e-

Molecular data for fusion (and other) plasmas

Jonathan Tennyson
University College London

Outer region

Inner region

IAEA
Vienna Centre
June 2019

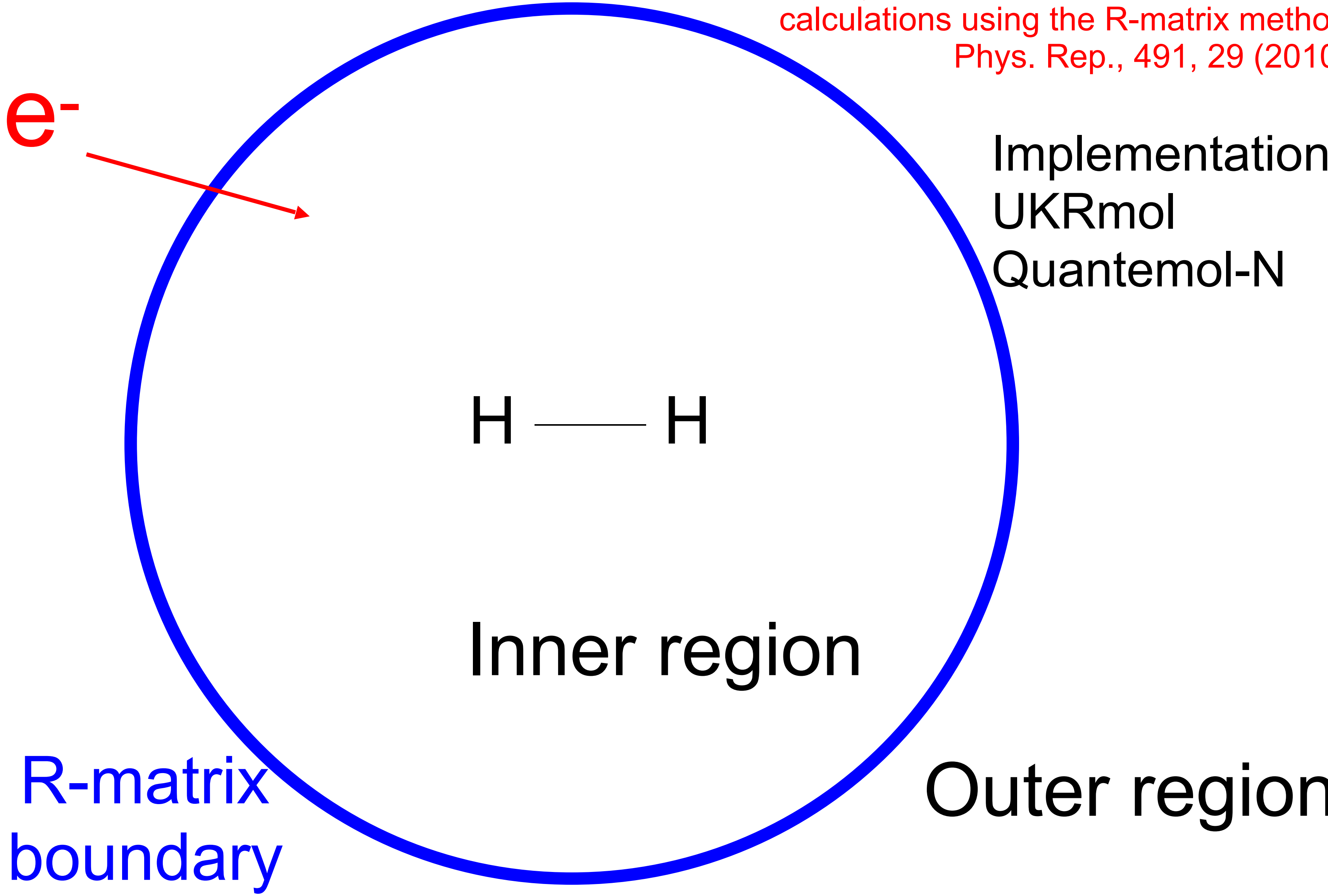
Contents

1. Formalisms: (a) the R-matrix method, (b) ExoMol
2. Electron collision applications:
   - Technological plasmas
   - Fusion plasmas: BeH, H_2
   - Atmospheric: space craft re-entry
   - Astrophysics (interstellar medium)
3. Future projects?

The R-matrix method

J. Tennyson, Electron - molecule collision calculations using the R-matrix method, Phys. Rep., 491, 29 (2010).

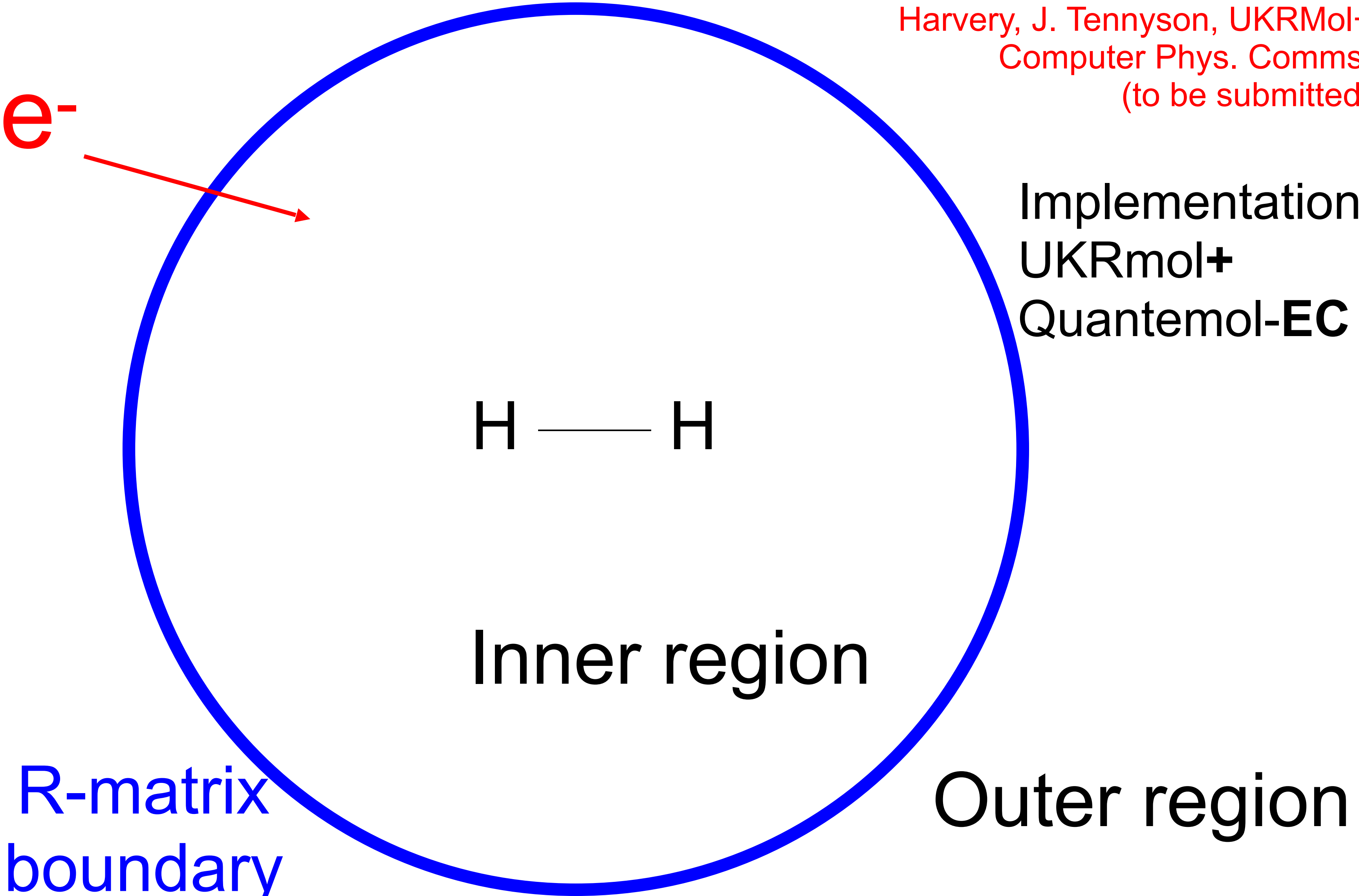
Implementation
UKRmol
Quantemol-N



The R-matrix method

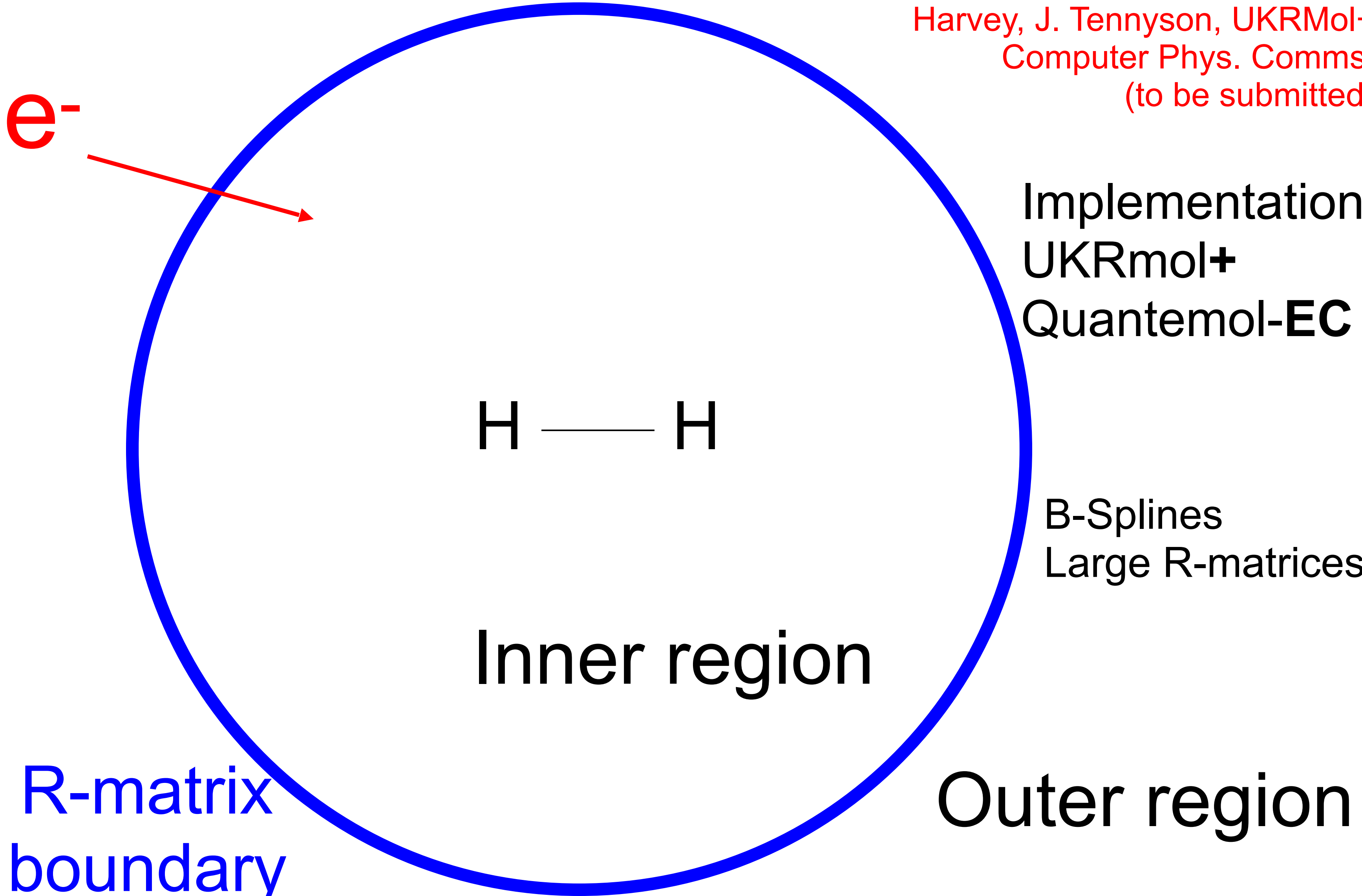
Z. Masin, J Benda, J.D. Gorfinkiel, A.G. Harvery, J. Tennyson, UKRMol+ Computer Phys. Comms. (to be submitted)

