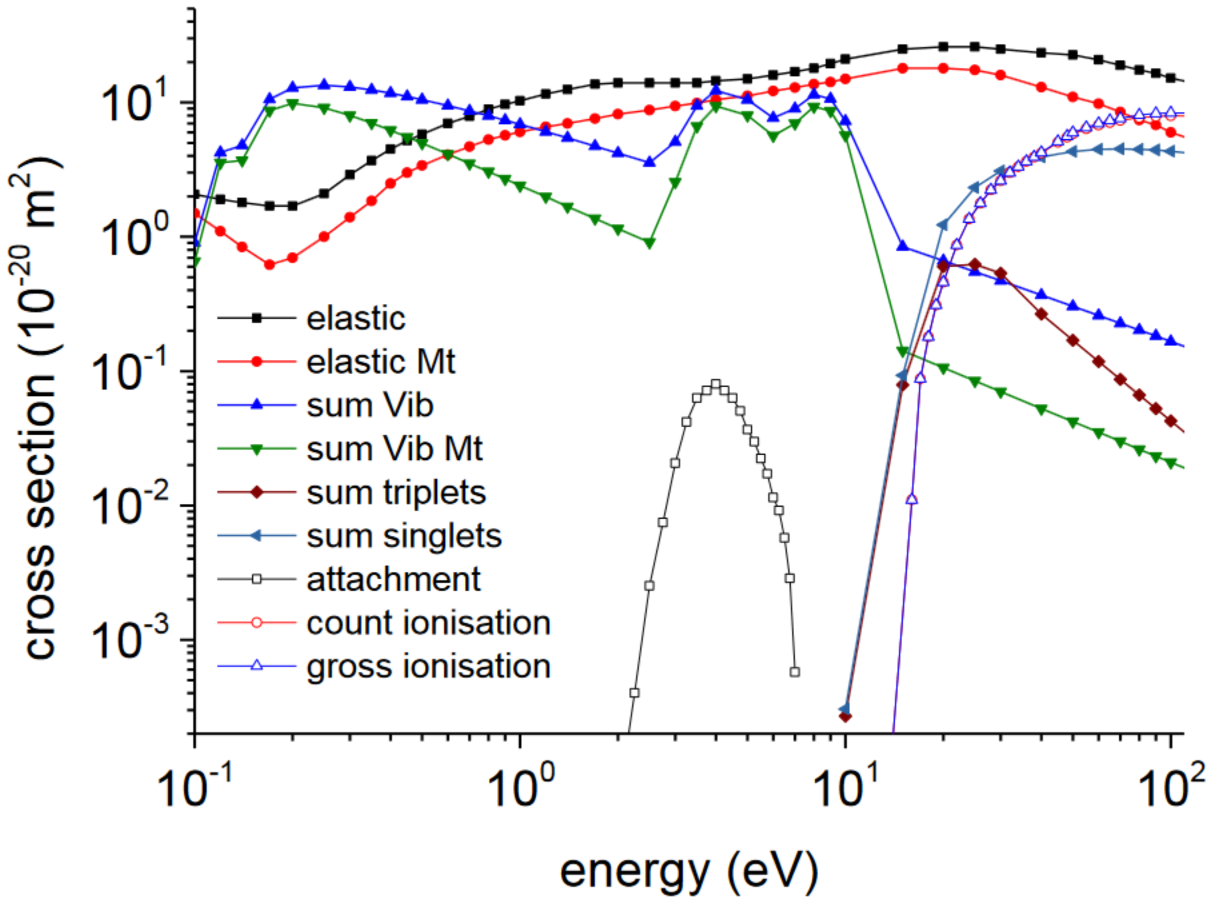
C3F8 drift velocity calculation and experiments



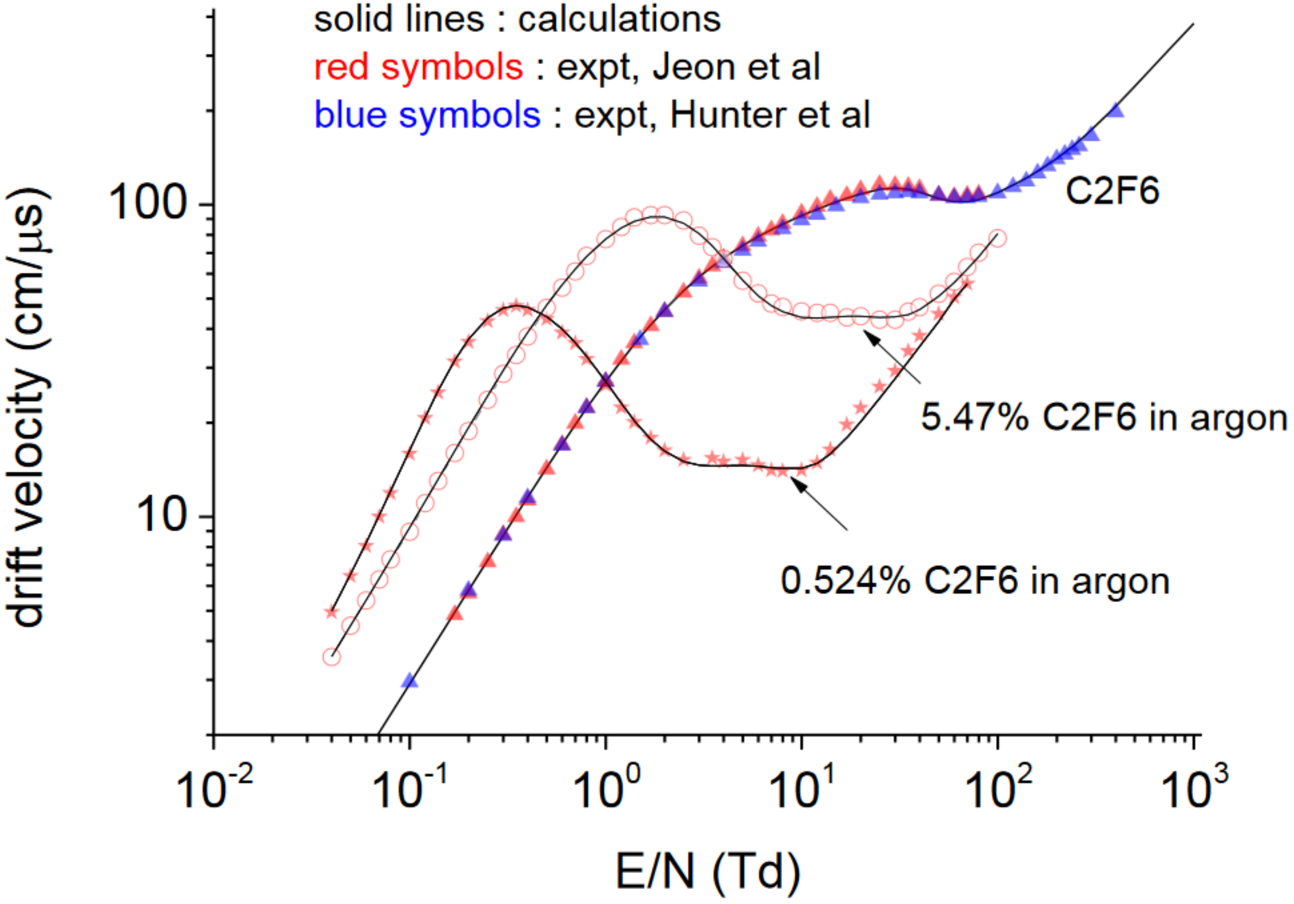
C3F8 Argon mixtures



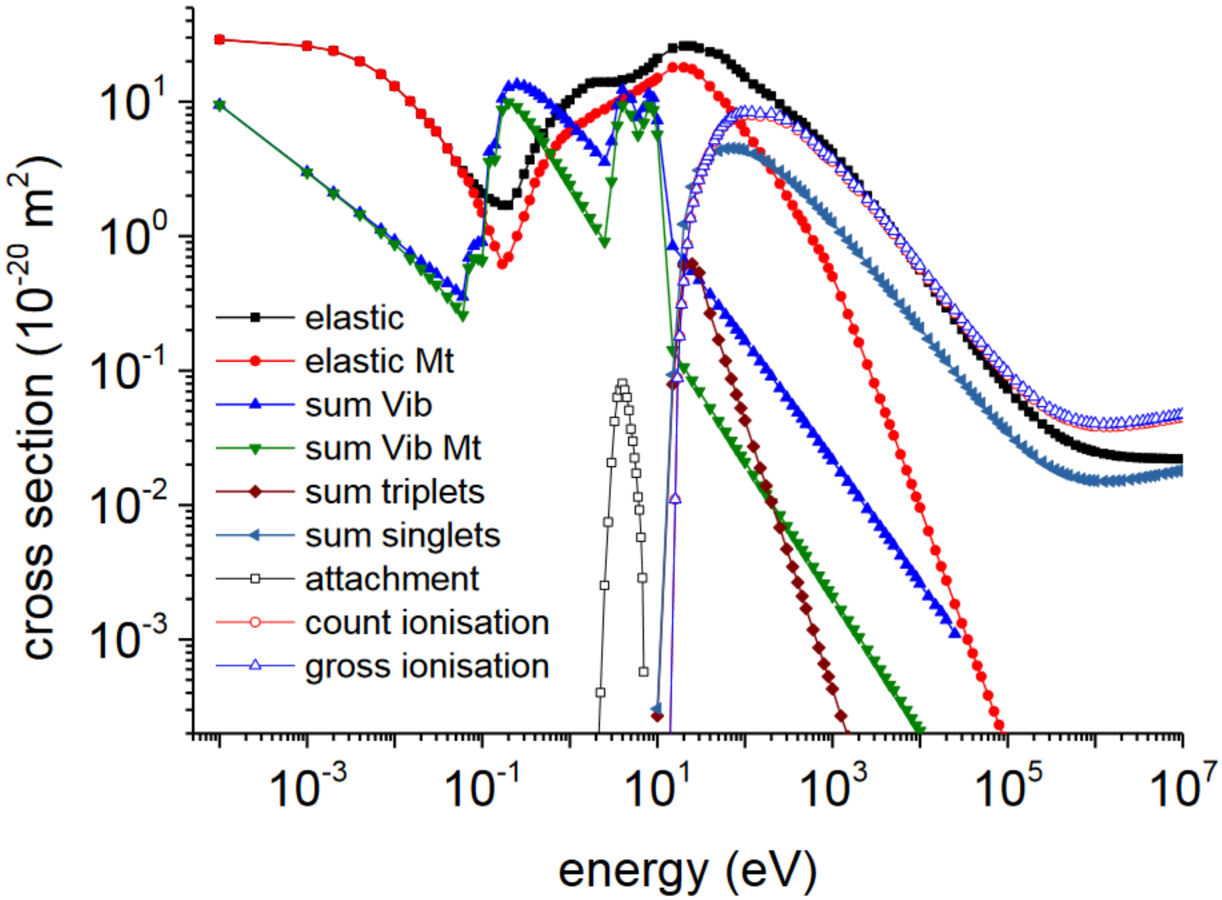
C2F6 2023 cross-sections on expanded scale



Fit of C2F6 2023 to transport data

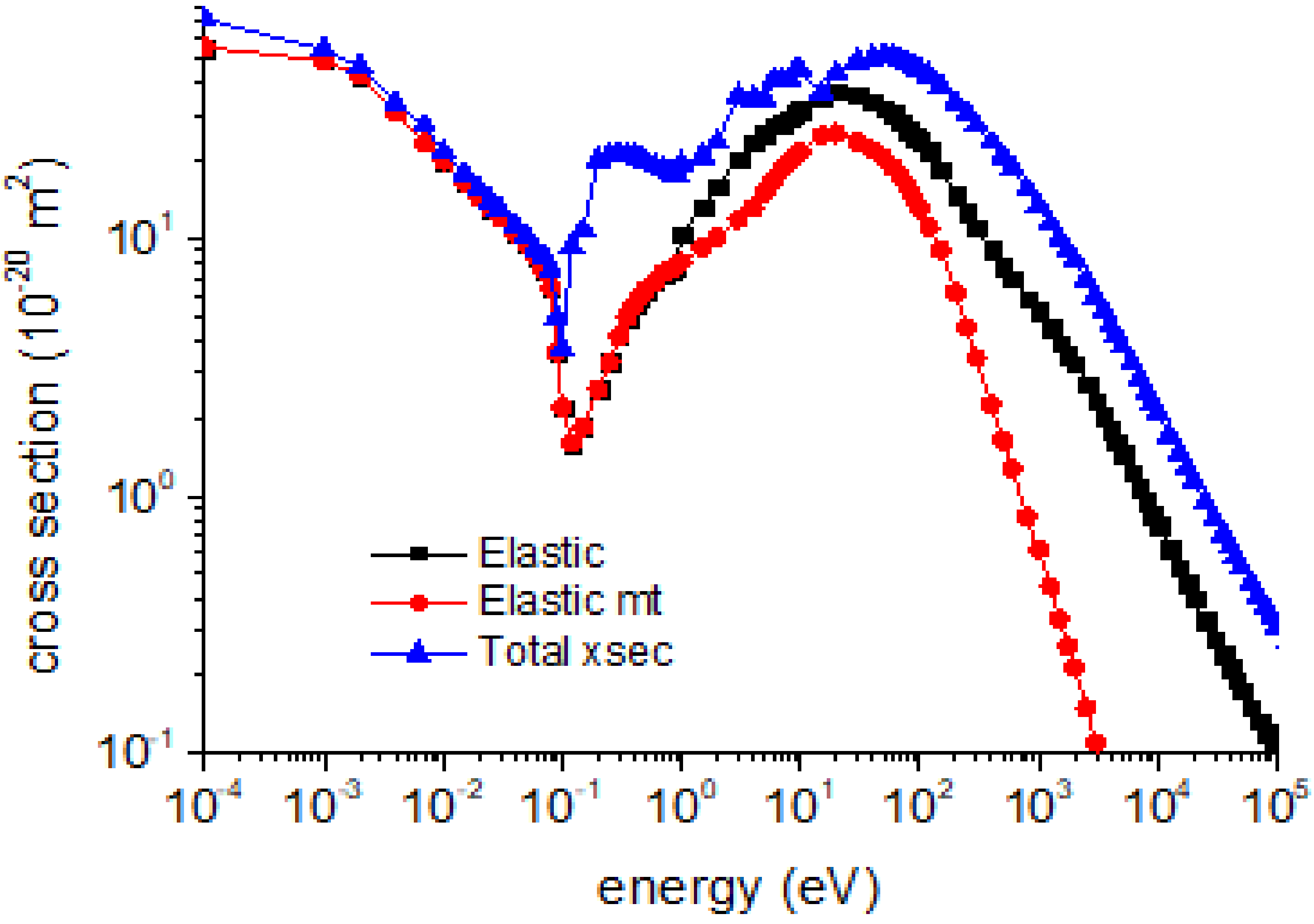


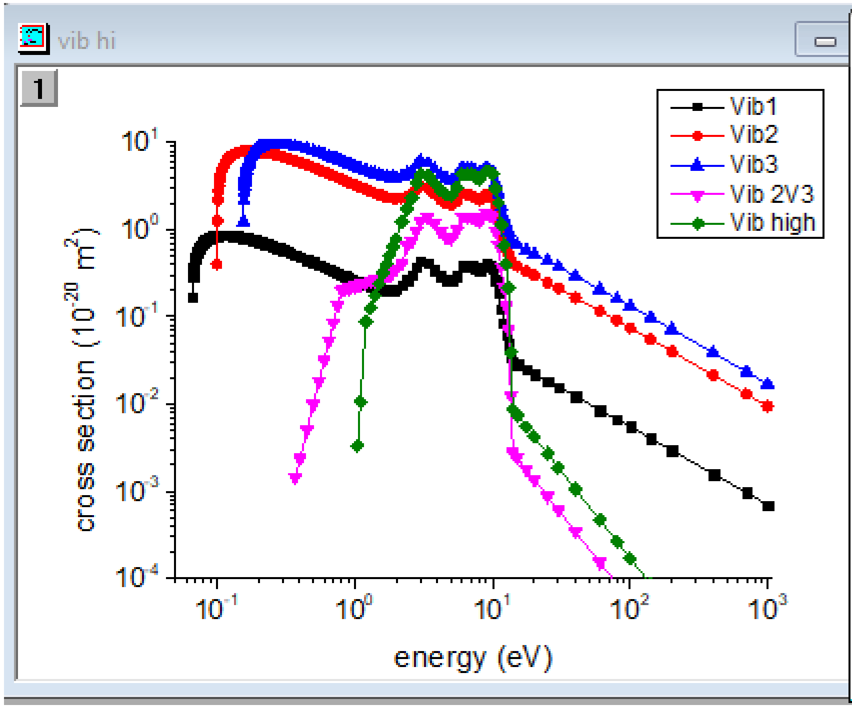
C2F6 2023

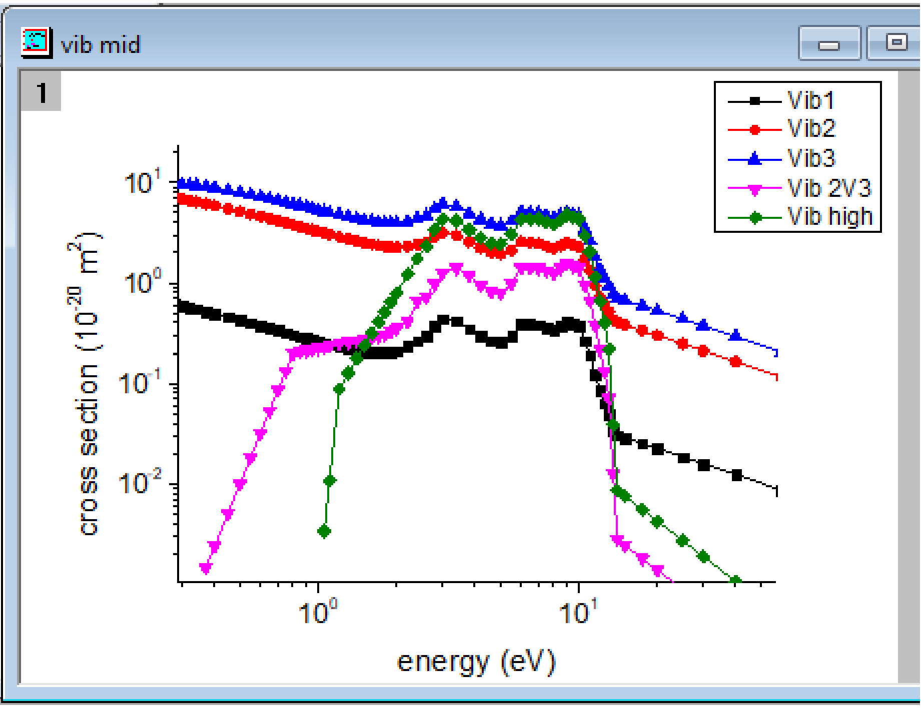


cross section (10^{-20} m^2)
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-3}
10^{-1}
10^1
10^3
10^5
10^7
energy (eV)
elastic
elastic Mt
sum Vib
sum Vib Mt
sum triplets
sum singlets
attachment
count ionisation
gross ionisation