Implementation
UKRmol**+**
Quantemol-**EC**



The R-matrix method

Z. Masin, J Benda, J.D. Gorfinkiel, A.G. Harvey, J. Tennyson, UKRMol+ Computer Phys. Comms. (to be submitted)



Implementation
UKRmol**+**
Quantemol-**EC**

B-Splines
Large R-matrices

Low-energy electron collision processes

Elastic scattering

AB + **e** ⟶ AB + **e**

Rotational excitation

AB(N") + **e** ⟶ AB(N') + **e**

Vibrational excitation

AB(v"=0) + **e** ⟶ AB(v') + **e**

Dissociative recombination/Dissociative attachment

AB + **e** ⟶ A + B

Electronic excitation

AB + **e** ⟶ AB* + **e**

Impact dissociation

AB + **e** ⟶ A + B + **e**

Impact ionisation (e,2e)

AB + **e** ⟶ AB^+ + **e** + **e**

Increasing Energy

ExoMol

Hot line lists for exoplanets and other astronomical bodies

Published in MNRAS

I. BeH, MgH, CaH
II. SiO
III. HCN/HNC
IV. CH_4
V. NaCl, KCl
VI.PN
VII. PH_3
VIII. H_2CO
IX. AlO
X. NaH
XI. HNO_3
XII. CS
XIII. CaO
XIV. SO_2
XV. HOOH
XVI. H_2S
XVII. SO_3
XVIII. VO
XIX. $H_2{}^{18}O$, $H_2{}^{17}O$
XX. H_3^+
XXI. NO
XXII. SiH_4
XXIII. PO, PS
XXIV. SiH
XXV. SiS
XXVI. SN, SH
XXVII. AlH
XXVIII. C_2H_4
XXIX. CH_3Cl
XXX. $H_2{}^{16}O$
XXXI. C_2
XXXII. TiO
XXXIII. MgO
XXXIV. PH
XXXV. NH_3

(Virtually) Complete
HCCH, CrH, MnH

In progress
C_3, TiH, SrH, NaO, YO, SiO_2, SO, SiO (UV)

Planned
NiH, FeH, ZnO, ZnS etc
CaOH

Larger
Hydrocarbons, “gasous rock”

J. Tennyson et al, 327, 73,
J. Mol. Spectrosc. (2016)

Science & Technology Facilities Council

erc

ExoMol

Hot line lists for exoplanets and other astronomical bodies

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I. **BeH**, MgH, CaH
II. SiO
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Planned
NiH, FeH, ZnO, ZnS etc
CaOH, **BeH_2 ?**

Larger
Hydrocarbons, “gasous rock”

J. Tennyson et al, 327, 73,
J. Mol. Spectrosc. (2016)

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erc

Low-energy electron collision processes

Elastic scattering

$AB + e \longrightarrow AB + e$

Rotational excitation

$AB(N'') + e \longrightarrow AB(N') + e$

Vibrational excitation

$AB(v''=0) + e \longrightarrow AB(v') + e$

Dissociative recombination/Dissociative attachment

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Electronic excitation

$AB + e \longrightarrow AB^* + e$

Impact dissociation

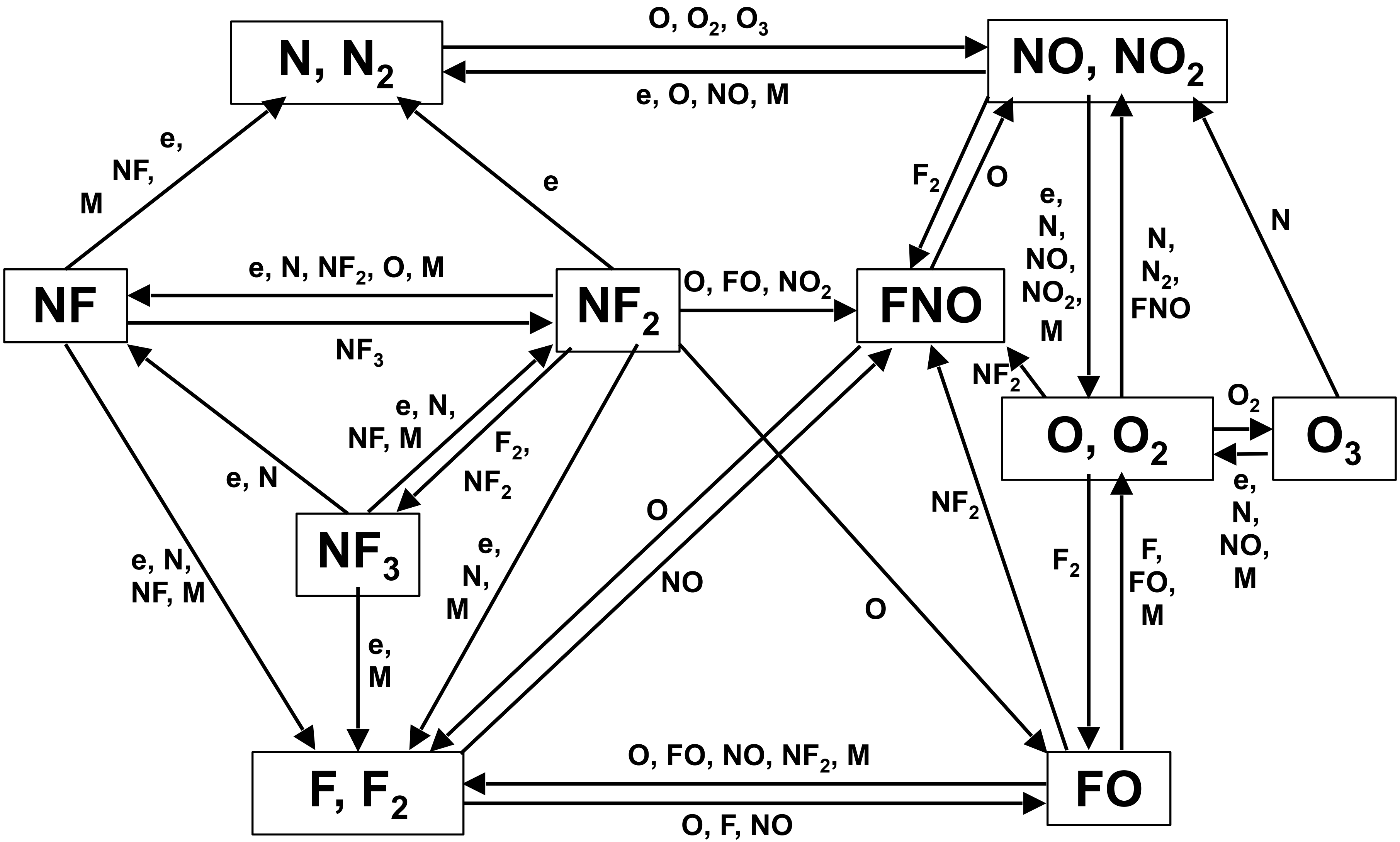
$AB + e \longrightarrow A + B + e$

Impact ionisation (e,2e)

$AB + e \longrightarrow AB^+ + e + e$

Increasing Energy

REACTION MECHANISM: NF_3/O_2



M represents 3rd body.

Diagram ignores ions which are also important.

Plasma chemistries:

Driven by a whole variety of
e – molecules
Heavy particle reactions

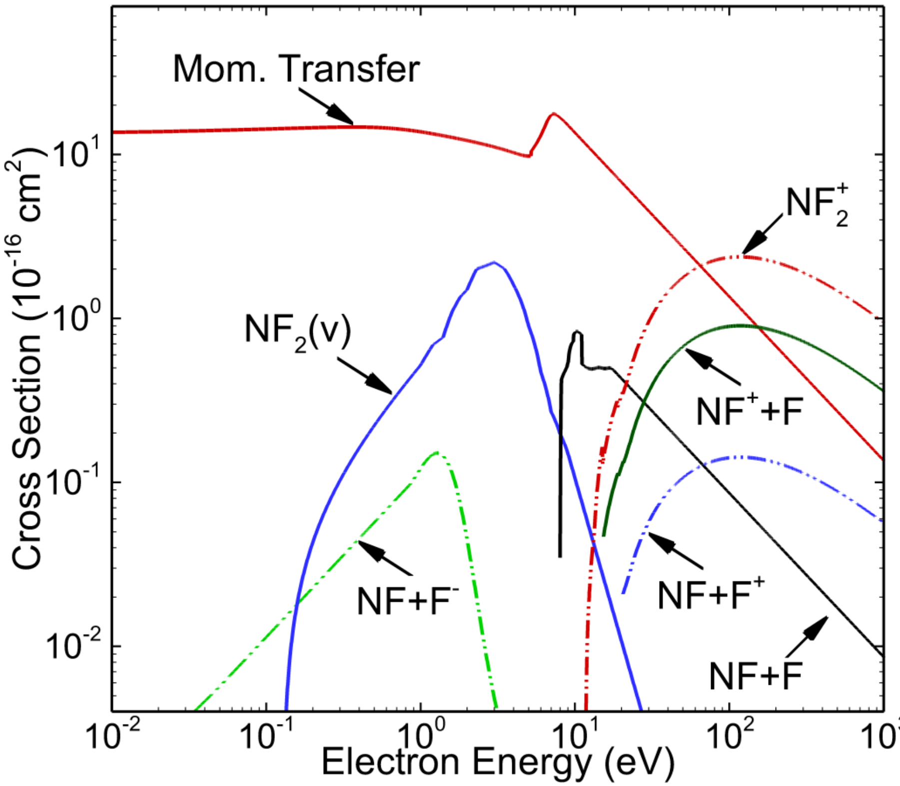
Eg NF_3/O_2 mixture

S. Huang, V. Volynets, J.R. Hamilton, S. Lee, I.-C. Song, S. Lu, J. Tennyson & M.J. Kushner, Insights to Scaling Remote Plasma Sources Sustained in NF_3 Mixtures, *J. Vac. Sci. Technol. A*, **35**, 031302 (2017)

Process	Rate Coefficient[b)]	Reference	ΔH (eV)[b)]
Electron Impact NF_x			
$e + NF_3 \rightarrow NF_3 + e$	c)	[17]	d)
$e + NF_3 \rightarrow NF_2 + F^-$	c), e)	[17]	-1.0
$e + NF_3 \rightarrow NF_3(v) + e$	c), f)	[17]	
$e + NF_3 \rightarrow NF_2 + F + e$	c)	[17]	-5.8
$e + NF_3 \rightarrow NF + F + F + e$	c)	[17]	-6.1
$e + NF_3 \rightarrow NF_3^+ + e + e$	c)	[17]	
$e + NF_3 \rightarrow NF_2^+ + F + e + e$	c)	[17]	-0.5
$e + NF_3 \rightarrow NF^+ + F + F + e + e$	c)	[17]	-4.2
$e + NF_3 \rightarrow F^+ + NF_2 + e + e$	c)	[17]	-1.1[g)]
$e + NF_2 \rightarrow NF_2 + e$	c)	[18]	
$e + NF_2 \rightarrow NF + F^-$	c)	[18]	-0.5
$e + NF_2 \rightarrow NF_2(v) + e$	c), f)	[18]	
$e + NF_2 \rightarrow NF + F + e$	c)	[18]	-5.1
$e + NF_2 \rightarrow NF_2^+ + e + e$	c)	[18]	
$e + NF_2 \rightarrow NF^+ + F + e + e$	c)	[18]	
$e + NF_2 \rightarrow F^+ + NF + e + e$	c)	[18]	
$e + NF \rightarrow NF + e$	c)	[18]	
$e + NF \rightarrow N + F^-$	c)	[18]	-0.6
$e + NF \rightarrow NF(v) + e$	c), f)	[18]	
$e + NF \rightarrow NF(^1\Delta) + e$	c), f)	[18]	
$e + NF \rightarrow NF(^1\Sigma^+) + e$	c), f)	[18]	
$e + NF \rightarrow N + F + e$	c)	[18]	-4.0
$e + NF \rightarrow NF^+ + e + e$	c)	[18]	
$e + NF \rightarrow N^+ + F + e + e$	c)	[18]	
$e + NF \rightarrow F^+ + N + e + e$	c)	[18]	
$e + NF_3^+ \rightarrow NF_2 + F$	1×10^{-7}	est. [29], h)	-11.1
$e + NF_2^+ \rightarrow NF + F$	1×10^{-7}	est. [29]	-6.3[g)]
$e + NF^+ \rightarrow N^* + F$	1×10^{-7}	est. [29]	-7.1
Electron Impact F_2/F			
$e + F_2 \rightarrow F_2 + e$	c)	[30]	
$e + F_2 \rightarrow F^- + F$	c)	[30]	-1.8
$e + F_2 \rightarrow F + F + e$	c)	[30]	-1.6
$e + F_2 \rightarrow F_2^* + e$	c)	[30]	
$e + F_2 \rightarrow F_2^+ + e + e$	c)	[30]	
$e + F_2^+ \rightarrow F + F^*$	1×10^{-7}	est. [29]	-0.6
$e + F \rightarrow F + e$	c)	[31]	
$e + F \rightarrow F^* + e$	c)	[31]	
$e + F \rightarrow F^+ + e + e$	c)	[31]	
$e + F^* \rightarrow F^+ + e + e$	c)	[31]	
$e + F^+ \rightarrow F^*$	$5.3 \times 10^{-12}\, T_e^{-0.5}$	est. [32]	
$e + e + F^+ \rightarrow F^* + e$	$5.12 \times 10^{-27}\, T_e^{-4.5}$	est. [32]	
Electron Impact N_xO_y			
$e + NO \rightarrow NO + e$	c)	[33]	

ELECTRON IMPACT NF_x CROSS SECTIONS

- **Electron impact cross sections for NF_x are not well known.**
- **Few direct measurements of NF_3 cross sections – mostly derived from swarm data.**
- **No direct (or swarm) measurements for NF_2, NF.**
- ***Ab initio* R-matrix method used to computationally generate self-consistent set of electron impact cross sections for NF_3, NF_2, NF.**

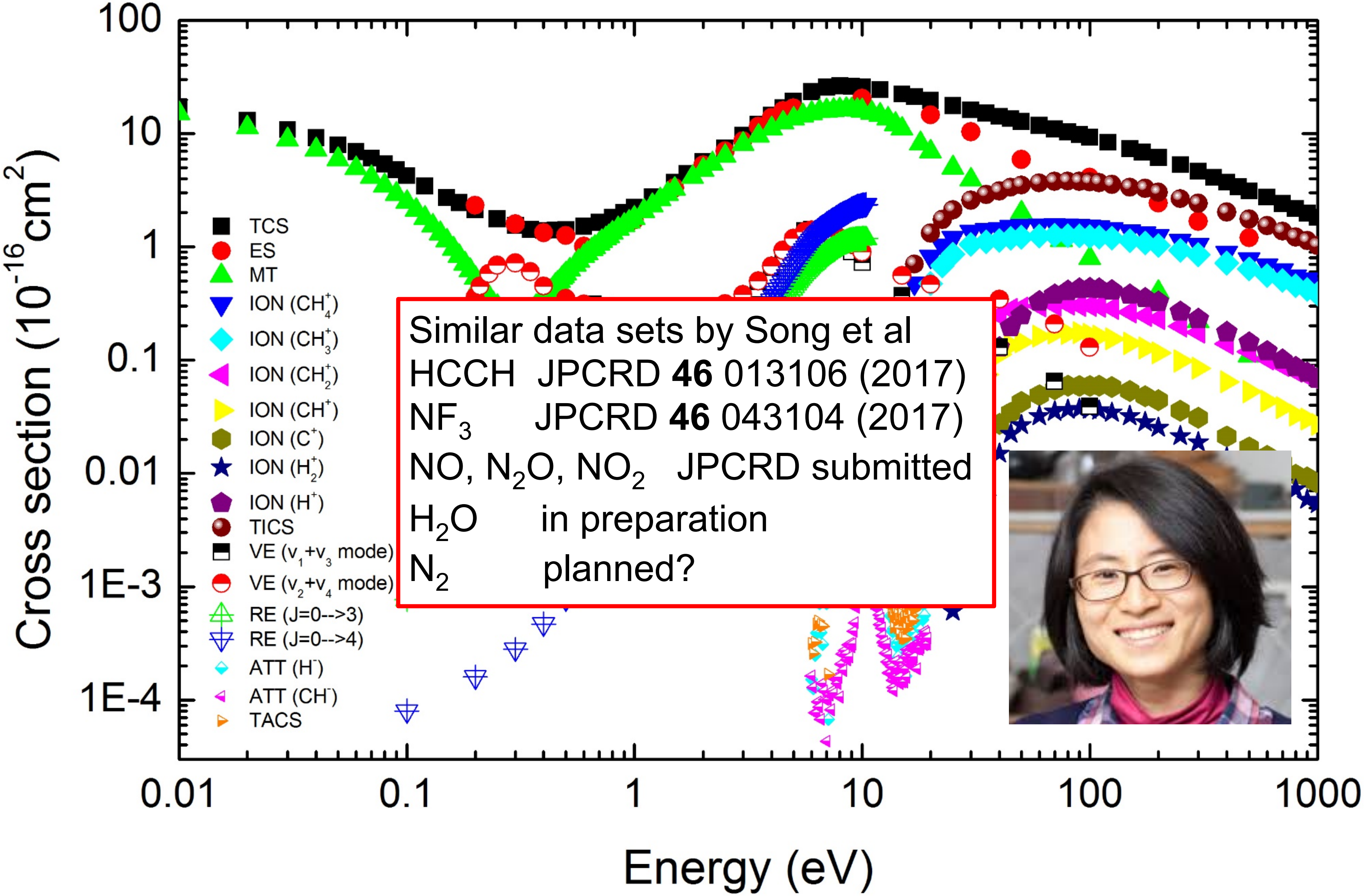


NF_2 cross sections obtained using R-matrix method.

James Hamilton

J.R. Hamilton, J. Tennyson, S. Huang and M.J. Kushner, Calculated cross sections for electron collisions with NF_3, NF_2 and NF, Plasma Sources Sci. Technol, 26, 065010 (2017).

Cross sections for electron collisions with methane



Similar data sets by Song et al
HCCH JPCRD **46** 013106 (2017)
NF_3 JPCRD **46** 043104 (2017)
NO, N_2O, NO_2 JPCRD submitted
H_2O in preparation
N_2 planned?

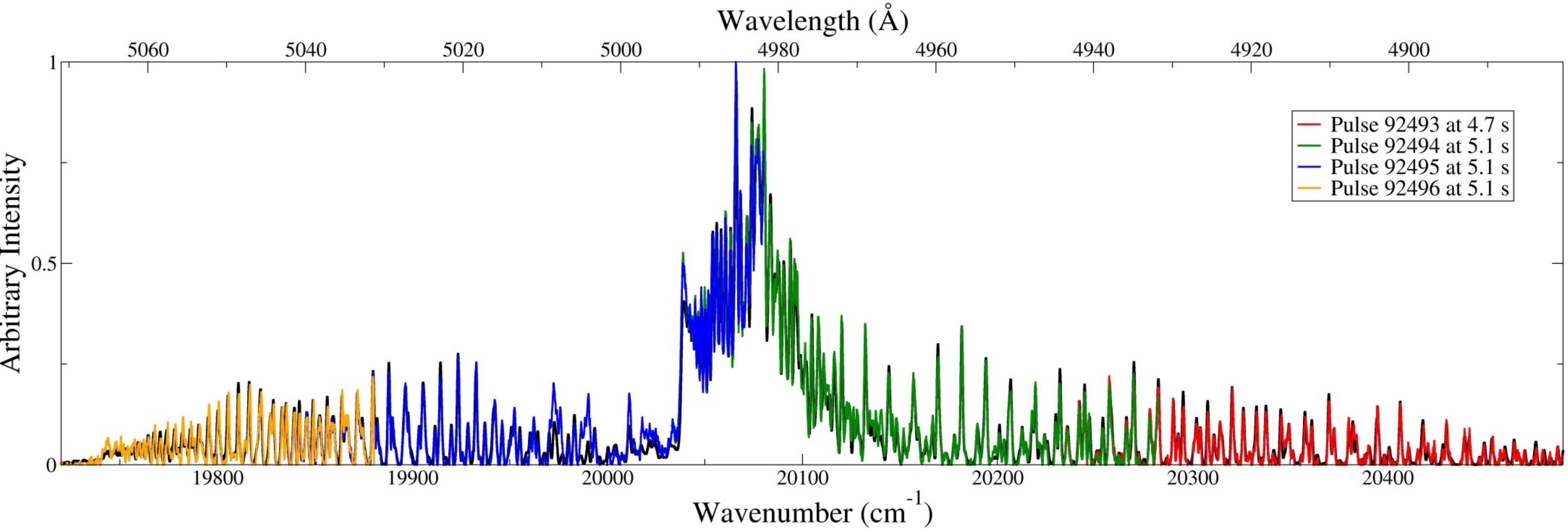
M.-Y. Song, J.S. Yoon, H. Cho, Y. Itikawa, G. Karwasz, V. Kokoouline, Y. Nakamura & J. Tennyson, J. Phys. Chem. Ref. Data, **44**, 023101 (2015)

Fusion appications: BeH / BeD / BeT

- Be coating of walls at JET (ITER)
- BeD observed product
- Monitor Be erosion

Daniel Darby-Lewis

BeD spectra measured in JET



Red, green, blue and orange regions are different pulses.

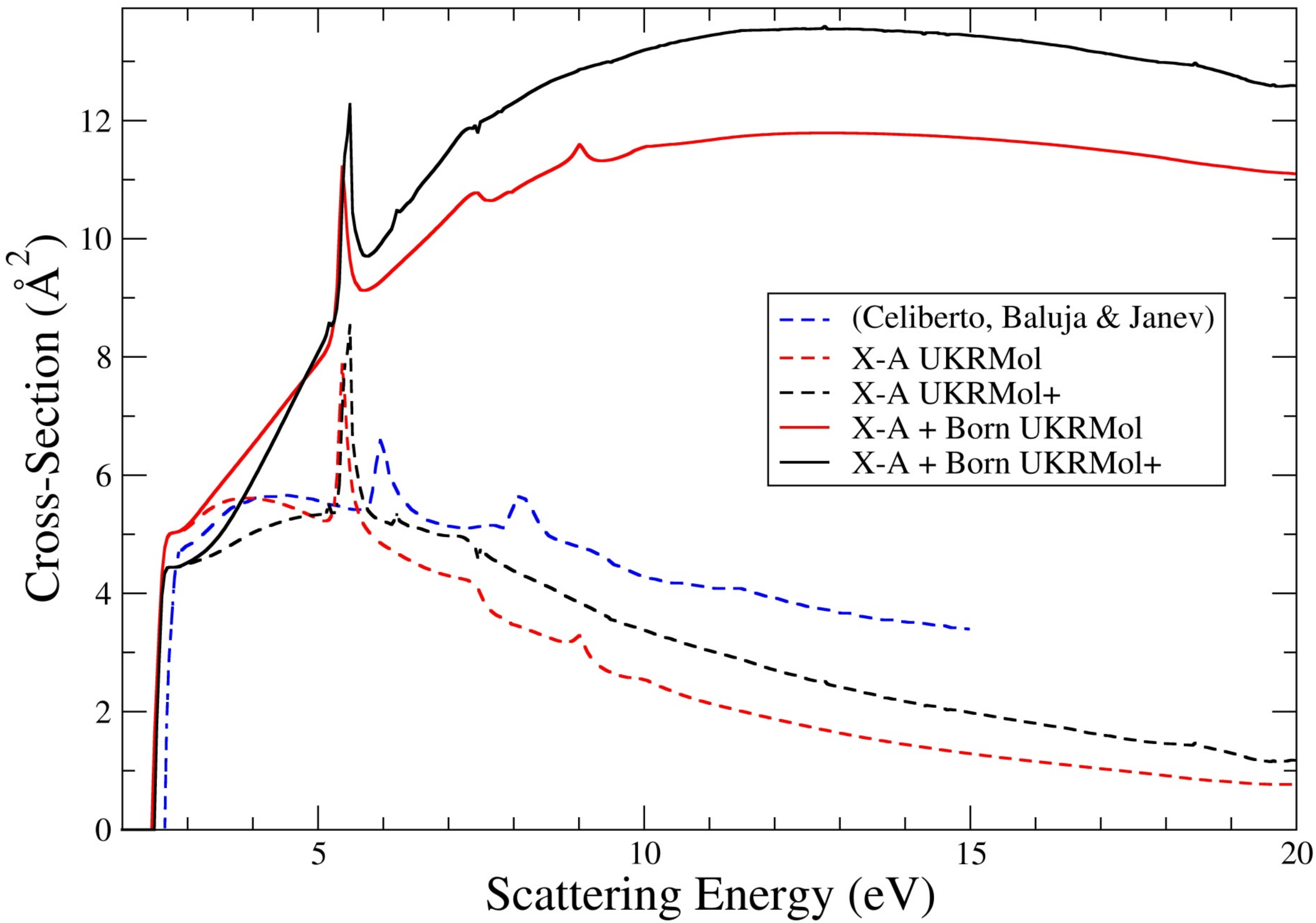
D. Darby-Lewis, J. Tennyson, K.D. Lawson, S.N. Yurchenko, M.F. Stamp, A. Shaw, S. Brezinsek and JET Contributor, Synthetic spectra of BeH, BeD and BeT for emission modelling in JET plasmas, *J. Phys. B: At. Mol. Opt. Phys.*, 51, 185701 (2018)