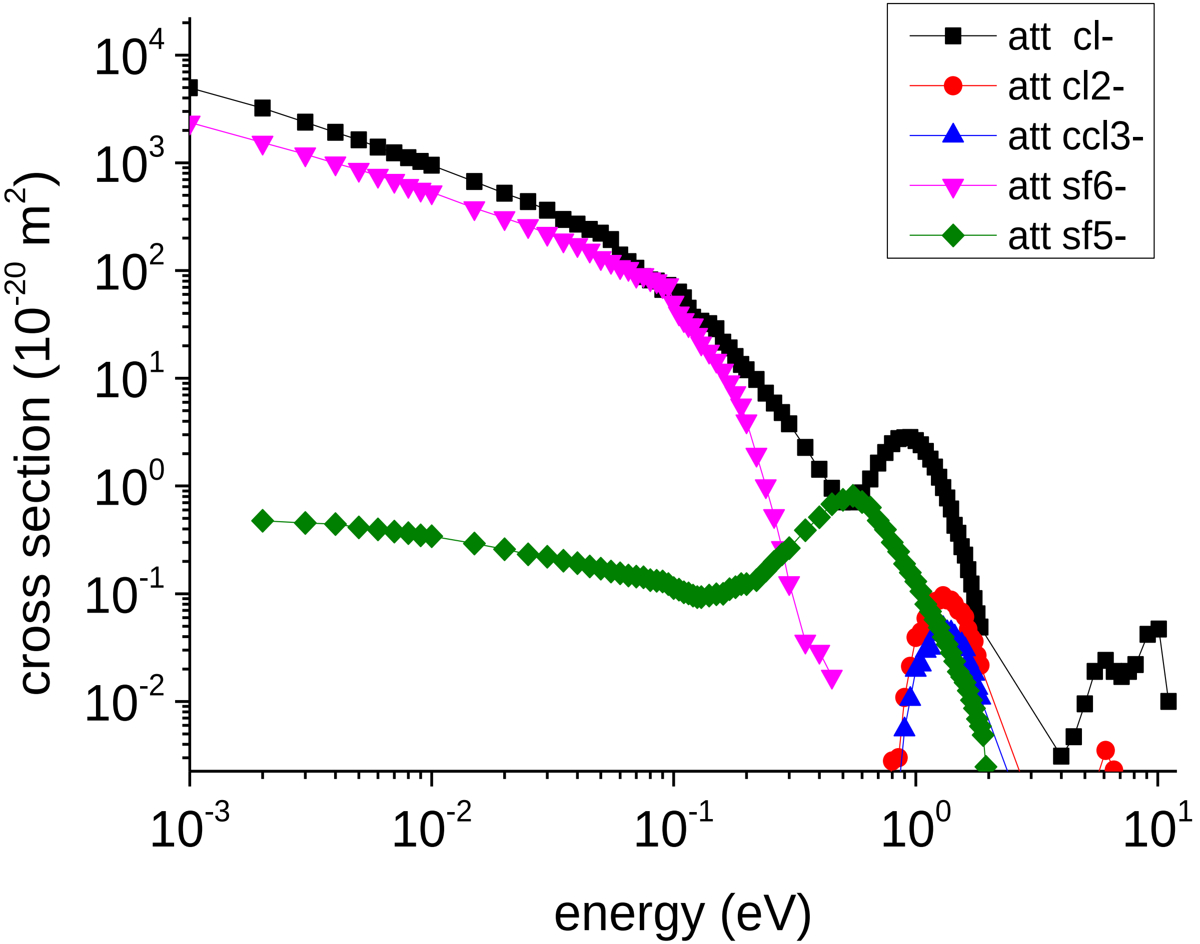
C3F8 elastic cross-sections



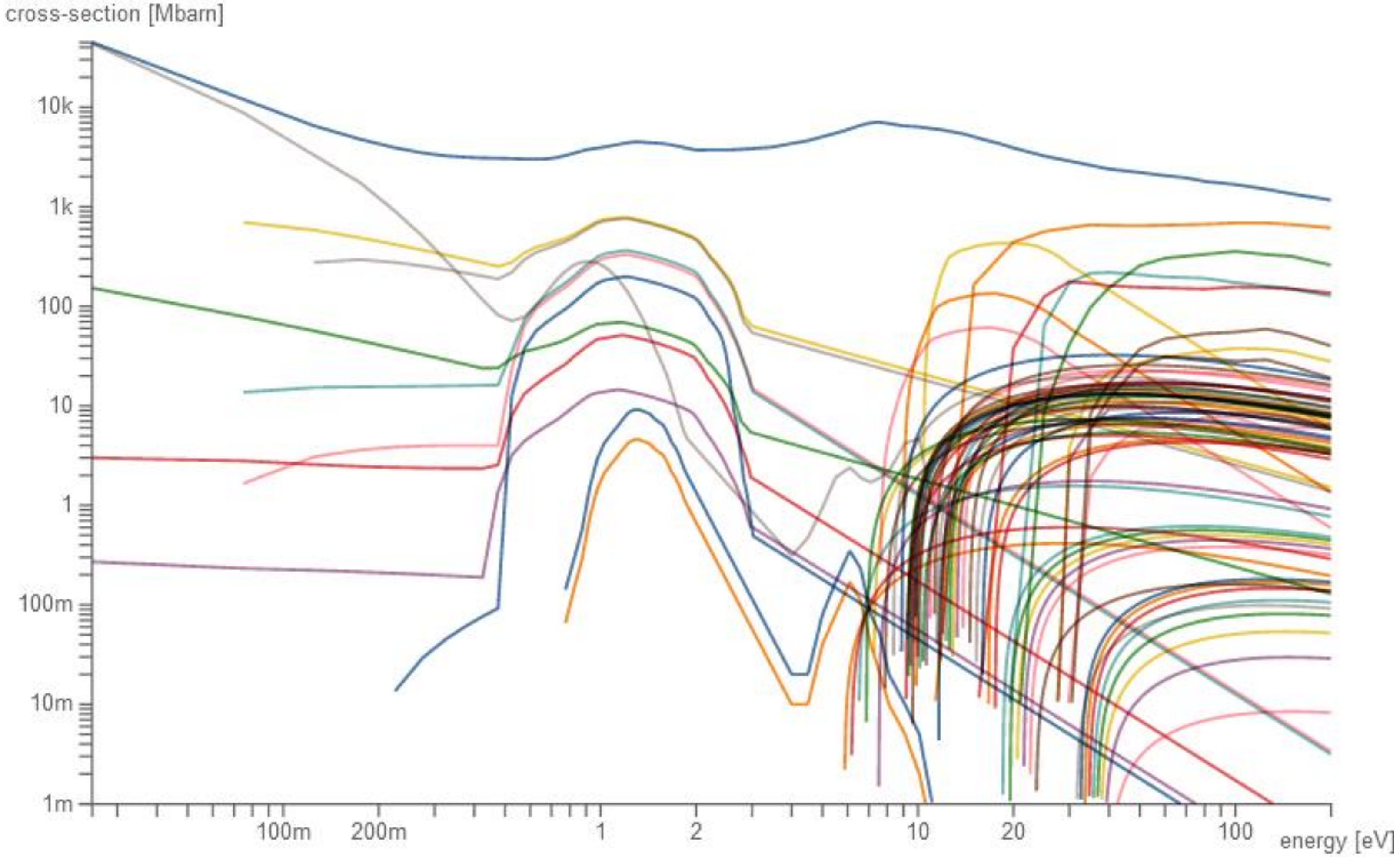

vib hi
1
Vib1
Vib2
Vib3
Vib 2V3
Vib high
cross section (10^-20 m^2)
10^1
10^0
10^-1
10^-2
10^-3
10^-4
10^-1
10^0
10^1
10^2
10^3
energy (eV)


vib mid
1
Vib1
Vib2
Vib3
Vib 2V3
Vib high
cross section (10^-20 m^2)
10^1
10^0
10^-1
10^-2
10^0
10^1
energy (eV)

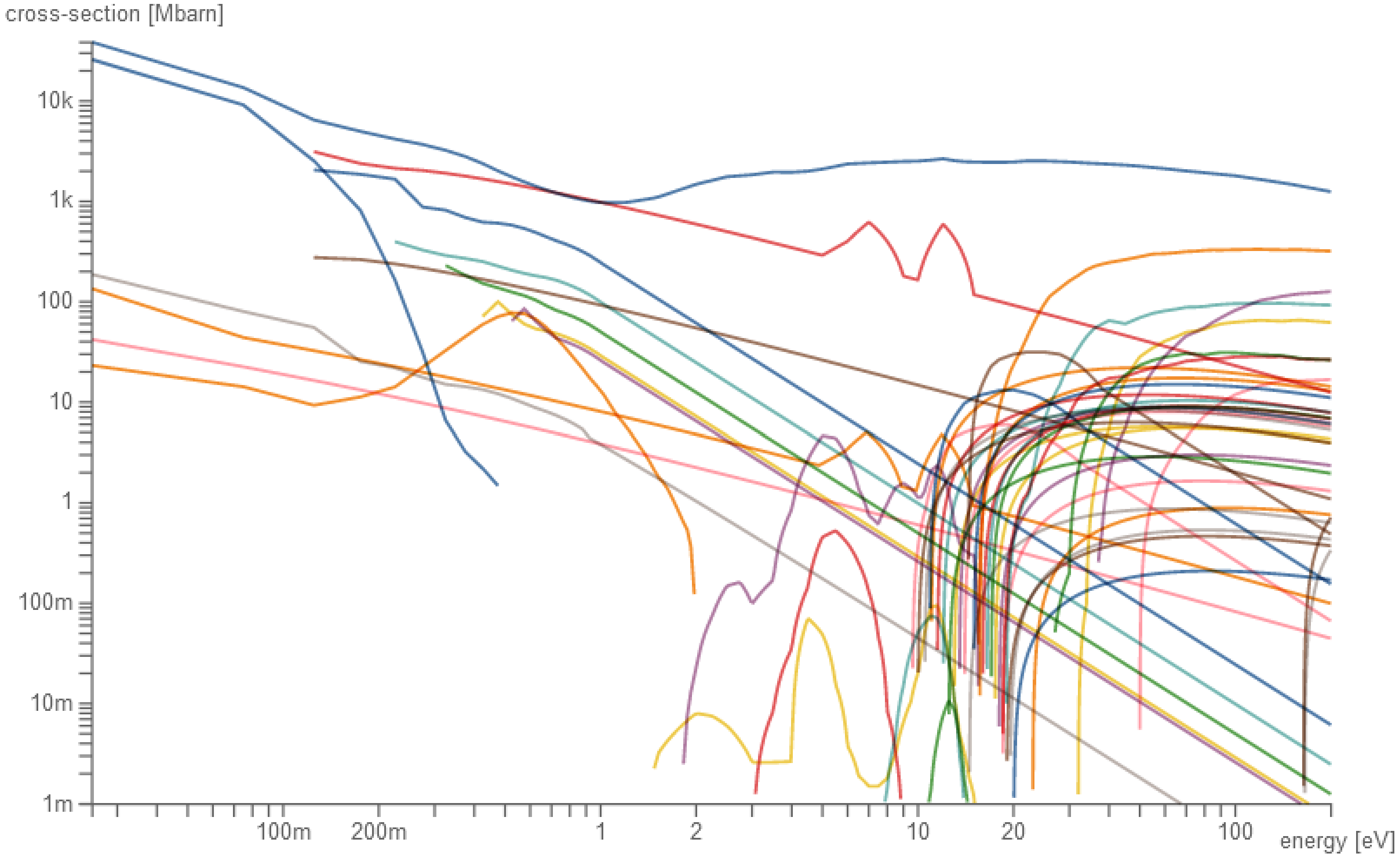
C Cl4 attachment cross-sections



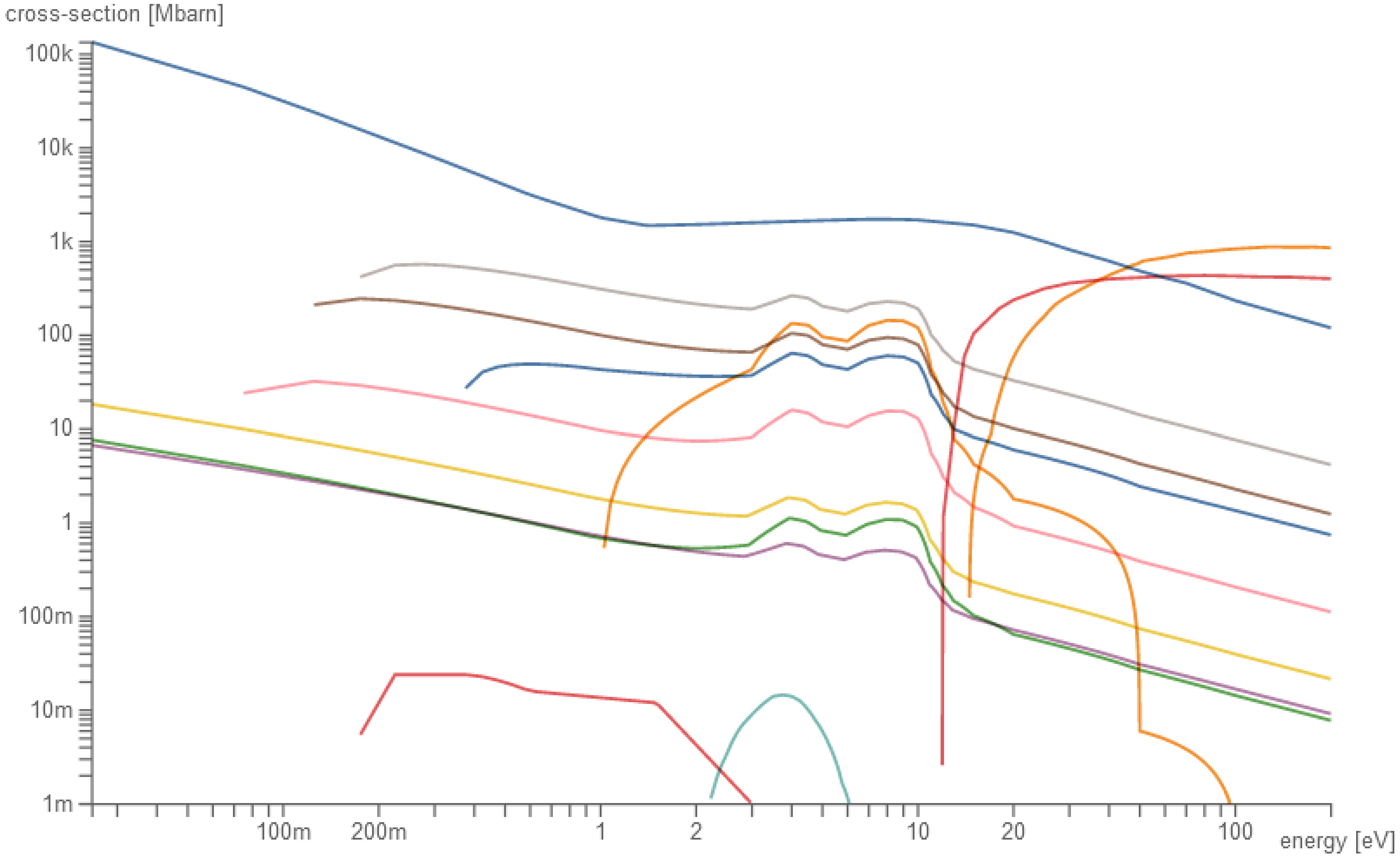
CCL4 carbon tetra chloride Attachment at low energy doubler that of SF6



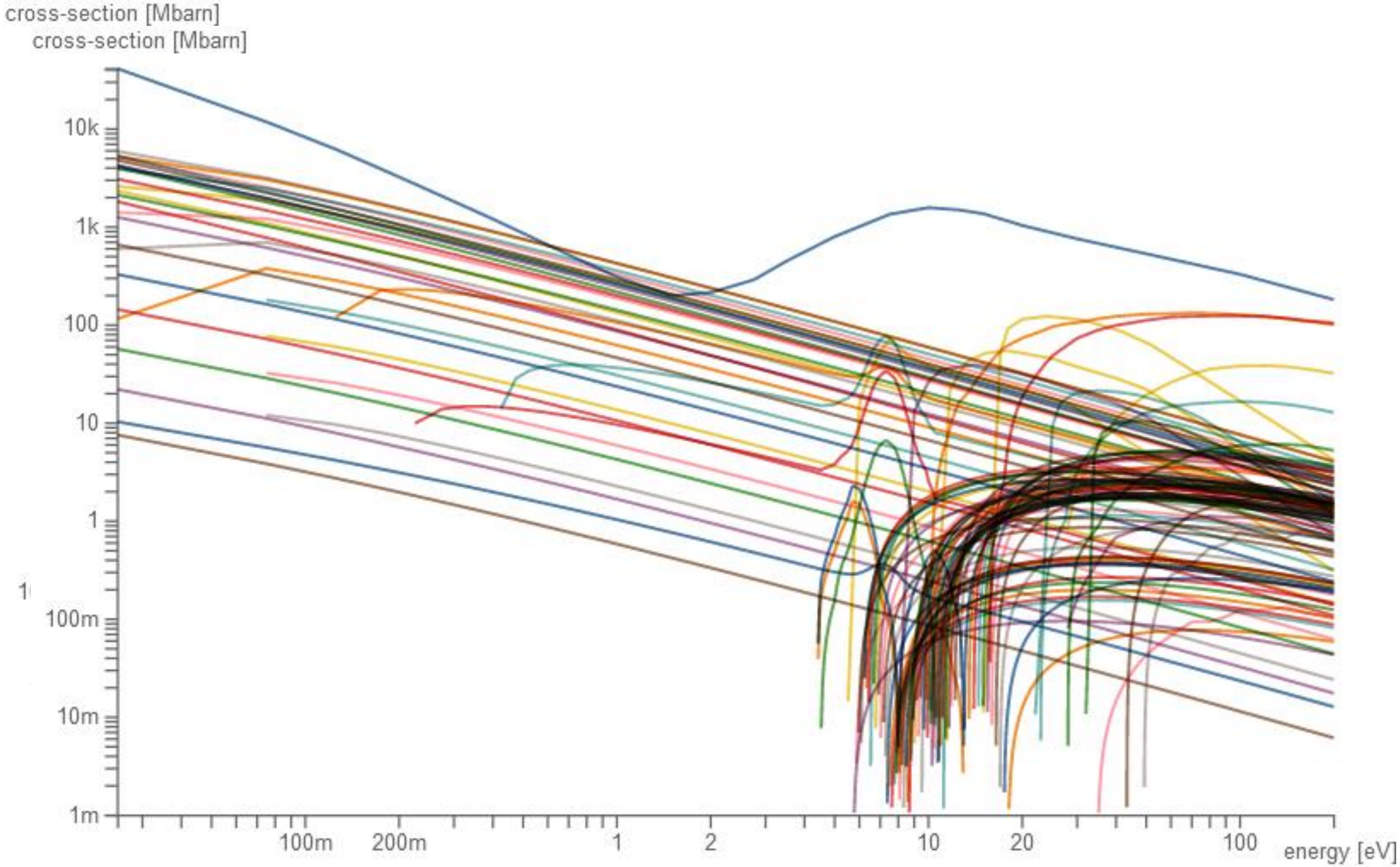
SF6 note large attachment cross-sections at low energy



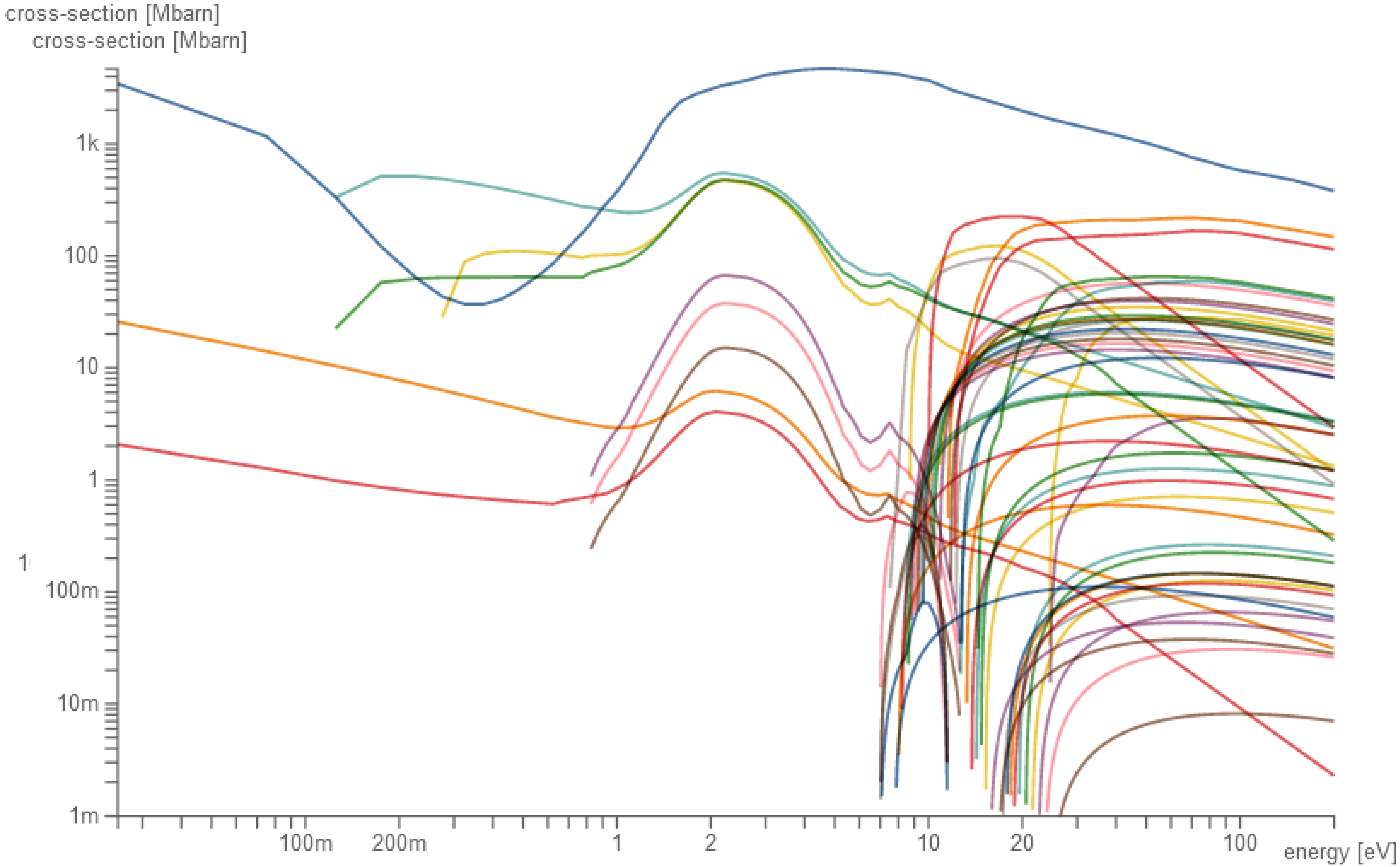
R134a C2H2F4 2010



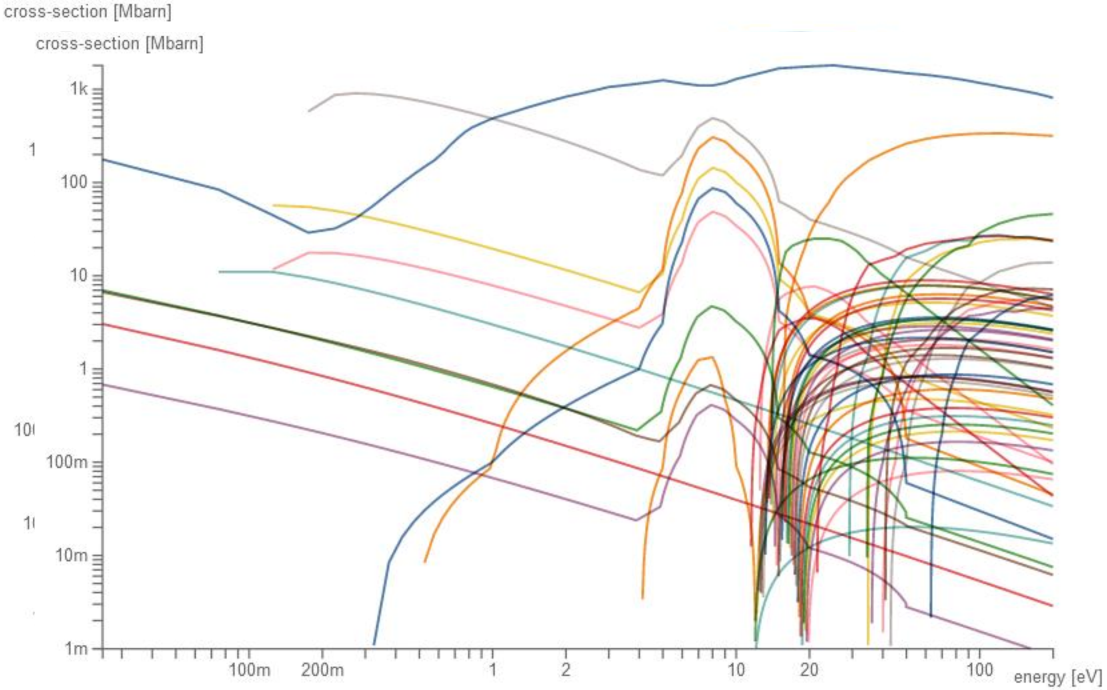
Ammonia NH3   note symmetric top rotational model => fewer transitions



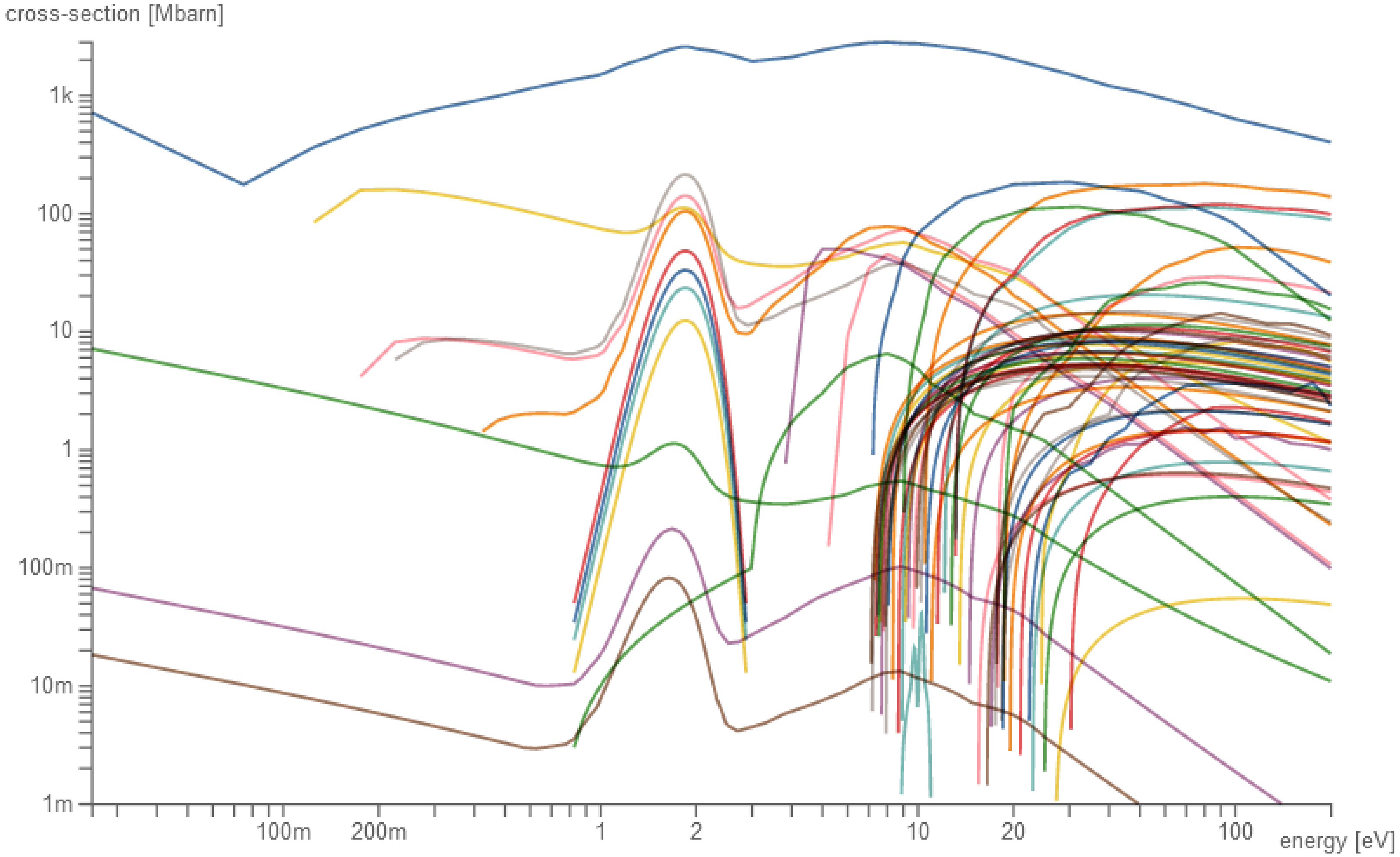
Silane SiH4 no rotation deep ramsauer dip



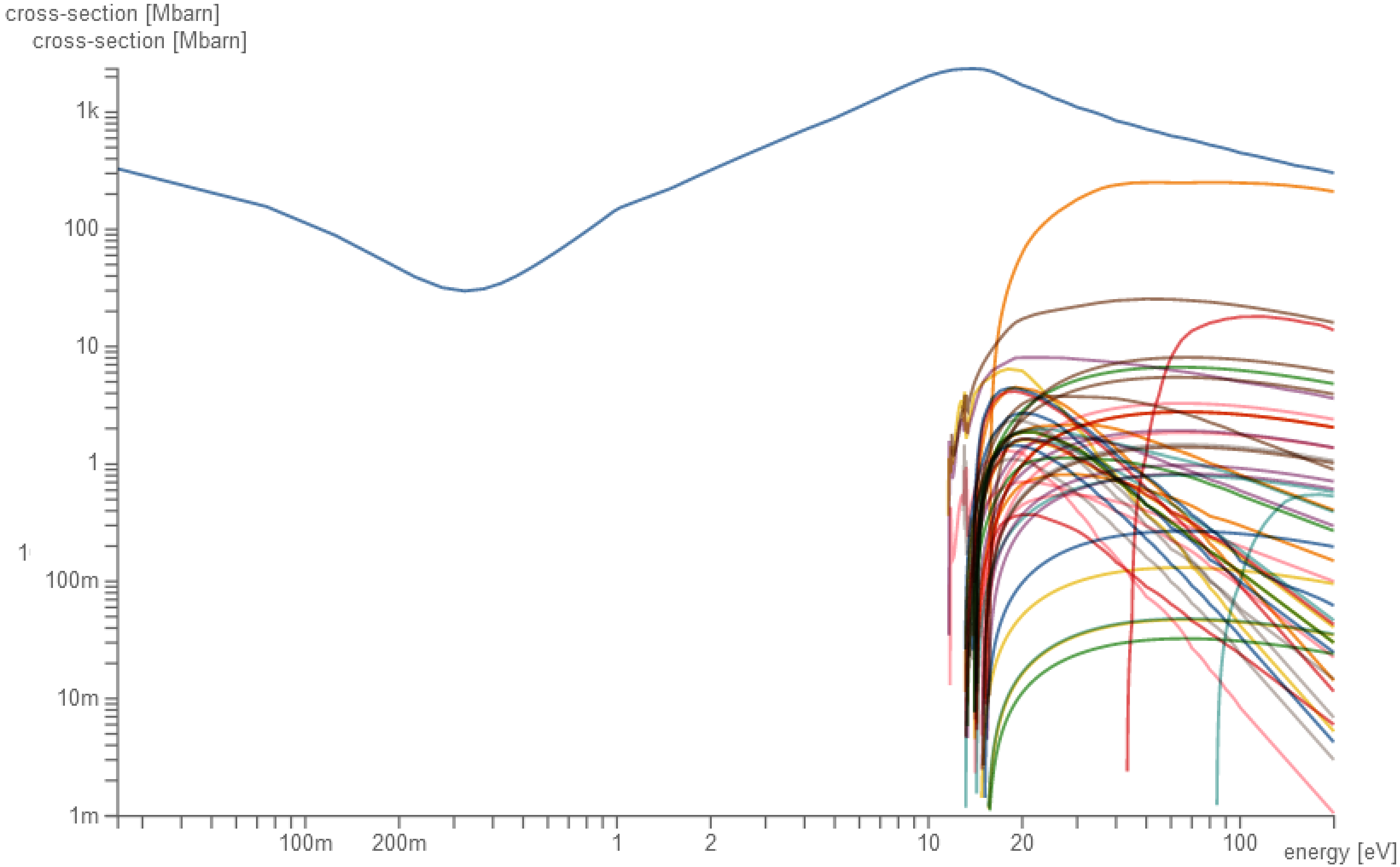
CF4 large stretch vibrations . Needs small modification to excitation and ionisation in order to increase the calculated W ev/ion pair from 29.8 ev to the expected value of 32 ev