Interpretation requires collisional-radiative model

Step 1 e + BeH (X $^2\Sigma^+$) → e + BeH (A $^2\Pi$)

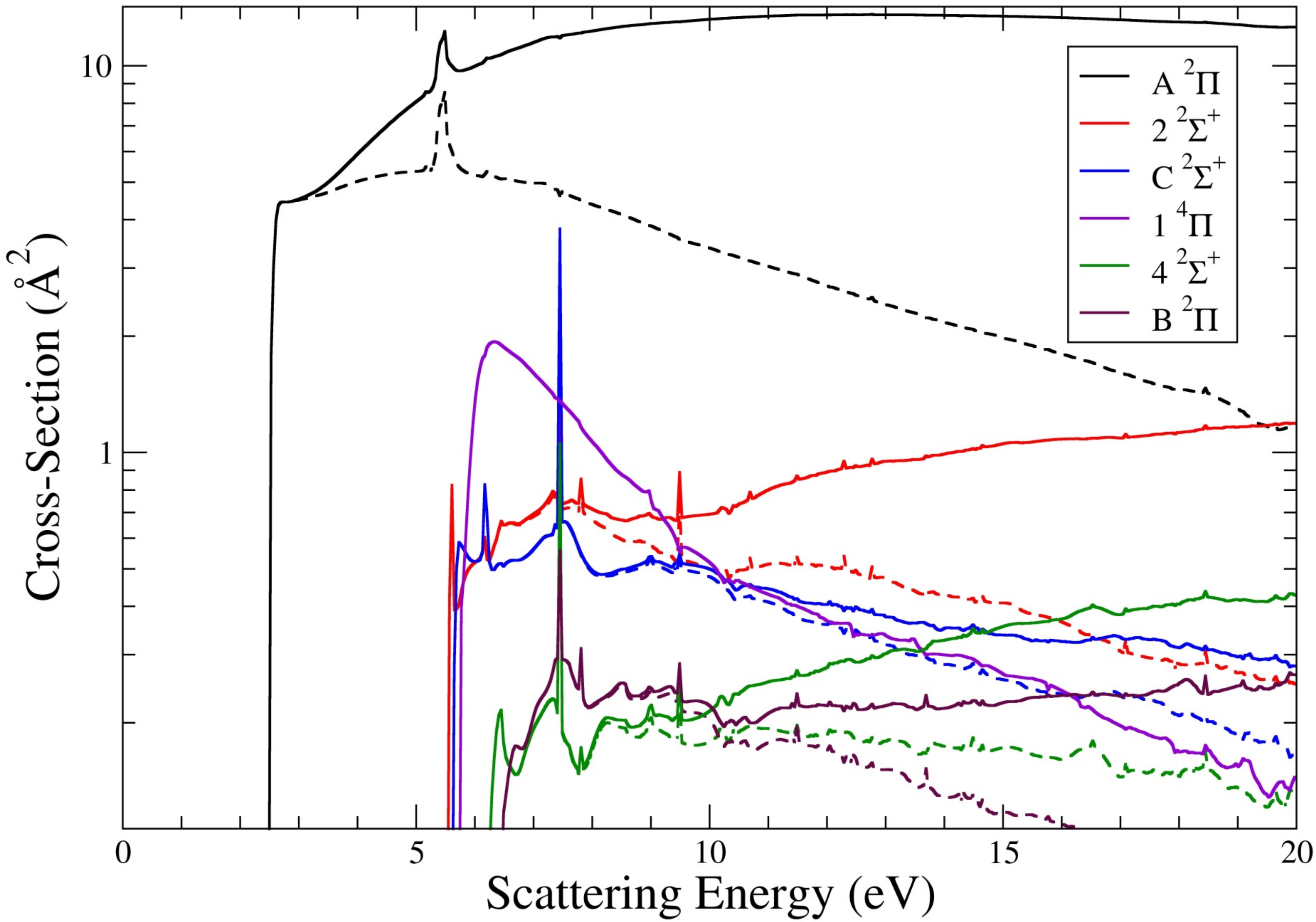
Step 2 BeH (A $^2\Pi$, *v'*,*J'*) → BeH (X $^2\Sigma^+$,*v''*,*J''*) + hν

e + BeH (X $^2\Sigma^+$) → e + BeH (A $^2\Pi$)



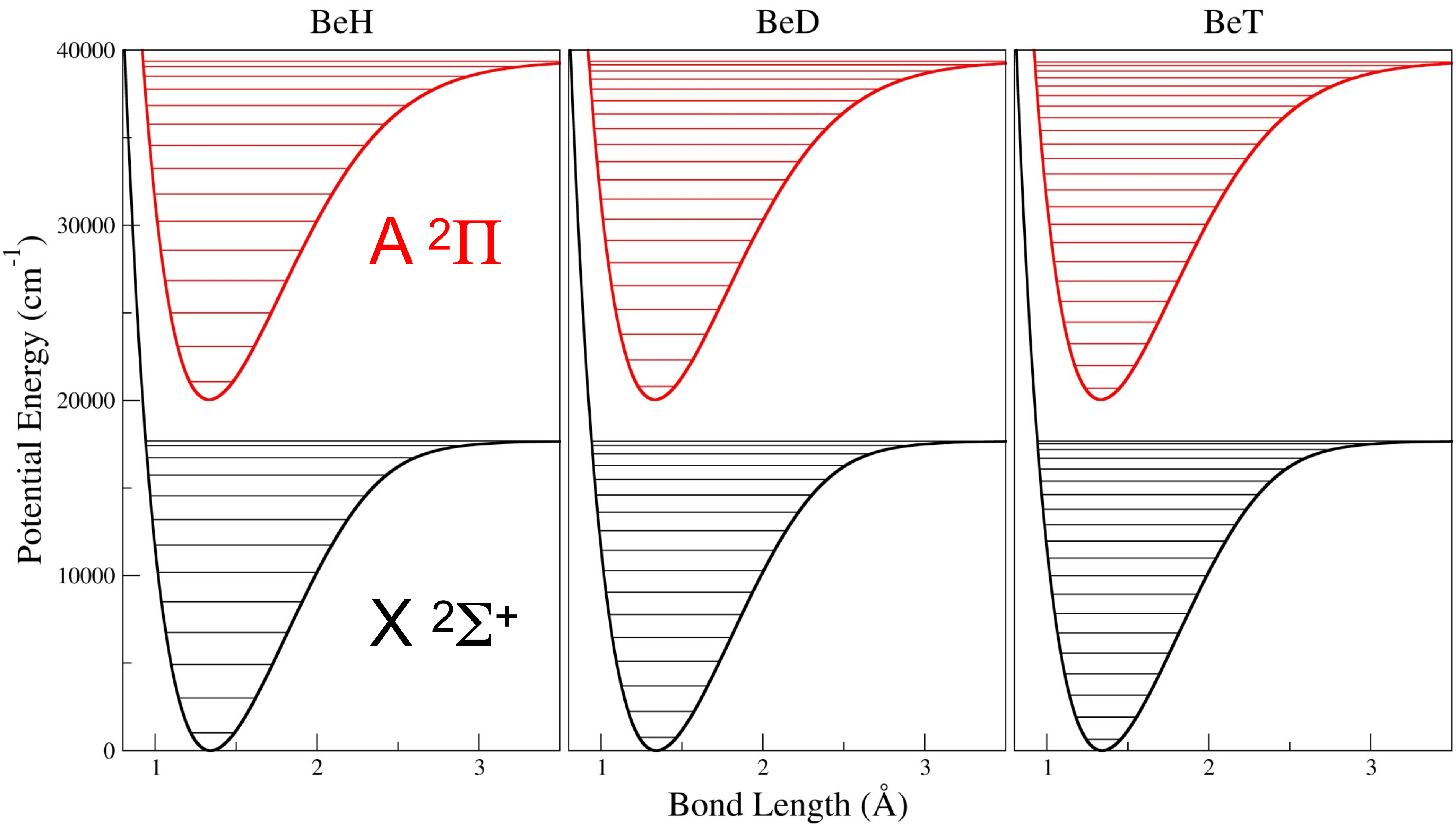
D. Darby-Lewis, Z. Masin & J. Tennyson, *J. Phys. B: At. Mol. Opt. Phys*, **50**, 175201 (2017).

Electron impact electronic excitation of the BeH (BeD)



D. Darby-Lewis, Z. Masin & J. Tennyson, *J. Phys. B: At. Mol. Opt. Phys*, **50**, 175201 (2017).

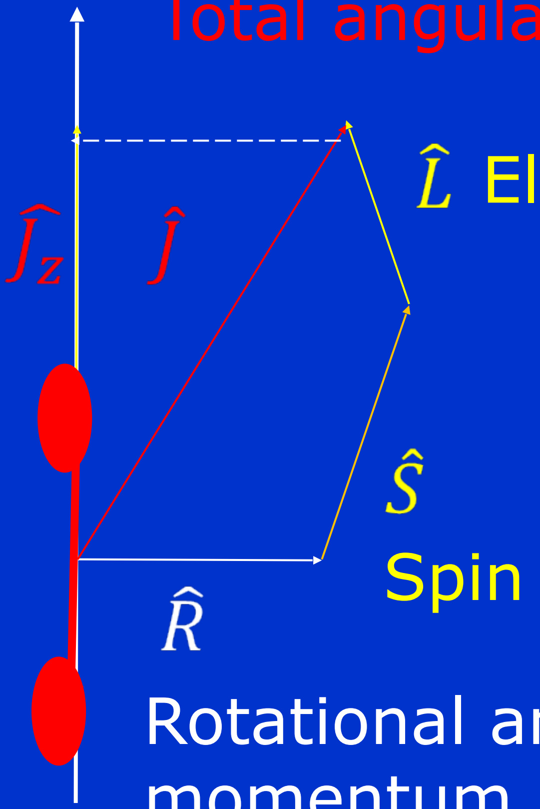
Spectroscopic model for BeH/BeD/BeT



D. Darby-Lewis, J. Tennyson, K.D. Lawson, S.N. Yurchenko, M.F. Stamp, A. Shaw, S. Brezinsek and JET Contributor, Synthetic spectra of BeH, BeD and BeT for emission modelling in JET plasmas, *J. Phys. B: At. Mol. Opt. Phys.*, **51**, 185701 (2018)

New general diatomic code: **Duo**

S.N. Yurchenko, L. Lodi, J. Tennyson & A.V. Stolyarov, Computer Phys. Comm. **202**, 262 (2016).



$$\hat{R}^2 = \hat{J}^2 - (\hat{L}^2 + \hat{S}^2)$$

$$\hat{H}_{ii} = \frac{\hbar^2}{2\mu r^2}\hat{R}^2 - \frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} + V_i(r)$$

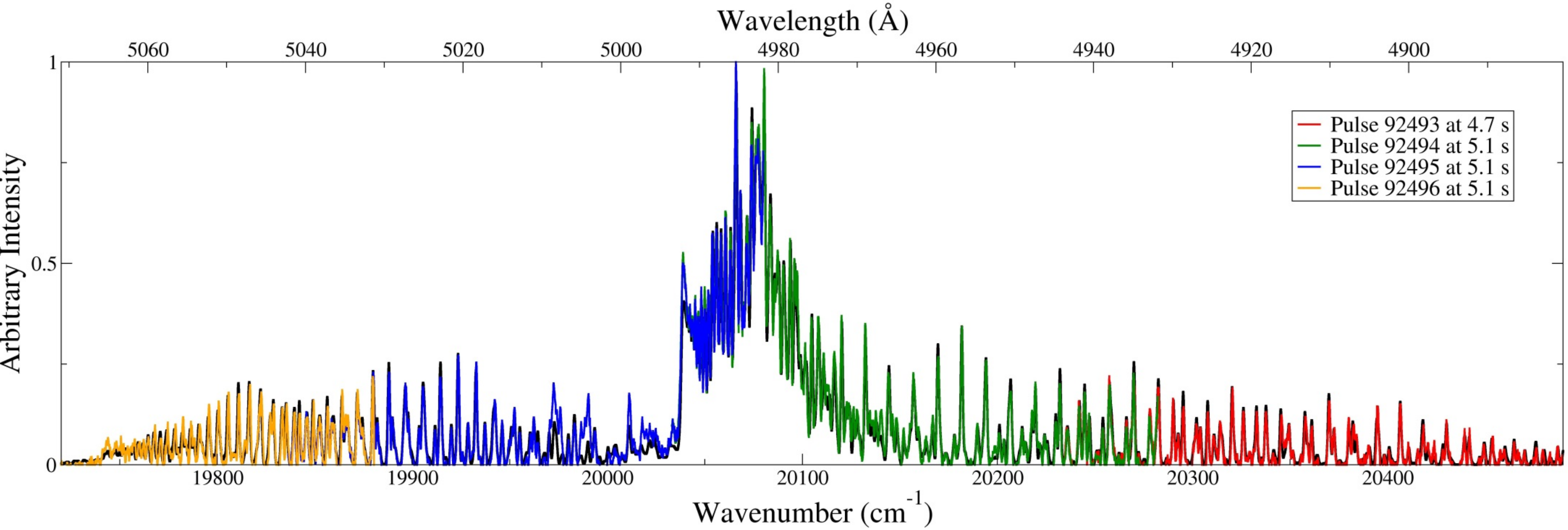
Variational basis set
Hund's case (a)