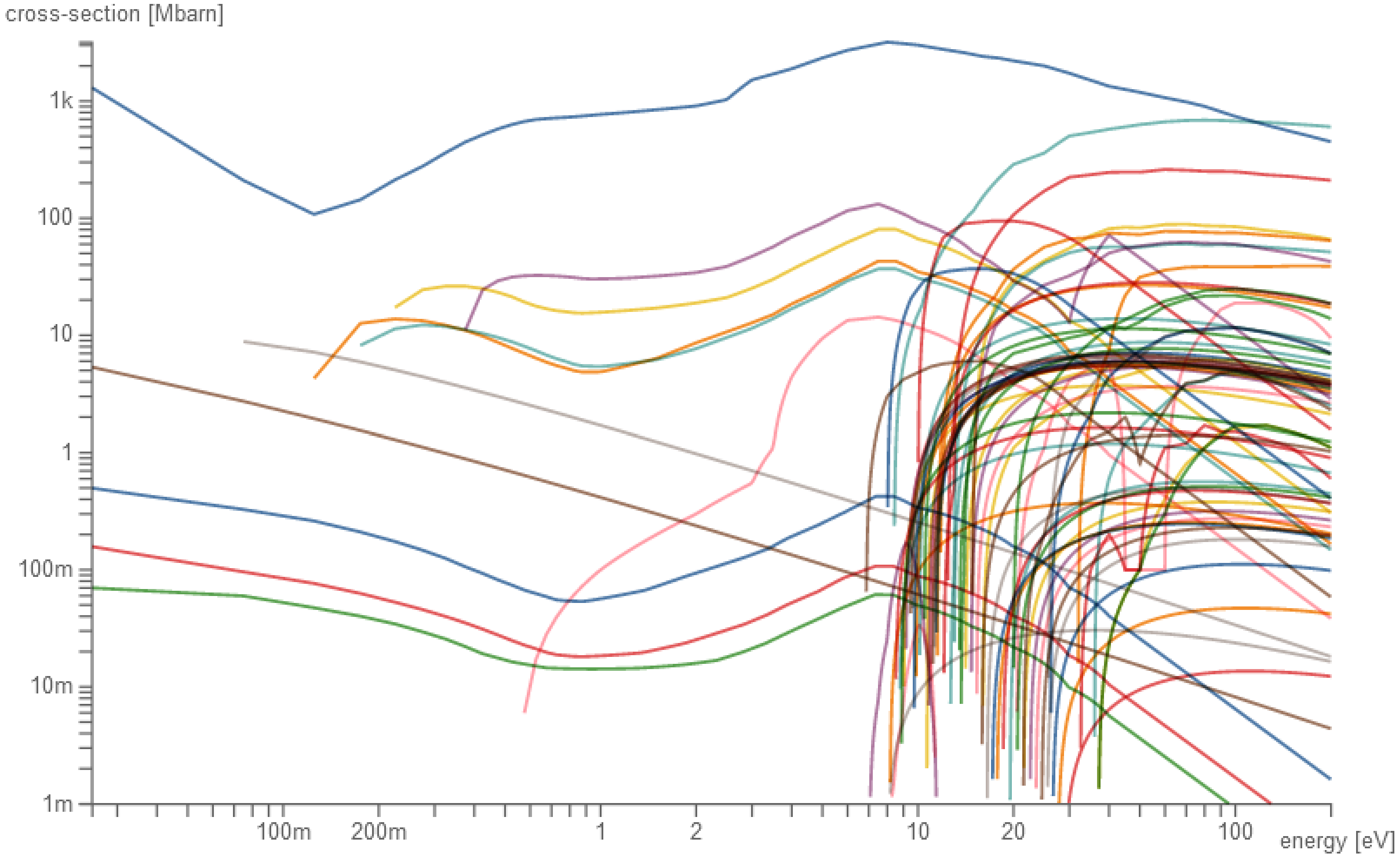
C2H4 ethene double bond pi excitation



Argon


cross-section [Mbarn]
cross-section [Mbarn]
1k
100
10
1
1
100m
10m
1m
100m
200m
1
2
10
20
100
energy [eV]

Ethane


cross-section [Mbarn]
1k
100
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10m
1m
100m
200m
1
2
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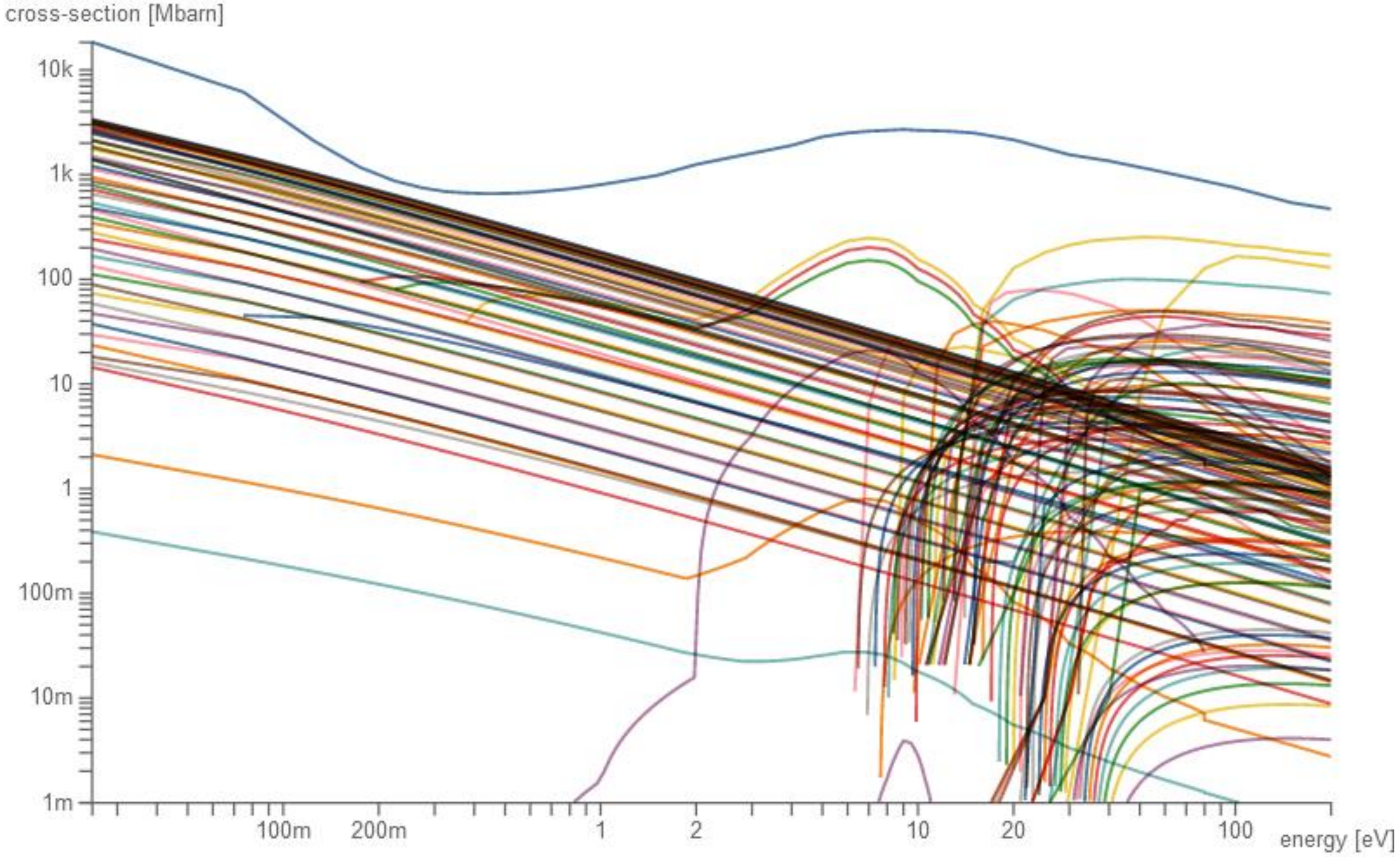
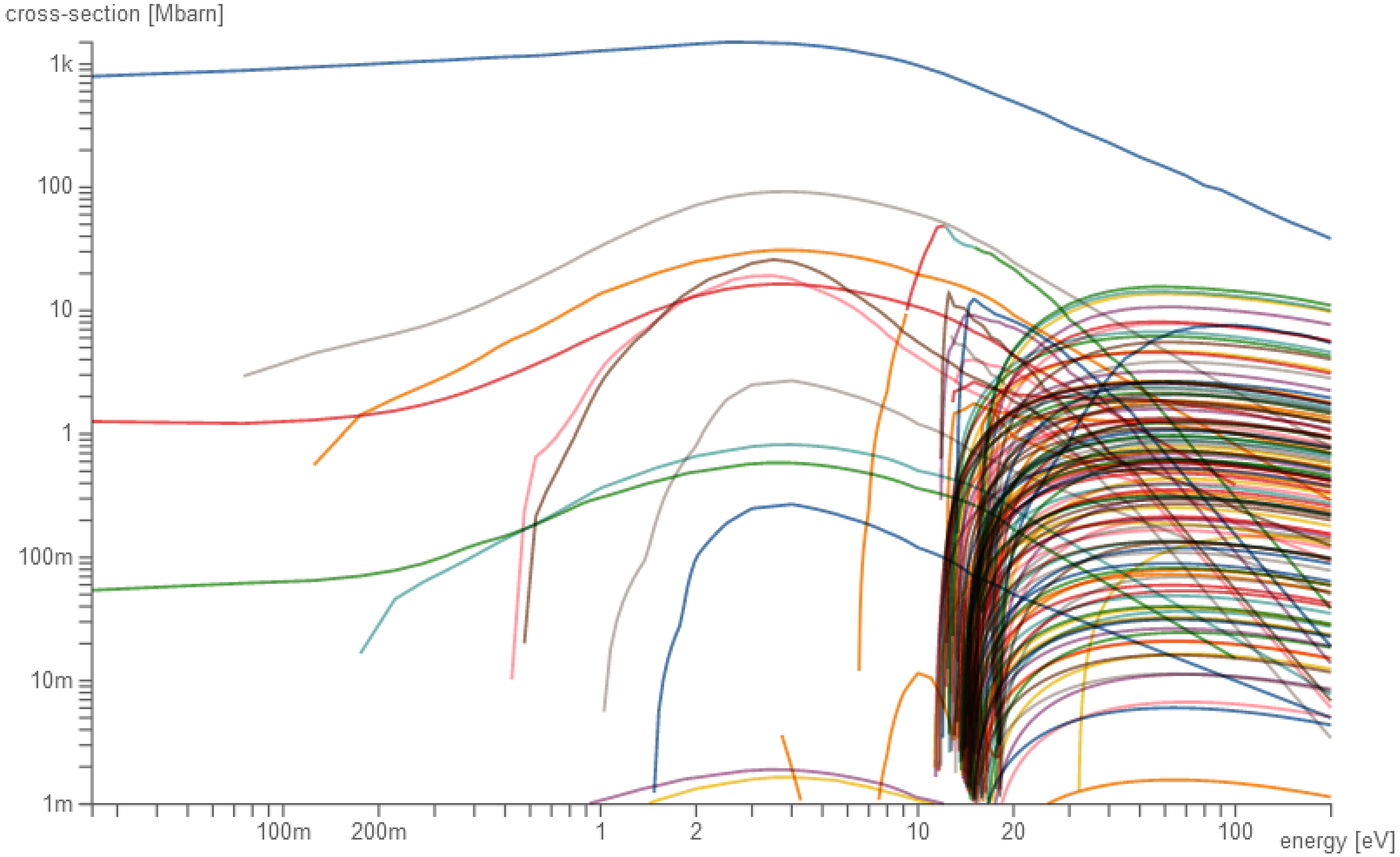
20
100
energy [eV]

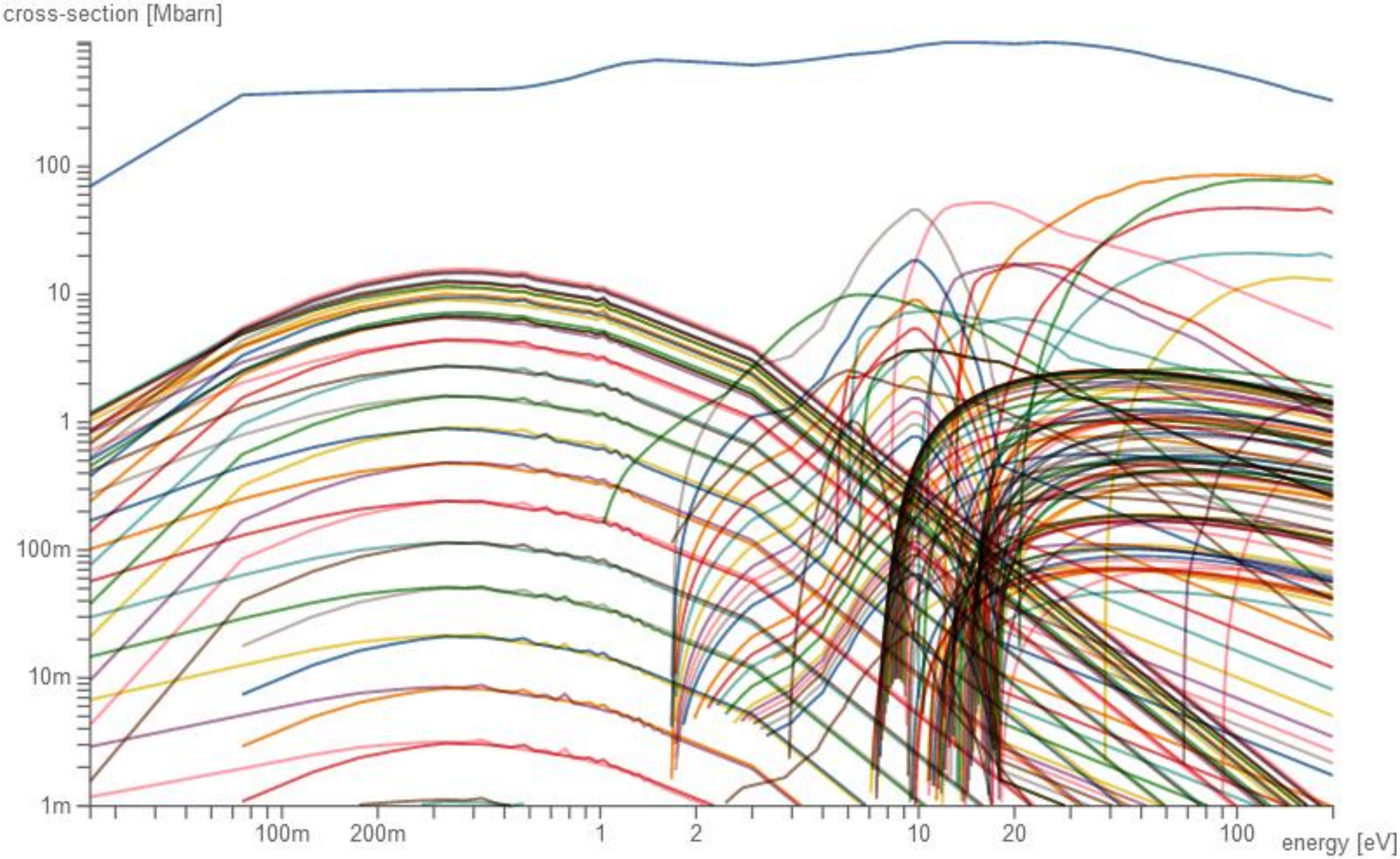
DI METHYL ETHER dme



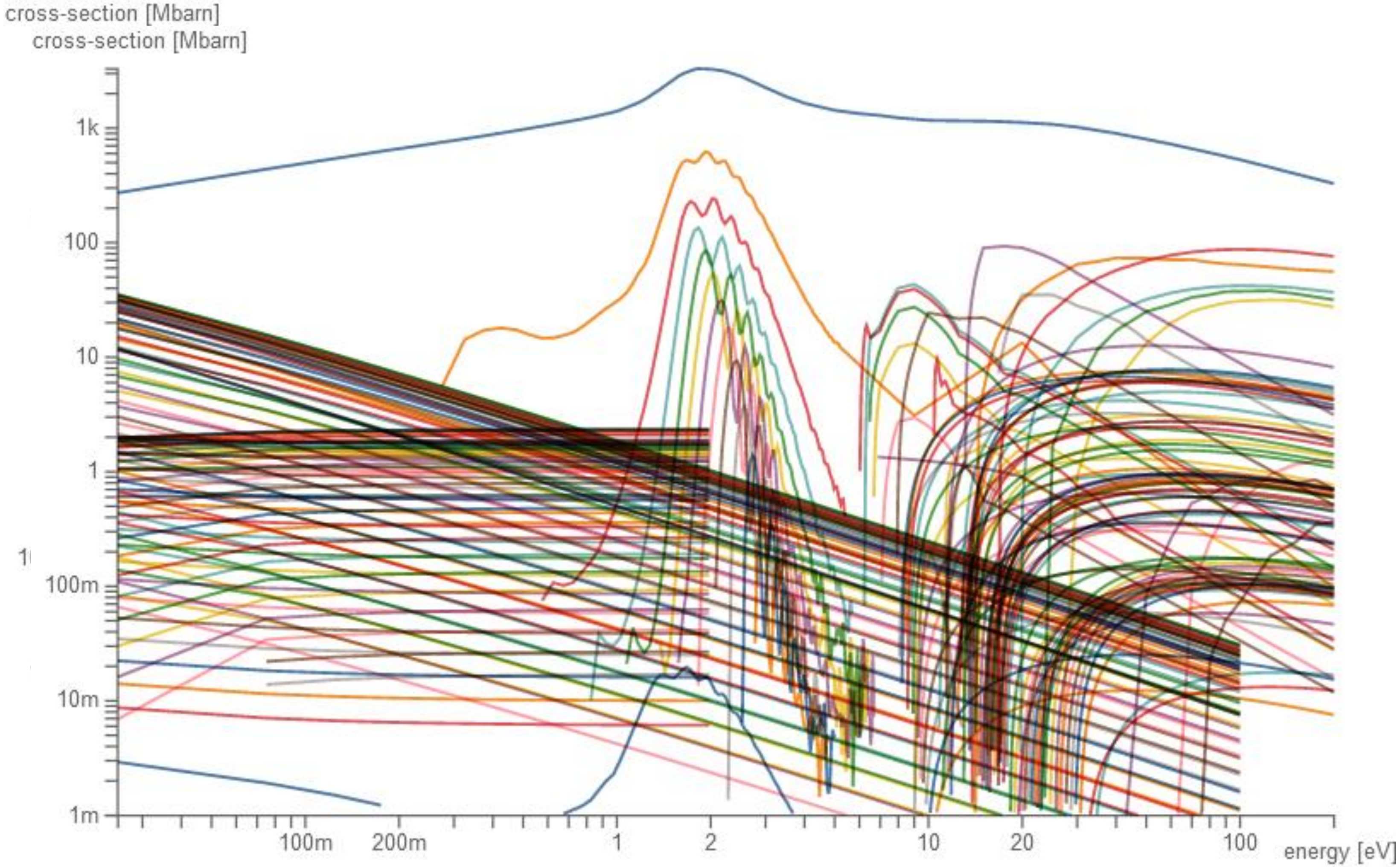
Hydrogen


cross-section [Mbarn]
1k
100
10
1
100m
10m
1m
100m
200m
1
2
10
20
100
energy [eV]

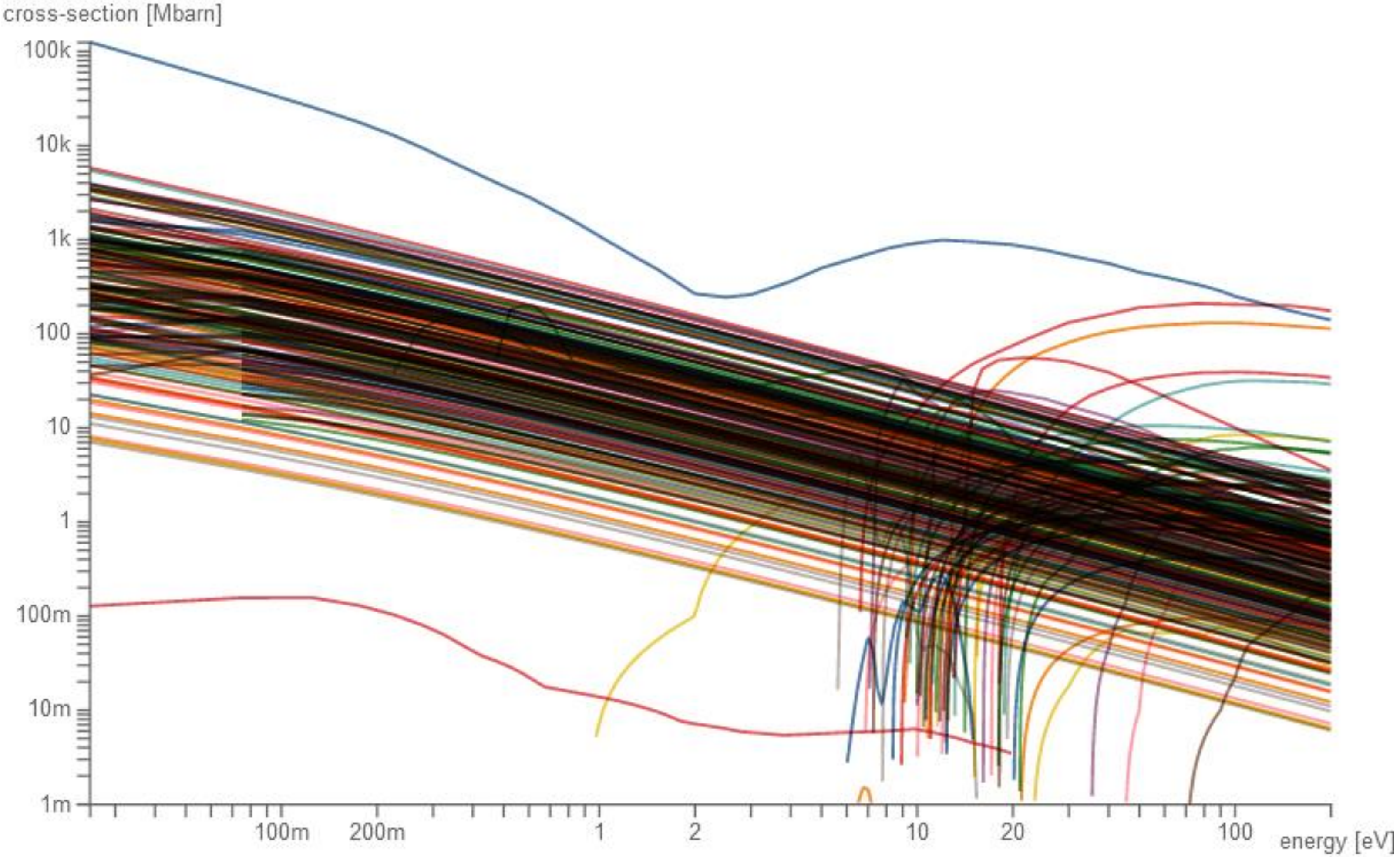
Oxygen


cross-section [Mbarn]
100
10
1
100m
10m
1m
100m
200m
1
2
10
20
100
energy [eV]

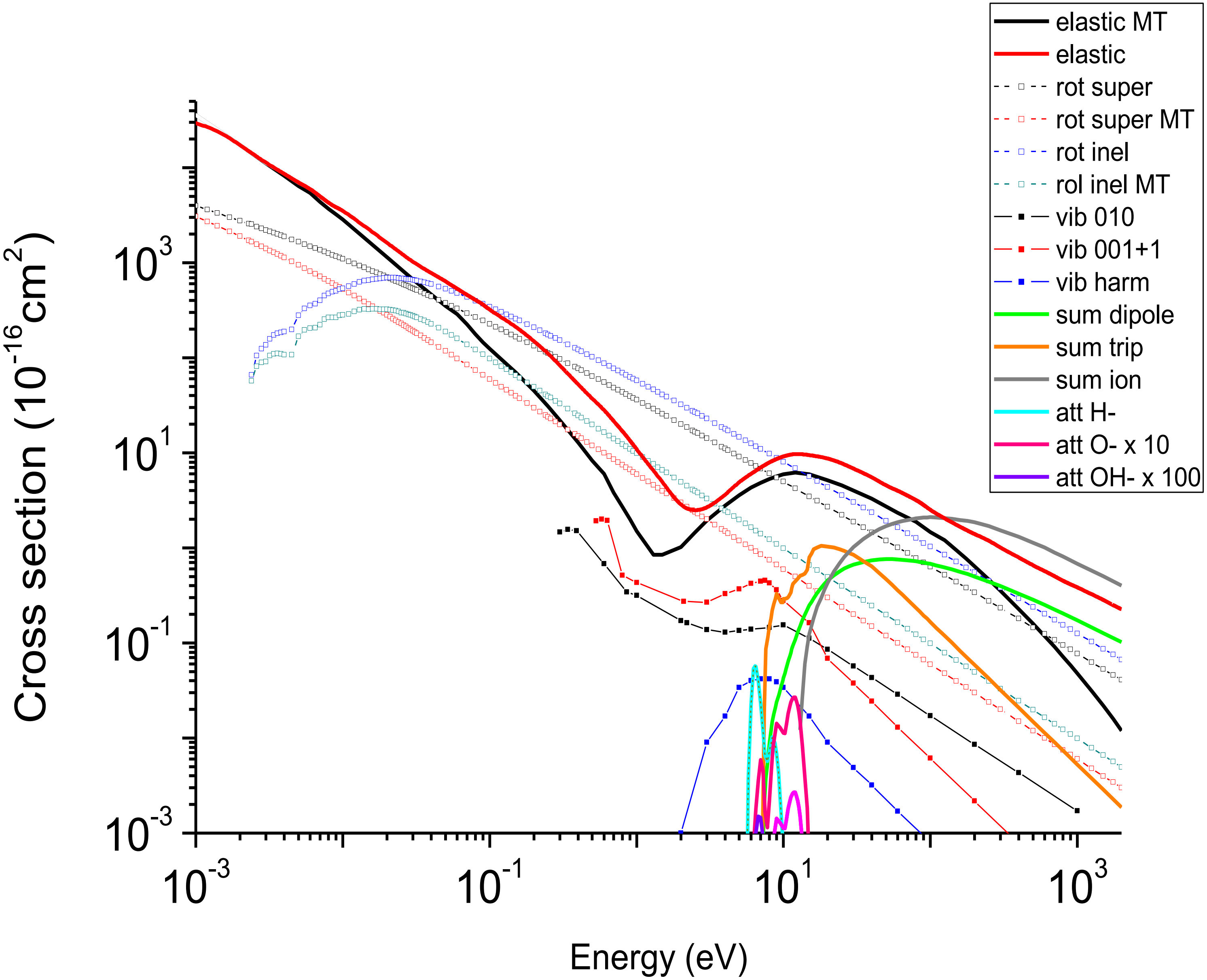
Carbon Monoxide fits transport data to +-0.3%



H2O


cross-section [Mbarn]
100k
10k
1k
100
10
1
100m
10m
1m
100m
200m
1
2
10
20
100
energy [eV]