Vibrational Spin

$$\phi_n = |v\rangle |J\Omega\rangle |S\Sigma\rangle |LS\Sigma\rangle$$

Rotational Electronic

BeD spectra measured in JET

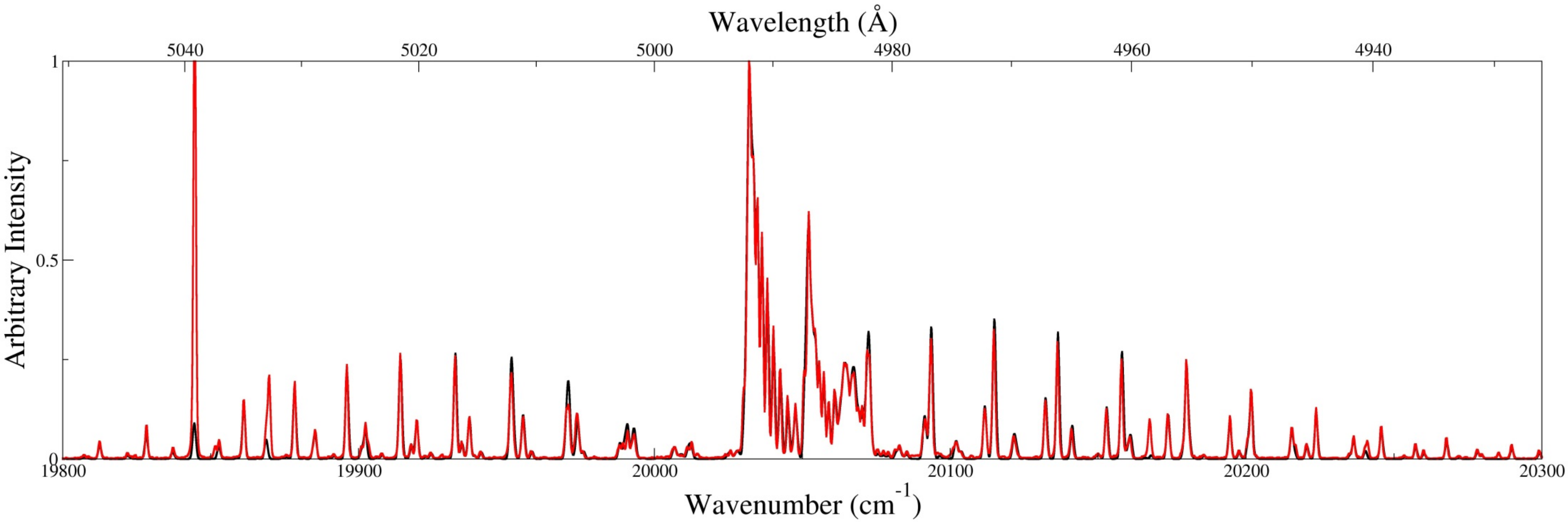


Red, green, blue and orange regions are different pulses.

Spectral fit: black lines. Gives: T_{rot} = 3800 K, T_{vib} = 4700 K

D. Darby-Lewis, J. Tennyson, K.D. Lawson, S.N. Yurchenko, M.F. Stamp, A. Shaw, S. Brezinsek and JET Contributor, Synthetic spectra of BeH, BeD and BeT for emission modelling in JET plasmas, *J. Phys. B: At. Mol. Opt. Phys.*, 51, 185701 (2018)

BeH spectra measured in Julich



Spectrum from a H doped lamp with a Be target: Measured red.
Black synthetic generated at T_{rot} = 540 K and T_{vib} = 3440 K

Interpretation requires collisional-radiative model

Step 1 e + BeH (X $^2\Sigma^+$) → e + BeH (A $^2\Pi$)

Step 2 BeH (A $^2\Pi$, v',J') → BeH (X $^2\Sigma^+$,v'',J'') + hν

Interpretation requires collisional-radiative model

Step 1 e + BeH (X $^2\Sigma^+$,*v'*,*J'*) → e + BeH (A $^2\Pi$,*v''*,*J''*)

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Interpretation requires collisional-radiative model

Step 1 e + BeH (X $^2\Sigma^+$,*v'*) → e + BeH (A $^2\Pi$,*v''*)

Step 2 BeH (A $^2\Pi$, *v'*,*J'*) → BeH (X $^2\Sigma^+$,*v''*,*J''*) + hν

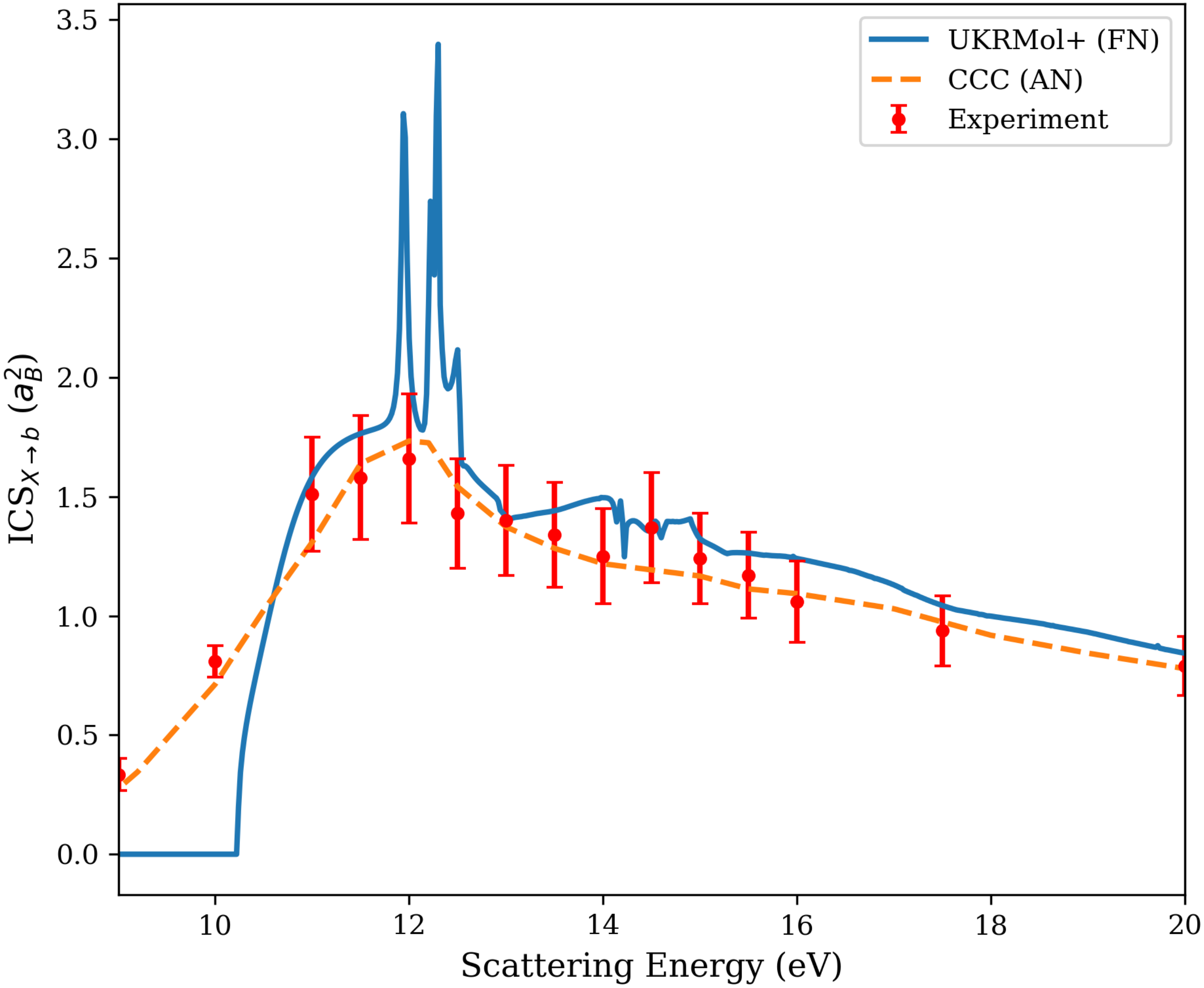
D. Darby-Lewis, PhD thesis

Fusion appications?: H_2/ D_2 /T_2 etc

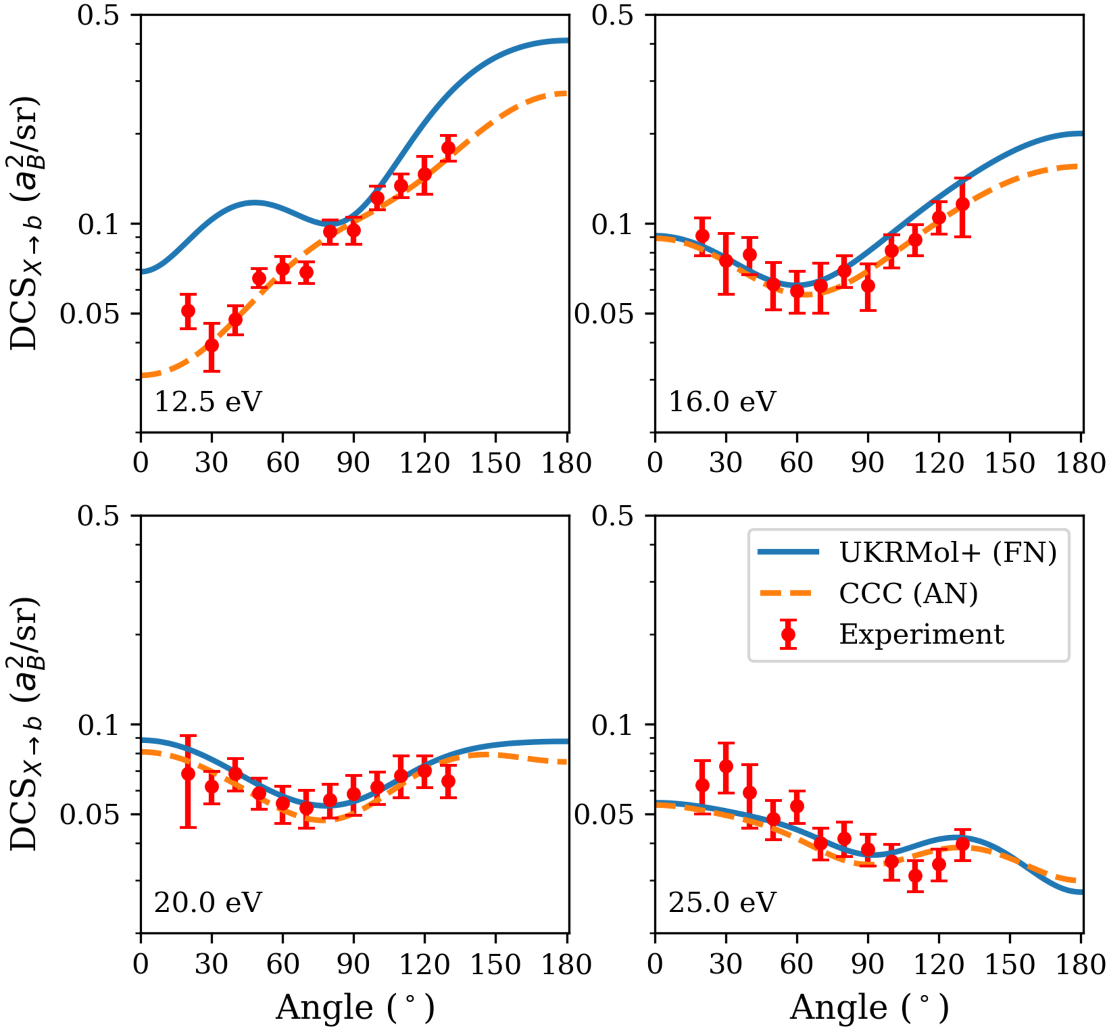
- New UKRmol+ allows study of diffuse targets
- Considering collisions going up H(n=3) states
- R-matrix sphere with a = 100 a.u. !