H2O


elastic MT
elastic
rot super
rot super MT
rot inel
rol inel MT
vib 010
vib 001+1
vib harm
sum dipole
sum trip
sum ion
att H-
att O- x 10
att OH- x 100
Cross section (10^{-16}cm^2)
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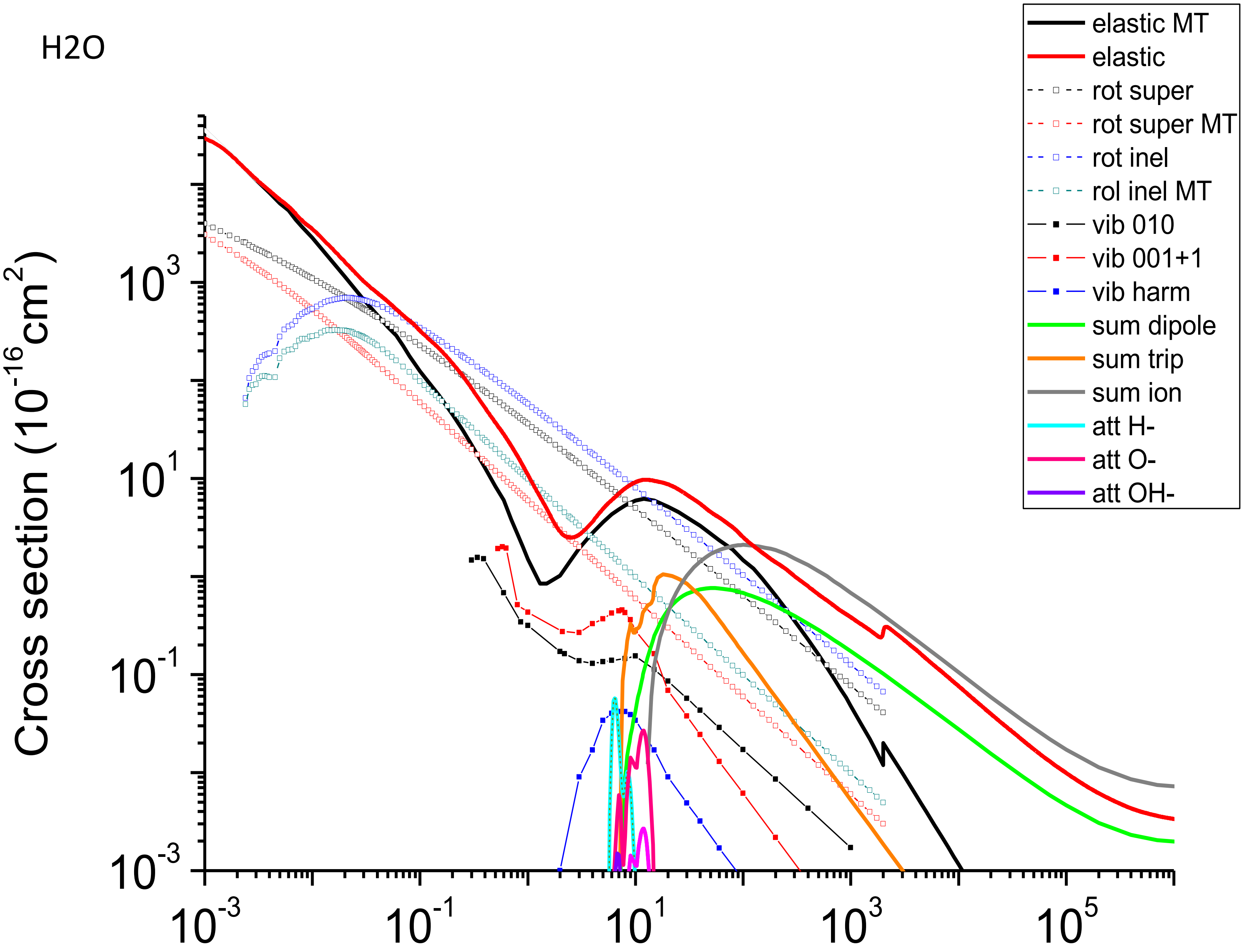
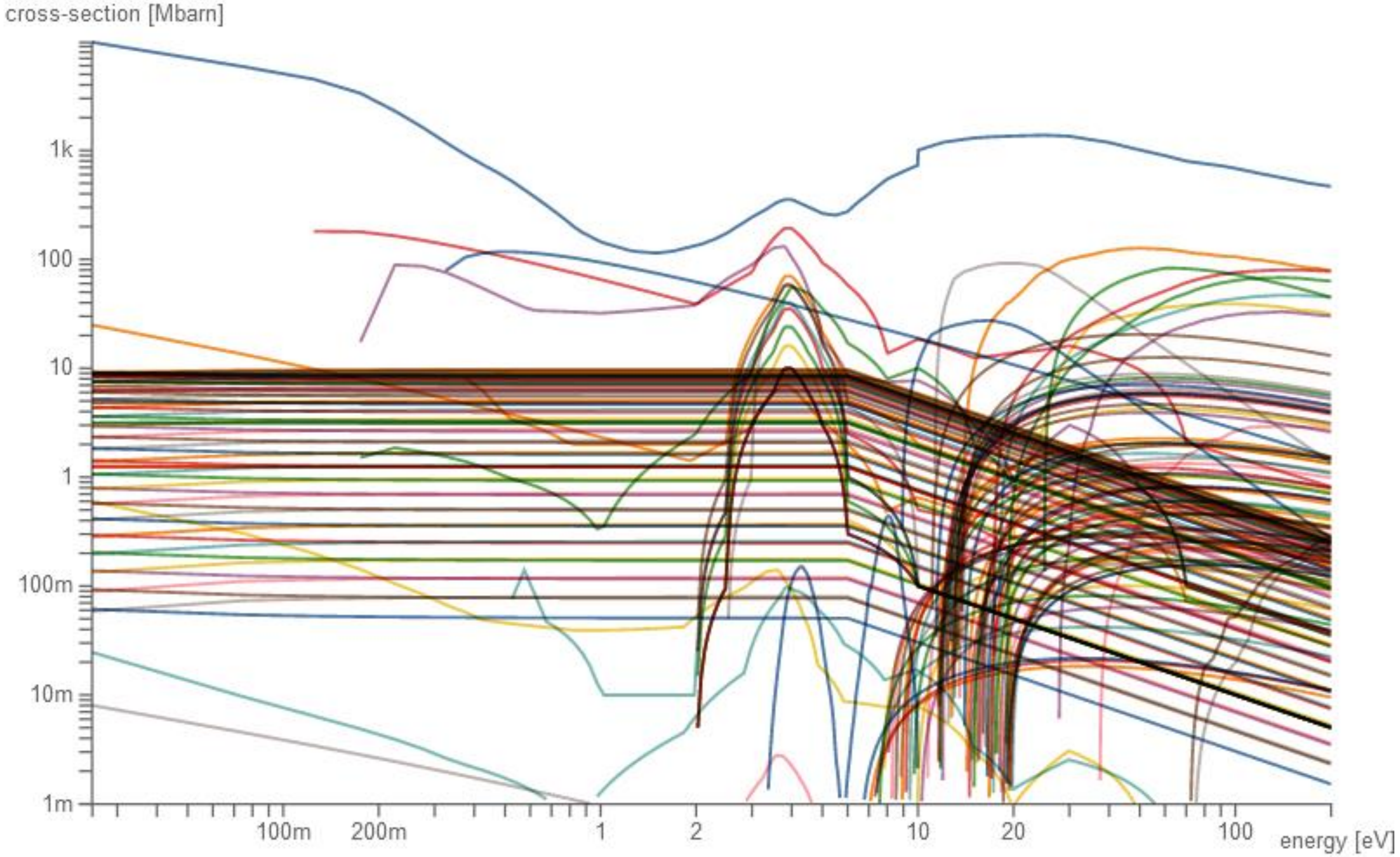
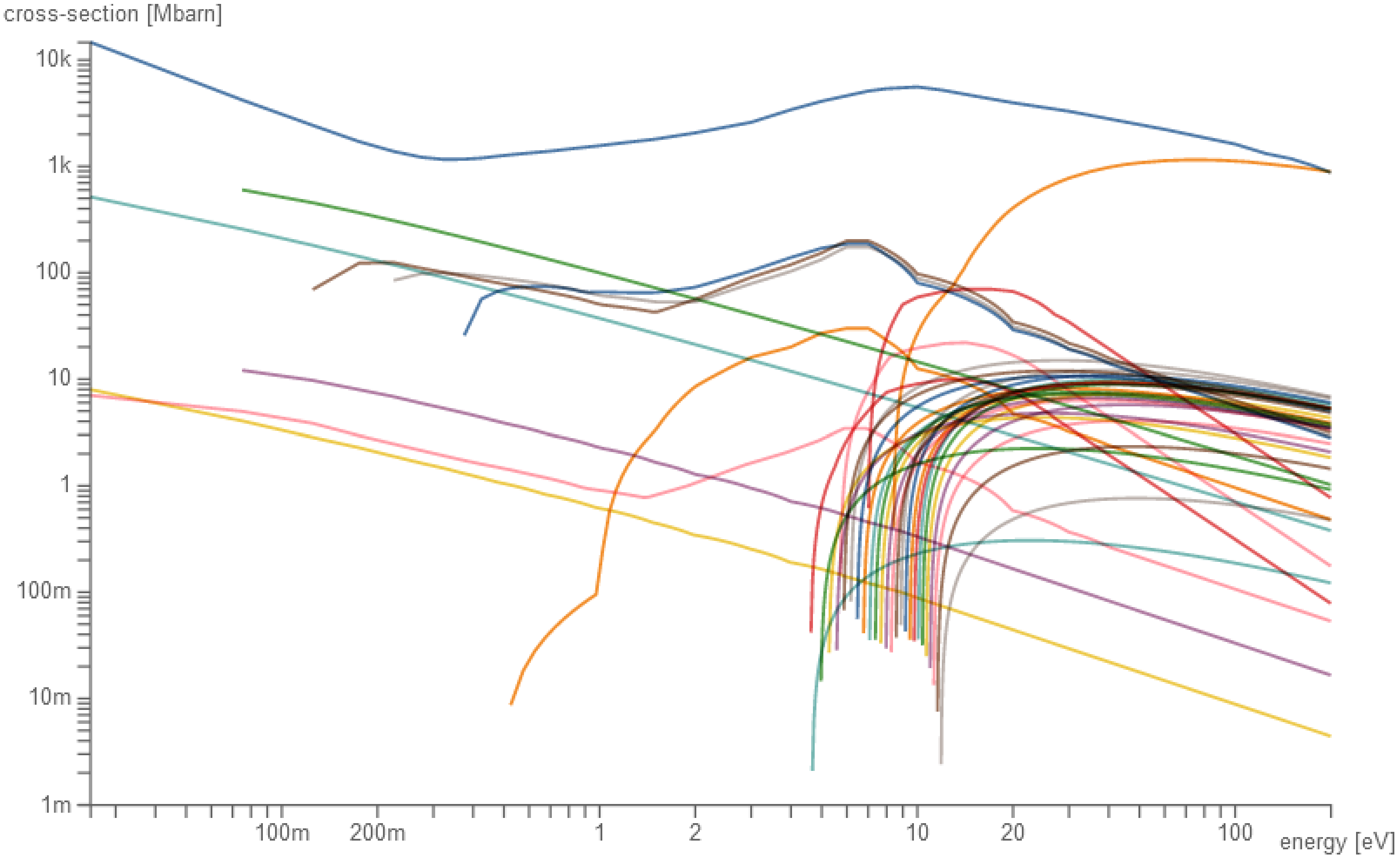
10^1
10^{-1}
10^{-3}
10^{-3}
10^{-1}
10^1
10^3
Energy (eV)


H2O
Cross section $(10^{-16}cm^2)$
10^3
10^1
10^{-1}
10^{-3}
10^{-3}
10^{-1}
10^1
10^3
10^5
Energy (eV)
elastic MT
elastic
rot super
rot super MT
rot inel
rol inel MT
vib 010
vib 001+1
vib harm
sum dipole
sum trip
sum ion
att H-
att O-
att OH-

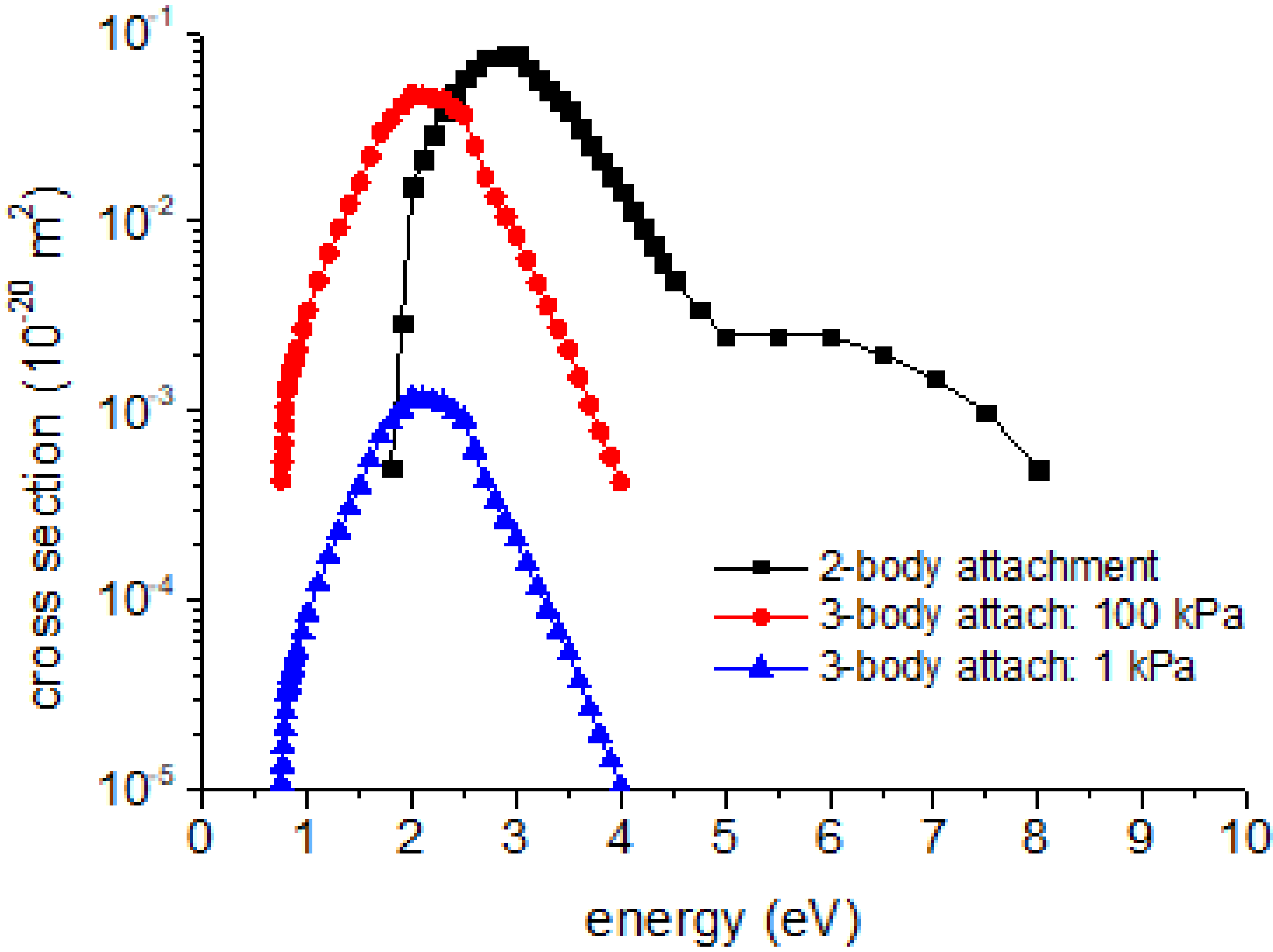
Carbon Dioxide Fits transport data to +- 0.3%



Tri methyl amine TMA



C3F8 2 and 3 body attachment



Oscillator strength

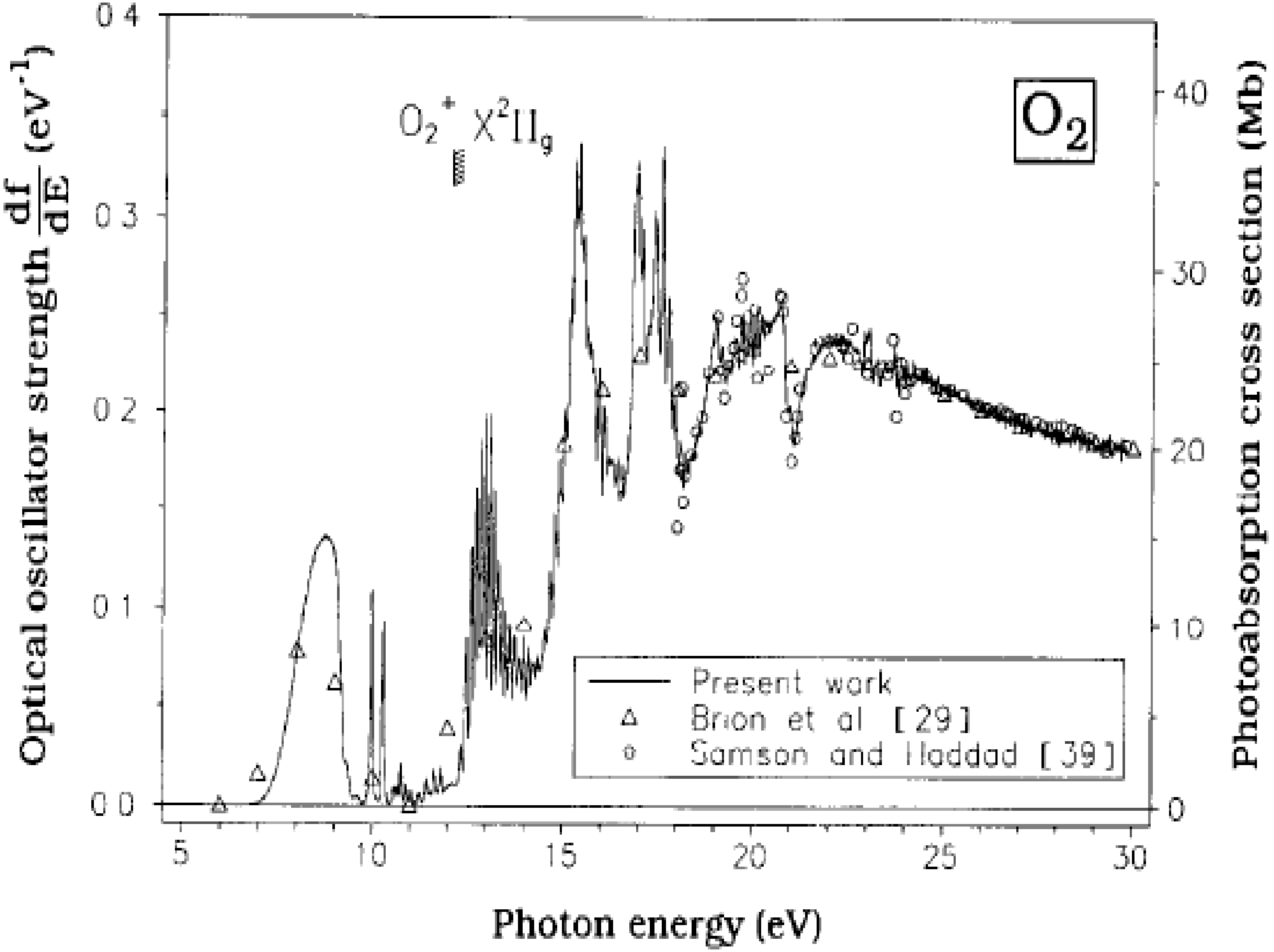
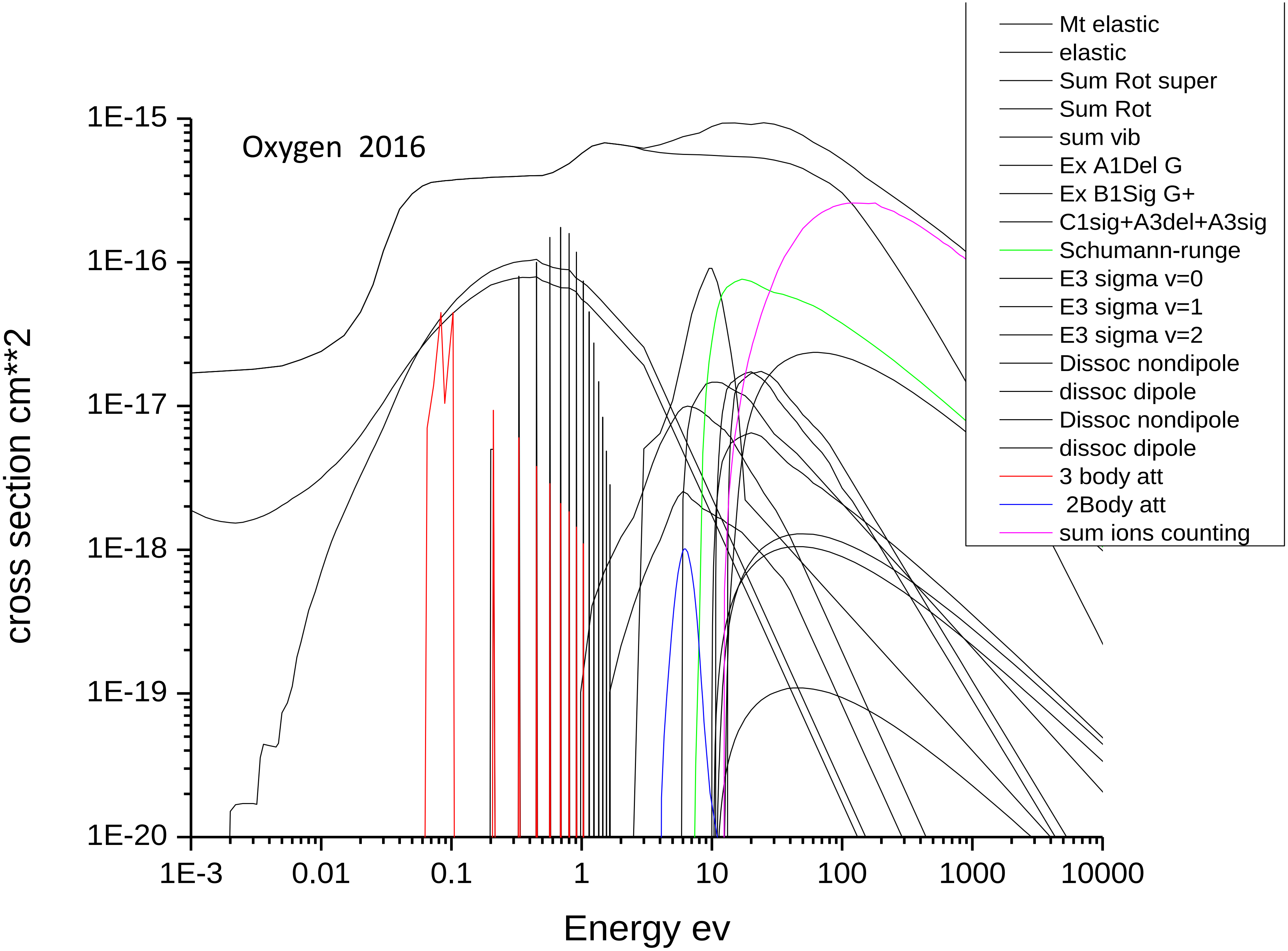
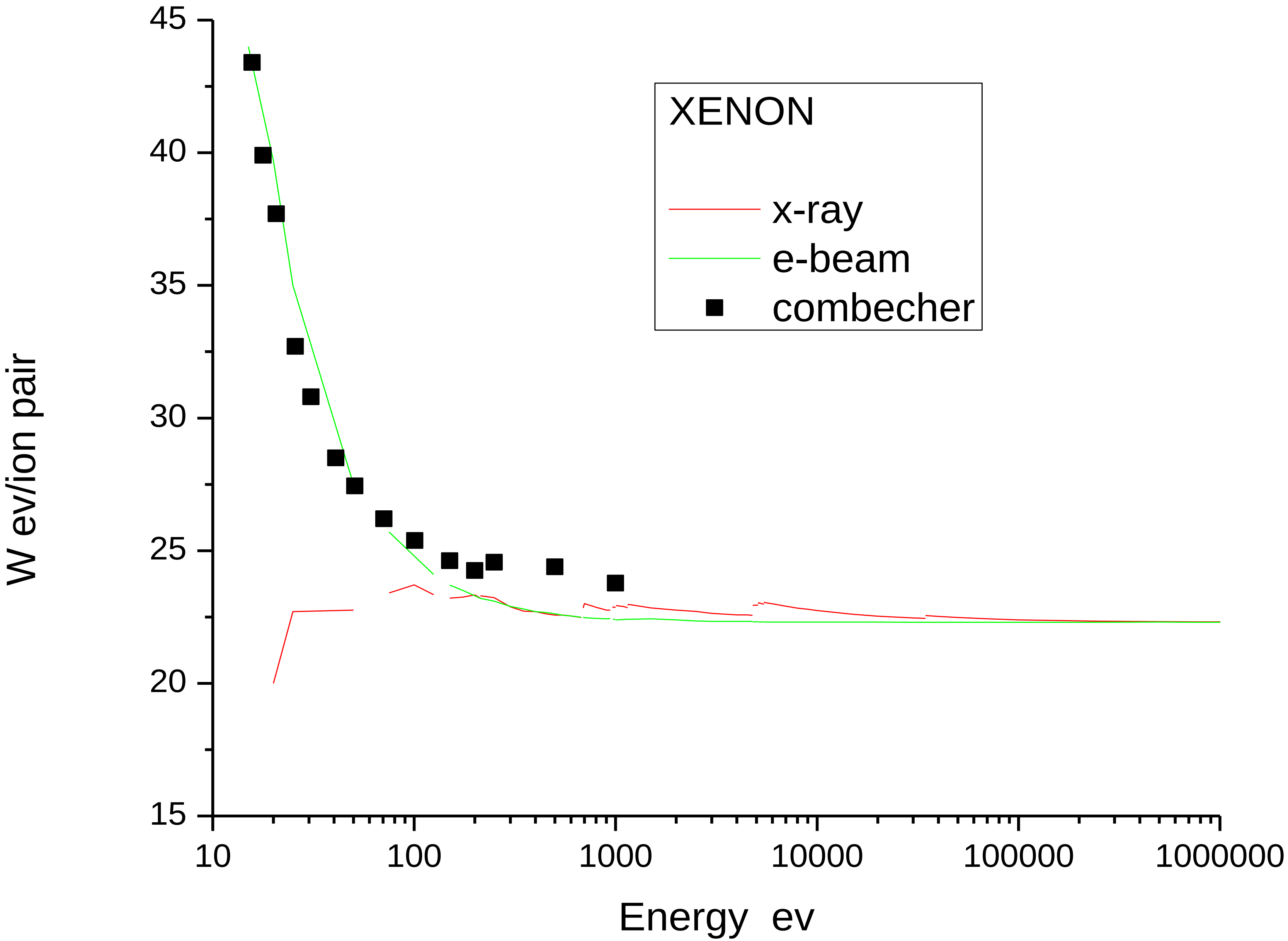
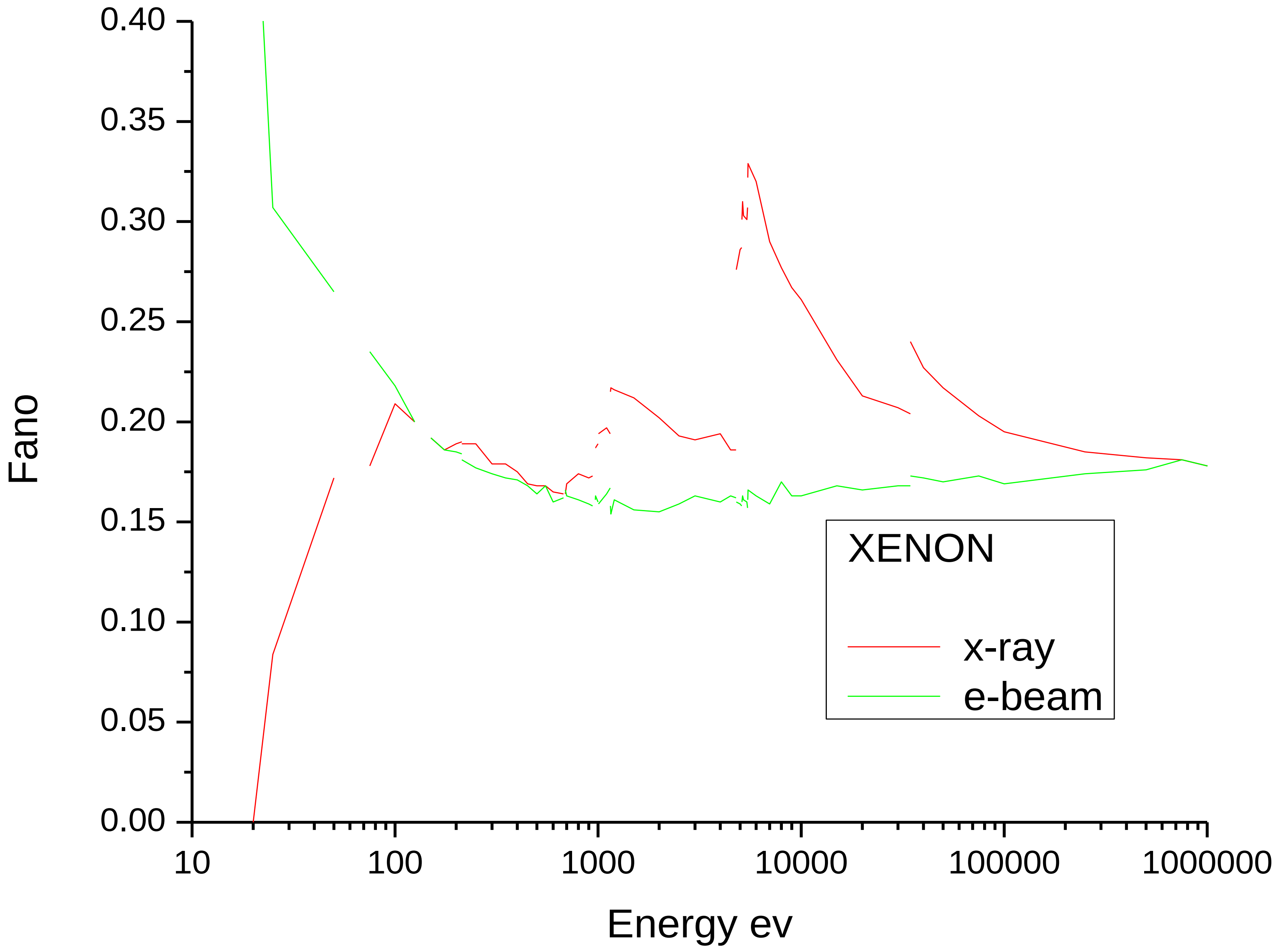
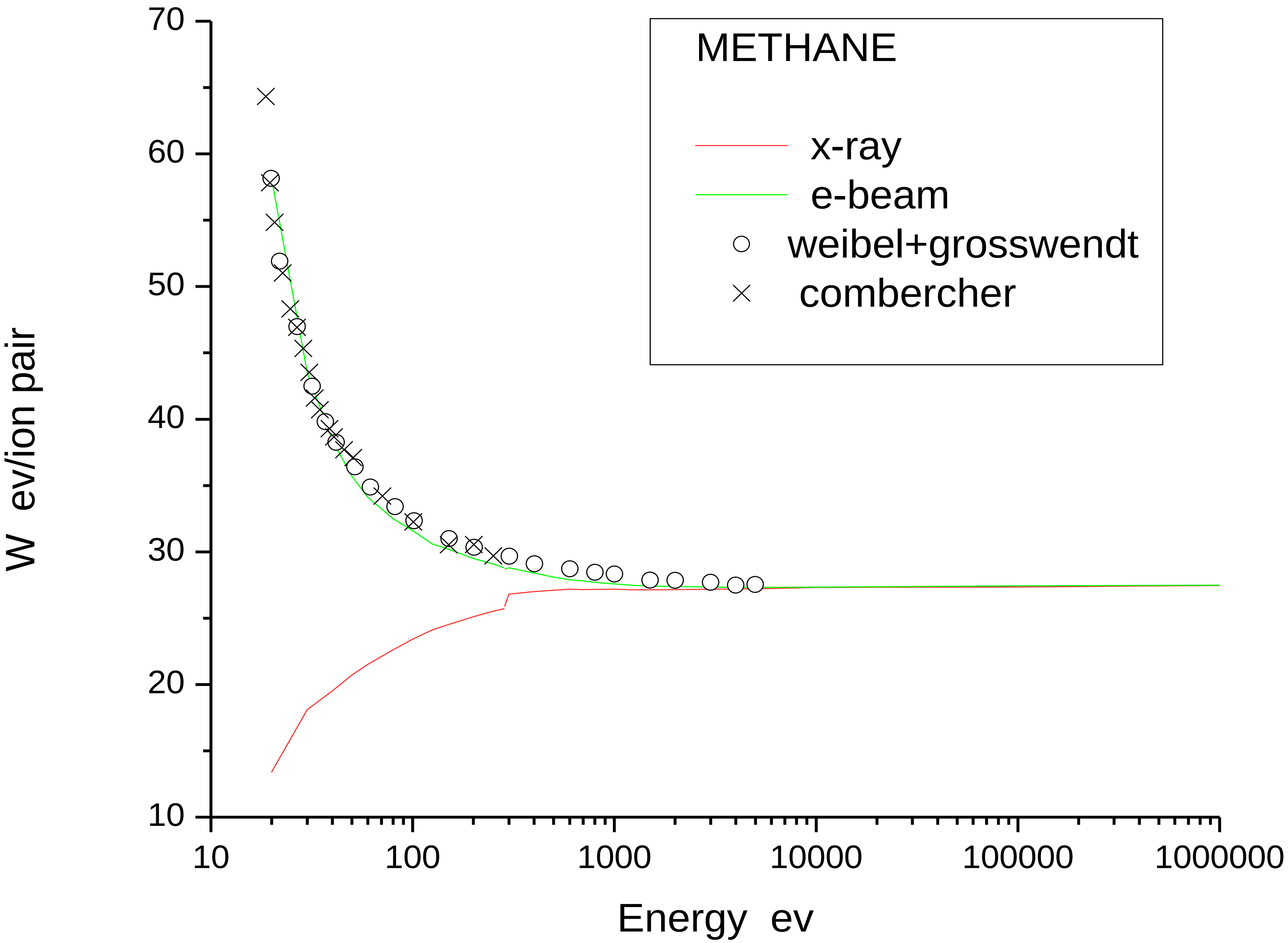


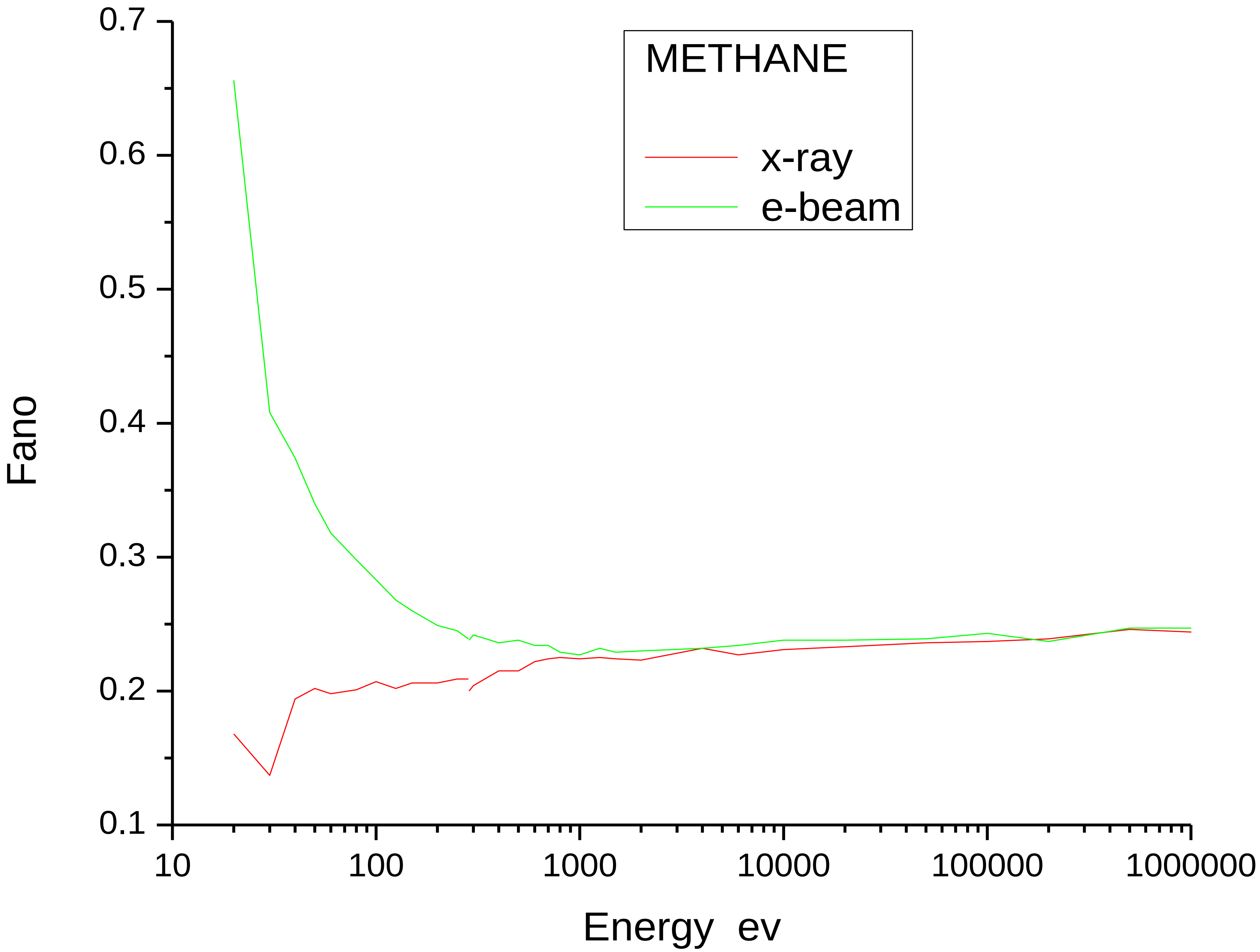
Fig. 1. Absolute oscillator strengths for the photoabsorption of molecular oxygen in the energy region 5–30 eV measured
resolution dipole (e, e) spectrometer (fwhm = 0.048 eV).