Tom Meltzer

H_2 X → b state electronic excitation cross sections



H_2 X → b state electronic excitation differential cross sections



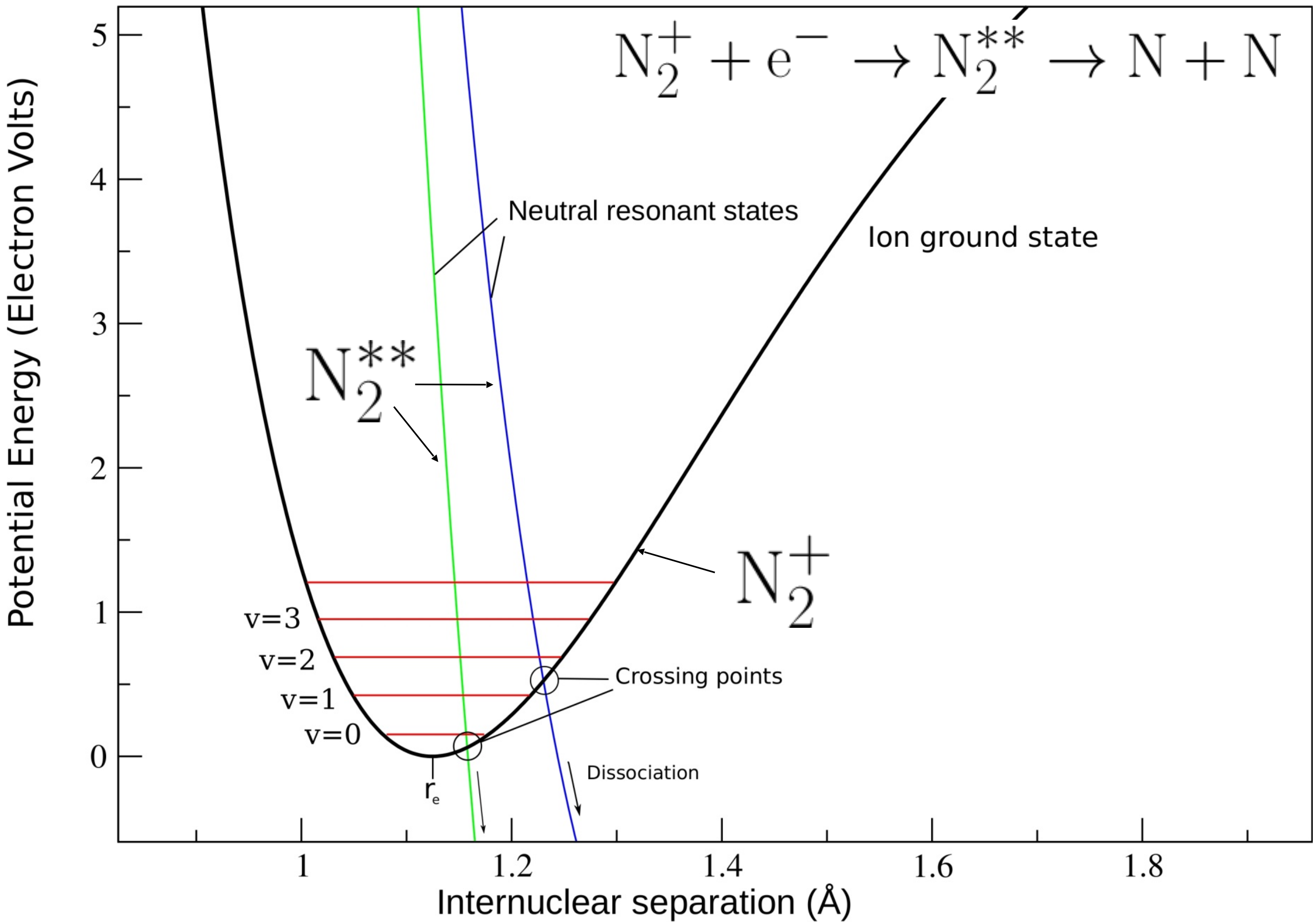
Future projects:

BeH_2 ?

Other systems (eg N_2) ?

Dissociative recombination (DR)

(Direct process)



PHYS4ENTRY

PLANETARY ENTRY INTEGRATED MODELS

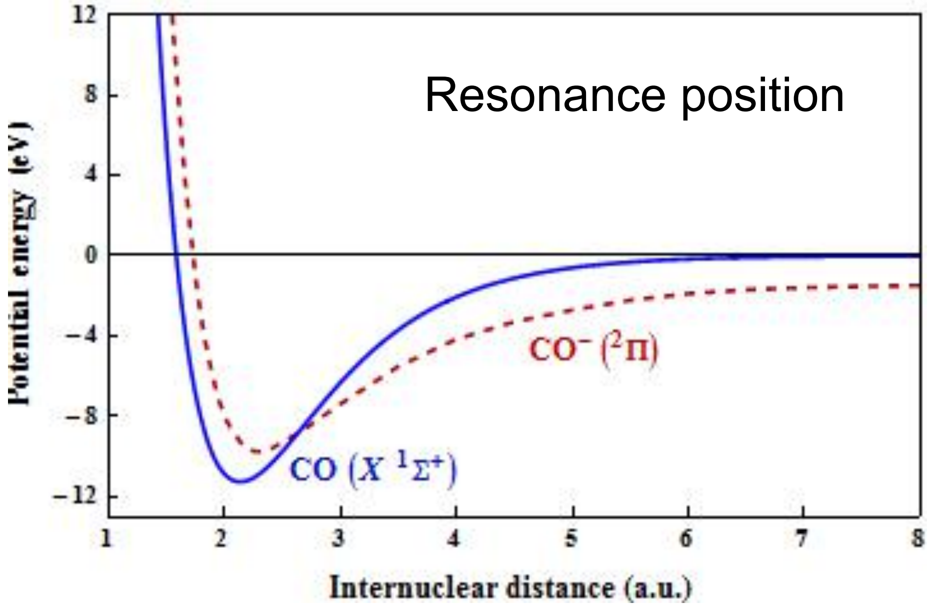
SEVENTH FRAMEWORK PROGRAMME

plasmas created on spacecraft (rocket) re-entry

Vibrational excitation of key molecule: Venus, Mars, Earth

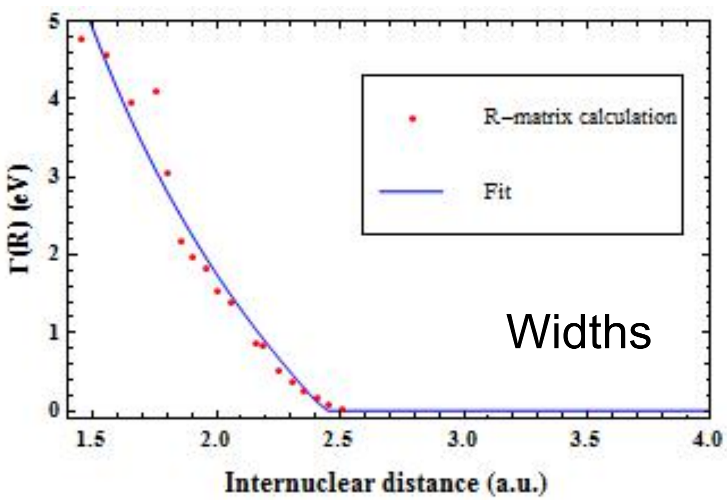
R. Celiberto et al, Atomic & molecular data for spacecraft re-entry plasmas, Plasma Sources Sci. Technol, **26**, 033004 (2016).

Electron – CO: $^2\Pi$ resonance



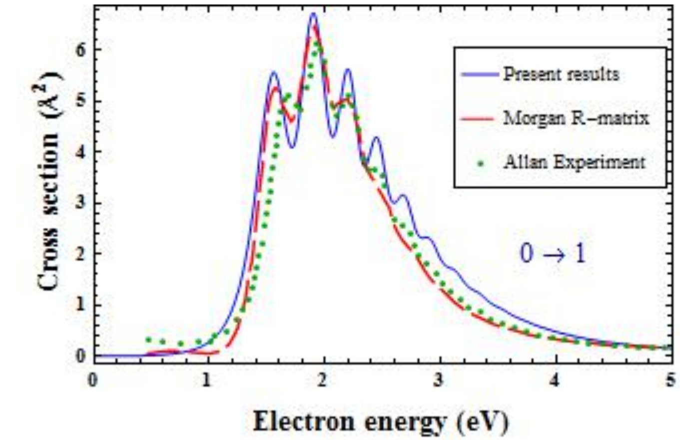
R-matrix resonance positions and widths

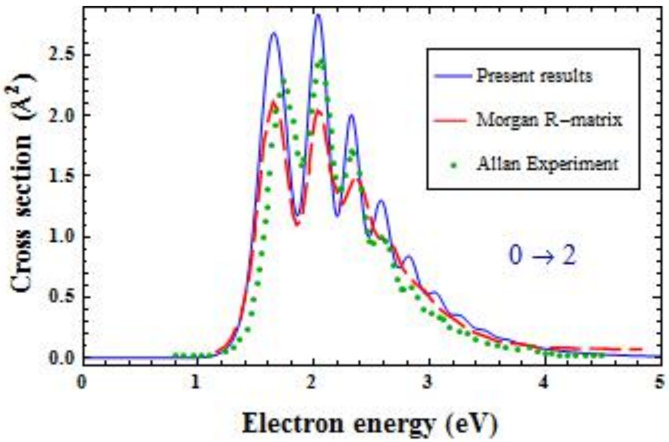
Static exchange plus polarisation (SEP) model

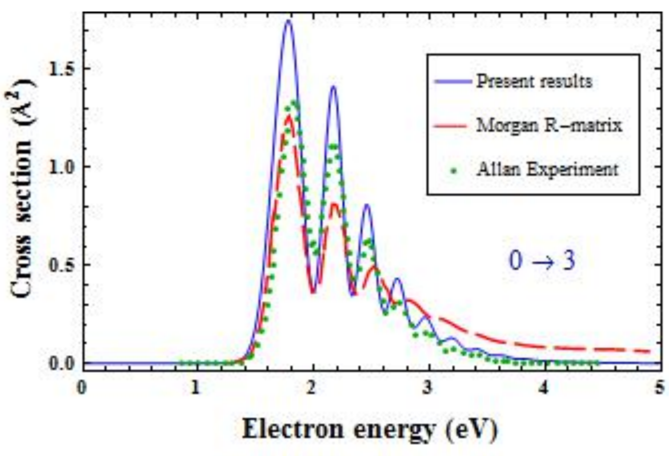


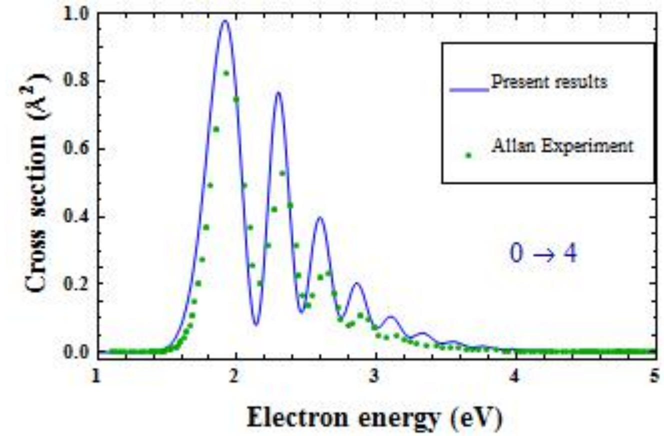
Electron – CO:

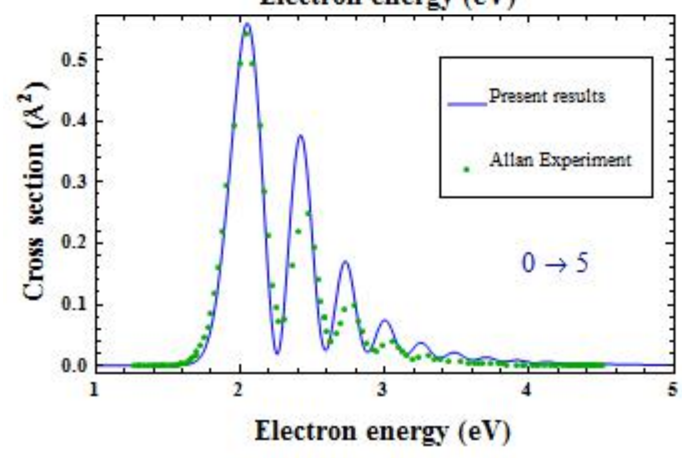
resonance enhanced vibrational excitation 0 → v’







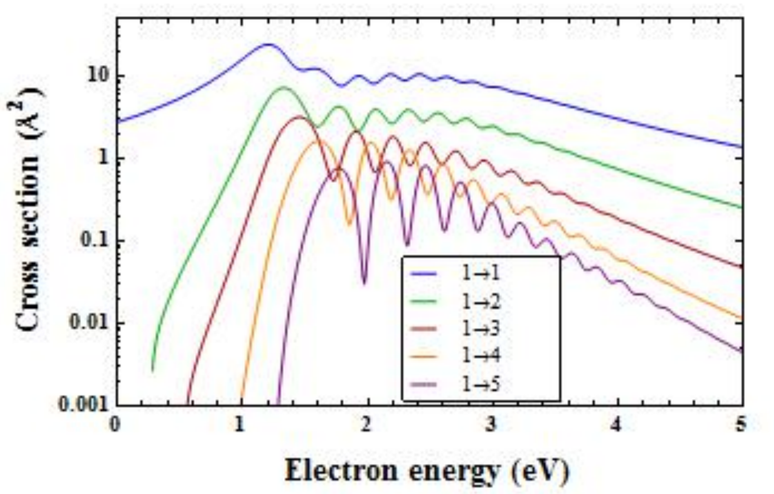


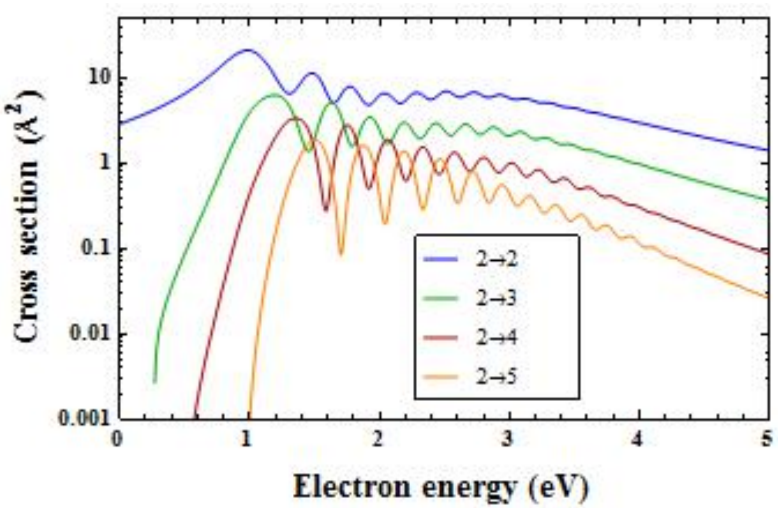


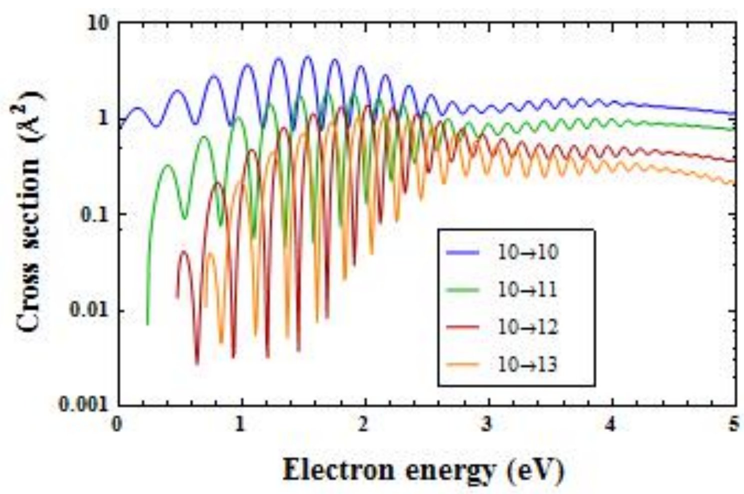
Electron – CO:

resonance enhanced vibrational excitation

High v' – v"(>0)



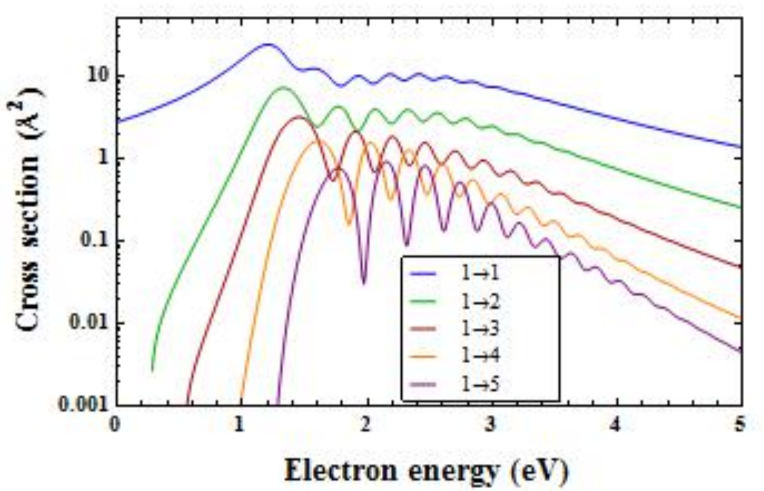




V Laporte, CM Cassidy, J Tennyson & R Celliberto,
Plasma Sources Sci. Technol. **21**, 045005 (2012)

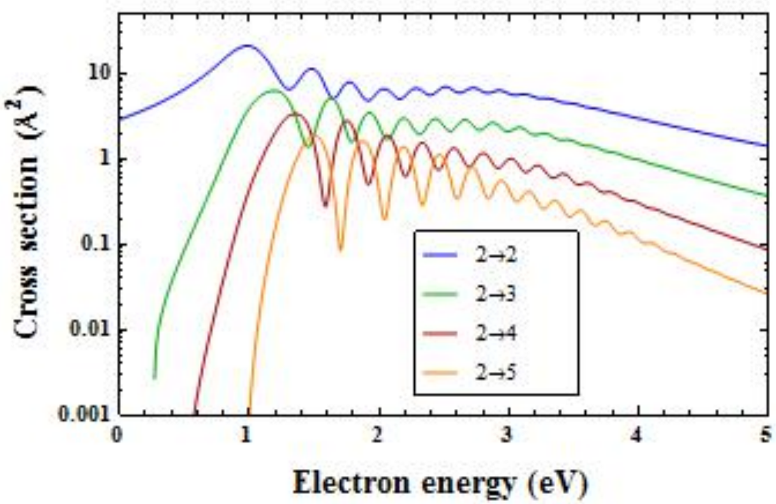
Electron – CO:

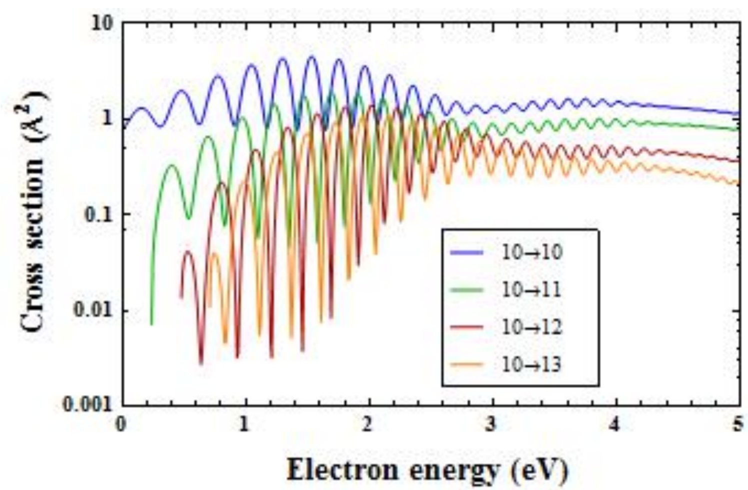
resonance enhanced vibrational excitation



High v' – v"(>0)

V Laporte, CM Cassidy, J Tennyson & R Celliberto, Plasma Sources Sci. Technol. **21**, 045005 (2012)





Dissociative attachment
+ impact dissociation of CO

V Laporte, J Tennyson & R Celliberto, Plasma Sources Sci. Technol., **25**, 01LT04 (2016).

Calculations extended to:

$e + NO(v'') \rightarrow e + NO(v')$

$e + NO(v'') \rightarrow N + O^-$

$e + O_2(v'') \rightarrow e + O_2(v')$

V. Laporta, R. Celiberto & J. Tennyson, Plasma Sources Sci. Technol., **22**, 025001 (2013)

$e + O_2(v'') \rightarrow O + O^-$

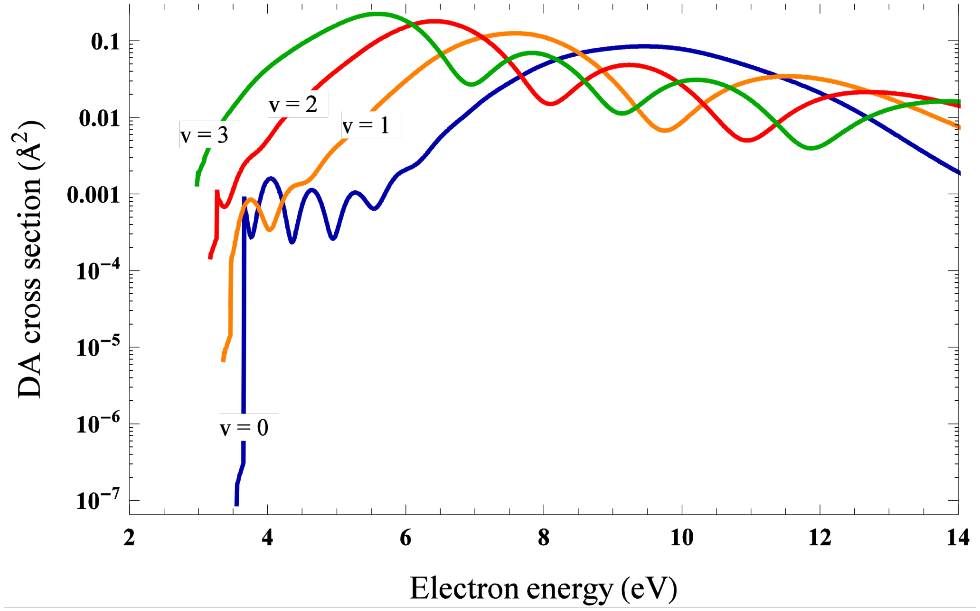
$e + N_2(v'') \rightarrow e + N_2(v')$

V. Laporta, D.A. Little, R. Celiberto & J. Tennyson, Plasma Sources Sci. Technol. **23**, 065002 (2014)

$e + CO_2(v'') \rightarrow e + CO_2(v')$

V. Laporta, J. Tennyson & R. Celiberto, *Plasma Sources Sci. Technol*, **25**, 06LT02 (2016).

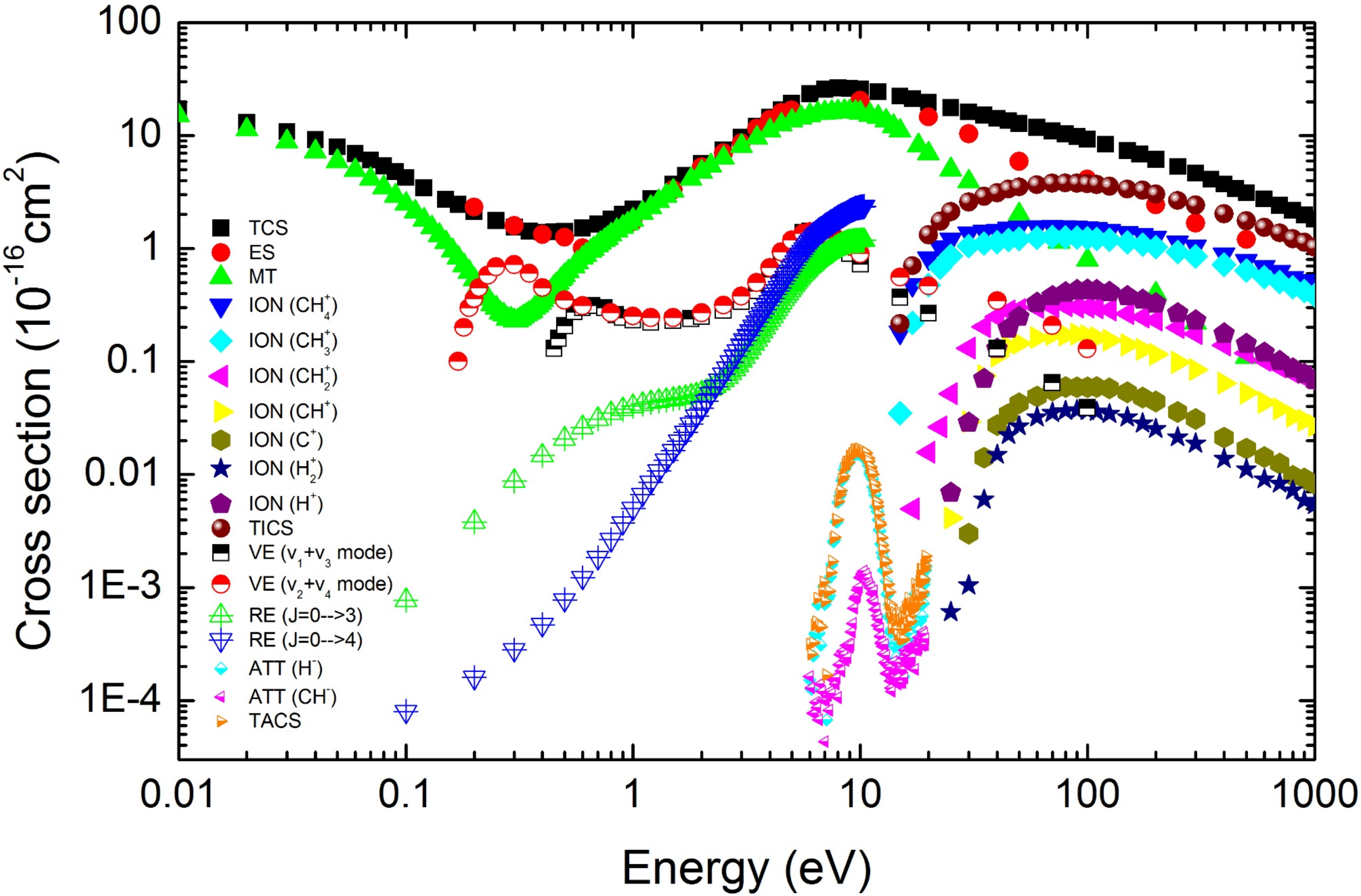
Dissociative attachment of O_2



V. Laporta, R. Celiberto & J. Tennyson, Phys. Rev. A, **91**, 012701 (2015)

Vincenzo Laporta

Cross sections for electron collisions with methane



M.-Y. Song, J.S. Yoon, H. Cho, Y. Itikawa, G. Karwasz, V. Kokoouline, Y. Nakamura & J. Tennyson, J. Phys. Chem. Ref. Data, **44**, 023101 (2015)

Static exchange (SE)

Target representation: Frozen 1-state

Interaction: static and exchange interactions only

$$\Psi_k = \mathcal{A} \; \Sigma_j \; a_{j,k} \, \phi^N \eta_j + \Sigma_i \, b_{j,k} \, \phi_j^{N+1}$$

ϕ^N Single Hartree-Fock target state

ϕ_j^{N+1} Simple form ϕ^N x *virtual*

Captures: Long-range physics

Resonances? Recovers shape resonances (usually too high)
No Feshbach resonances

Energy range: Unlimited (works at high energy)

Other comments: Well-defined model,
same answer with all codes

SE plus polarisation (SEP)

Target representation: 1-state

Interaction: polarisation via single excitation from target wavefunction

$$\Psi_k = \mathcal{A} \sum_j a_{j,k} \phi^N \eta_j + \sum_i b_{j,k} \phi_j^{N+1}$$

ϕ^N Single Hartree-Fock target state

ϕ_j^{N+1} Complicated ϕ^N x *virtual* plus 1 hole – 2 particle excitations

Captures: Short-range polarisation effects

Resonances? Good for shape resonance
Can capture Feshbach resonances (no parent states)

Energy range: Only up to first excitation threshold

Other comments: Model implementation dependent
Can be unbalanced (eg resonances too low)

Close-coupling (CC)

Target representation: Many-state, usually CI

Interaction: polarisation via coupling between target states

$$\Psi_k = \mathcal{A} \sum_{i,j} a_{i,j,k} \phi_i^N \eta_{i,j} + \sum_i b_{j,k} \phi_j^{N+1}$$

ϕ_i^N Configuration interaction (CI); orbitals?

eg Complete Active Space CI

ϕ_j^{N+1} $(\text{CAS-CI})^{N+1}$

Captures: Short-range polarisation effects,
channel-coupling effects

Resonances? Shape resonance (Often less good than SEP)
Feshbach resonances (parent states)

Energy range: Only up to first missing excitation threshold

Other comments: Electron impact electronic excitation
Hard to recover full polarisation effects

Close-coupling with pseudostates (RMPS)

Target representation: Many physical states + pseudostates

Interaction: polarisation via coupling between target (pseudo)states

$$\Psi_k = \mathcal{A} \; \Sigma_{i,j} \; a_{i,j,k} \, \phi_i^N \, \eta_{i,j} + \Sigma_i \, b_{j,k} \, \phi_j^{N+1}$$

ϕ_i^N Complete Active Space CI

+ single excitations to pseudo-orbitals

ϕ_j^{N+1} $(\text{CAS-CI})^{N+1}$

+ occupation of pseudo-orbitals

Captures: All polarisation effects, state coupling, ionisation

Resonances? All (+ pseudo-resonances at high energy)

Energy range: Above ionisation

Other comments: Converged treatment of polarisation

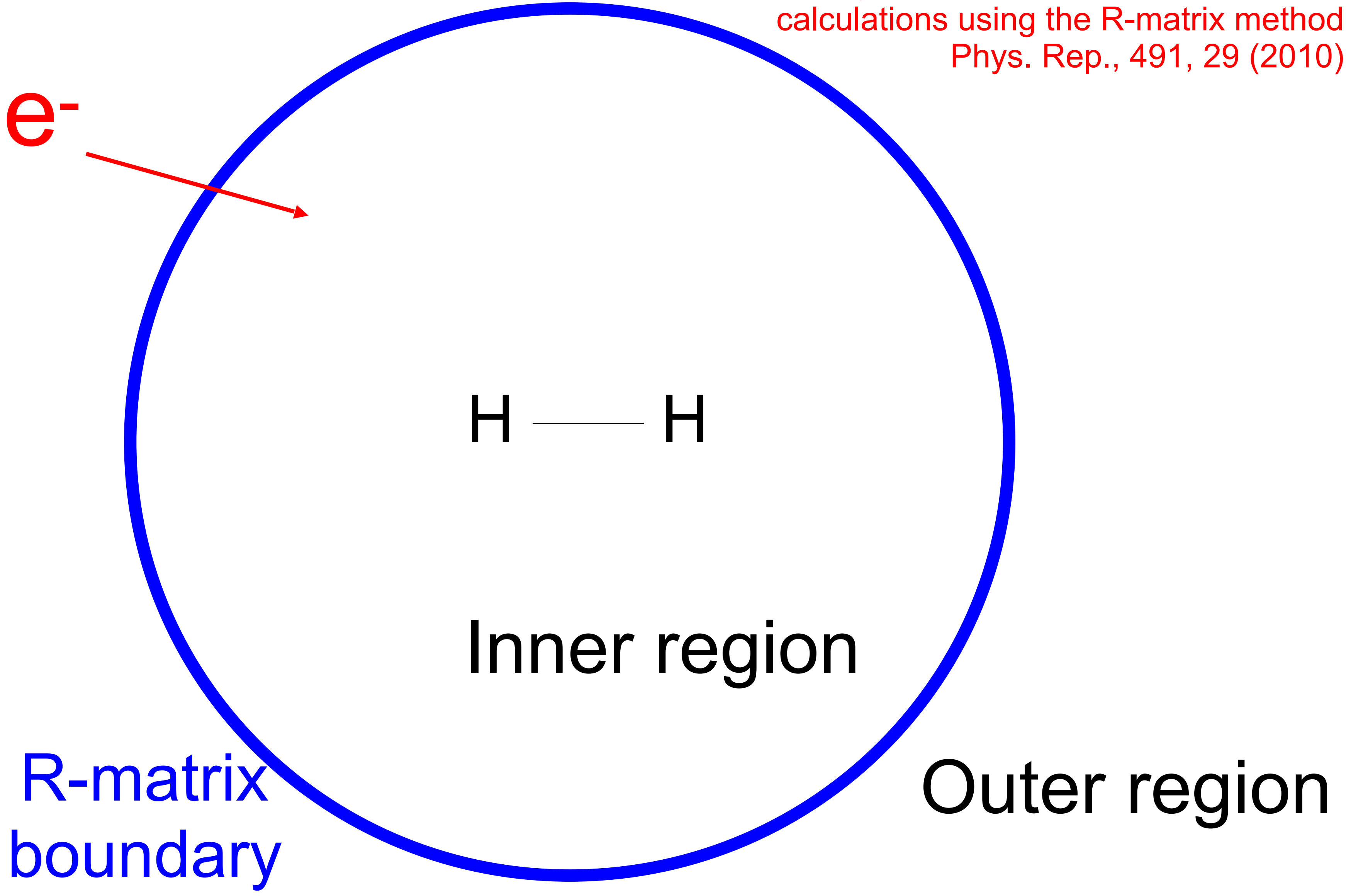
Computationally expensive

RMPS is R-matrix method; designed to treat many electrons

Similar in spirit to convergent close-coupling

The R-matrix method

J. Tennyson, Electron - molecule collision calculations using the R-matrix method, Phys. Rep., 491, 29 (2010).



Dominant interactions

Inner region

Exchange
Correlation

Adapt quantum chemistry codes

High ℓ functions required

Integrals over finite volume

Include continuum functions

Special measures for orthogonality

configuration generation must be appropriate

Boundary

Target wavefunction has zero amplitude

Outer region

Adapt electron-atom codes

Long-range multipole potential

Many degenerate channels

Born approx for long-range dipole coupling

R-matrix method for electrons: inner region wavefunction

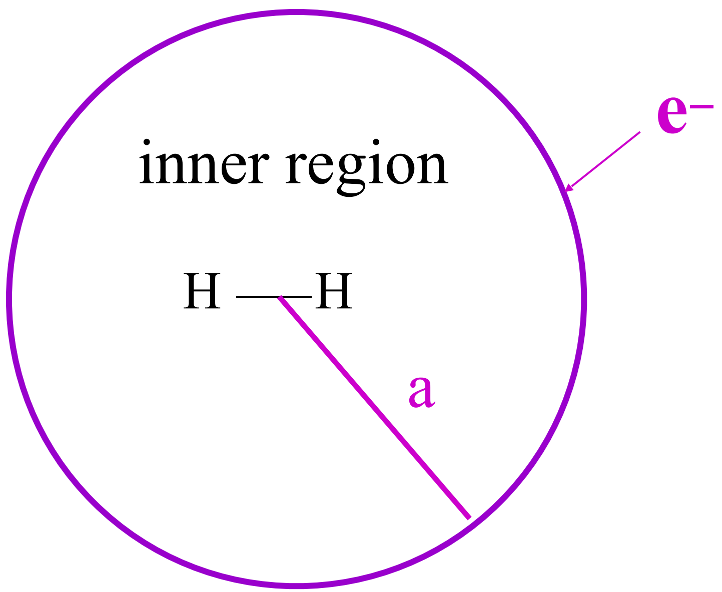
(within the Fixed-Nuclei approximation)

$$\Psi_k = \mathcal{A} \ \Sigma_{i,j} \ a_{i,j,k} \phi_i^N \eta_{i,j} + \Sigma_i \ b_{j,k} \phi_j^{N+1}$$

$\phi_i^N =$ *target states* = CI target built from nuclear centred GTOs

$\phi_j^{N+1} = L^2$ *functions*

$\eta_{i,j}$ = *continuum orbitals* =
GTOs centred on centre of mass



$\mathcal{A}$ = Anti-symmetriser

$a_{i,j,k}$ and $b_{j,k}$ variationally determined coefficients