Oxygen 2016
cross section cm**2
1E-15
1E-16
1E-17
1E-18
1E-19
1E-20
1E-3
0.01
0.1
1
10
100
1000
10000
Energy ev
Mt elastic
elastic
Sum Rot super
Sum Rot
sum vib
Ex A1Del G
Ex B1Sig G+
C1sig+A3del+A3sig
Schumann-runge
E3 sigma v=0
E3 sigma v=1
E3 sigma v=2
Dissoc nondipole
dissoc dipole
Dissoc nondipole
dissoc dipole
3 body att
2Body att
sum ions counting

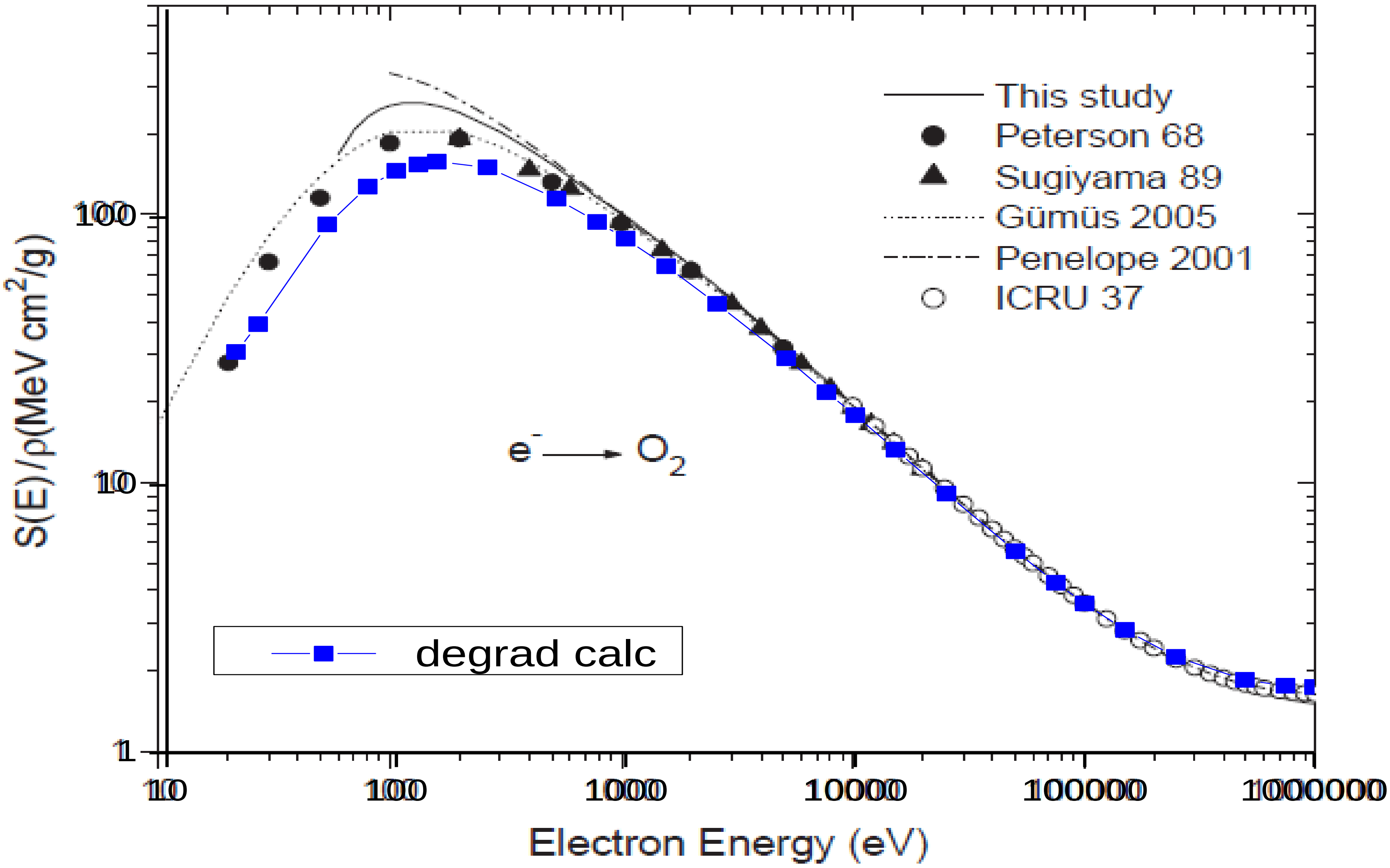

XENON
x-ray
e-beam
combecher
W ev/ion pair
Energy ev
45
40
35
30
25
20
15
10
100
1000
10000
100000
1000000

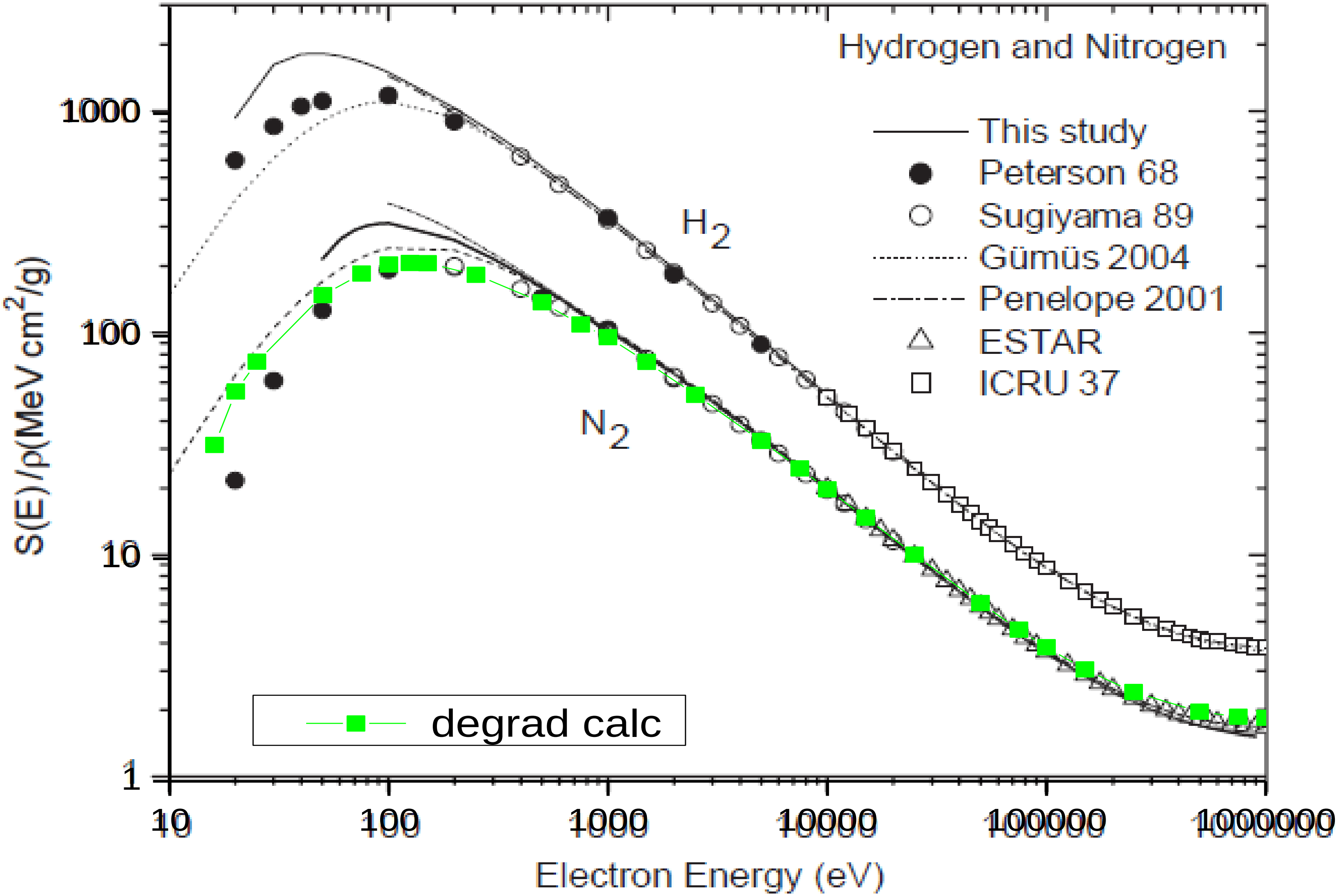

Fano
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
10
100
1000
10000
100000
1000000
Energy ev
XENON
x-ray
e-beam

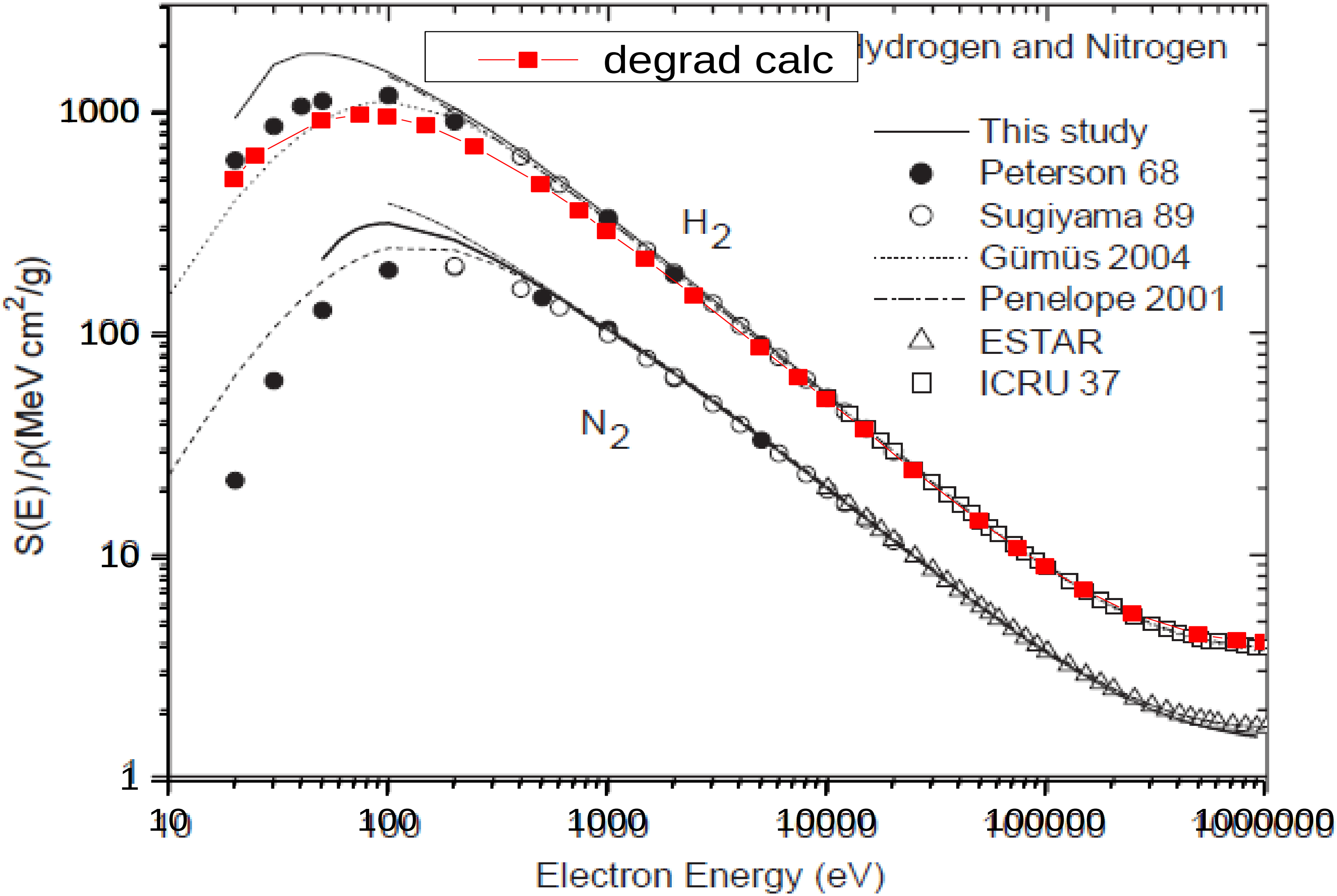

METHANE
x-ray
e-beam
weibel+grosswendt
combercher
W ev/ion pair
70
60
50
40
30
20
10
10
100
1000
10000
100000
1000000
Energy ev

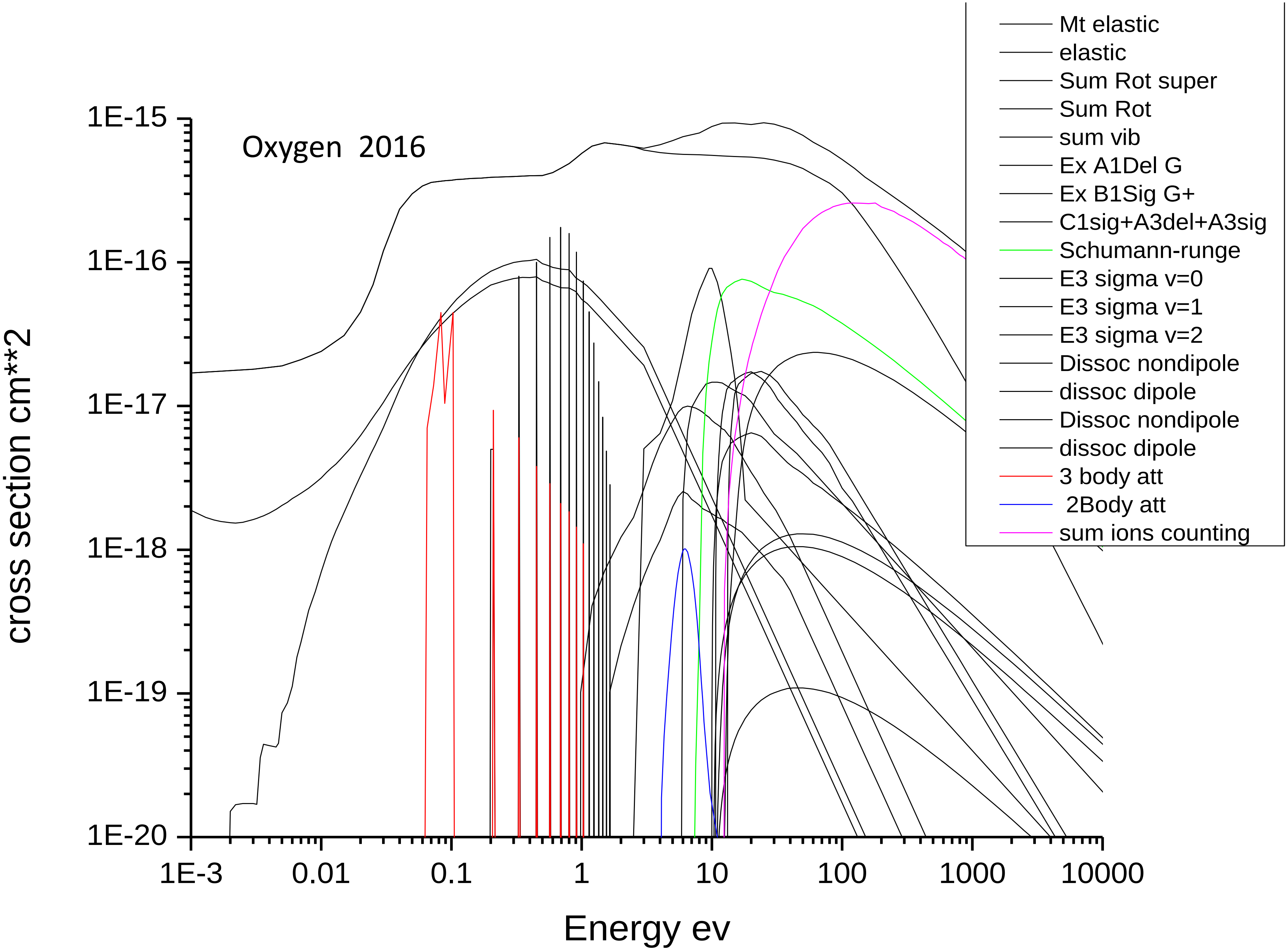

METHANE
x-ray
e-beam
Fano
0.7
0.6
0.5
0.4
0.3
0.2
0.1
10
100
1000
10000
100000
1000000
Energy ev

A.Akar and H.Gumus
Radiat. Phys. Chem. 73(2005)196




Hydrogen and Nitrogen
This study
Peterson 68
Sugiyama 89
Gümüs 2004
Penelope 2001
ESTAR
ICRU 37
H_2
N_2
degrad calc
$S(E)/\rho(MeV\,cm^2/g)$
Electron Energy (eV)
1000
100
10
1
10
100
1000
10000
100000
1000000


degrad calc
ydrogen and Nitrogen
This study
Peterson 68
Sugiyama 89
Gümüs 2004
Penelope 2001
ESTAR
ICRU 37
H_2
N_2
$S(E)/\rho (MeV\,cm^2/g)$
1000
100
10
1
10
100
1000
10000
100000
1000000
Electron Energy (eV)

Oxygen 2016
cross section cm**2
Energy ev
1E-15
1E-16
1E-17
1E-18
1E-19
1E-20
1E-3
0.01
0.1
1
10
100
1000
10000
Mt elastic
elastic
Sum Rot super
Sum Rot
sum vib
Ex A1Del G
Ex B1Sig G+
C1sig+A3del+A3sig
Schumann-runge
E3 sigma v=0
E3 sigma v=1
E3 sigma v=2
Dissoc nondipole
dissoc dipole
Dissoc nondipole
dissoc dipole
3 body att
2Body att
sum ions counting