ExoMol

UCL

e^-

Collisional and radiative molecular data for plasma models

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Outer region

Inner region

April 2021

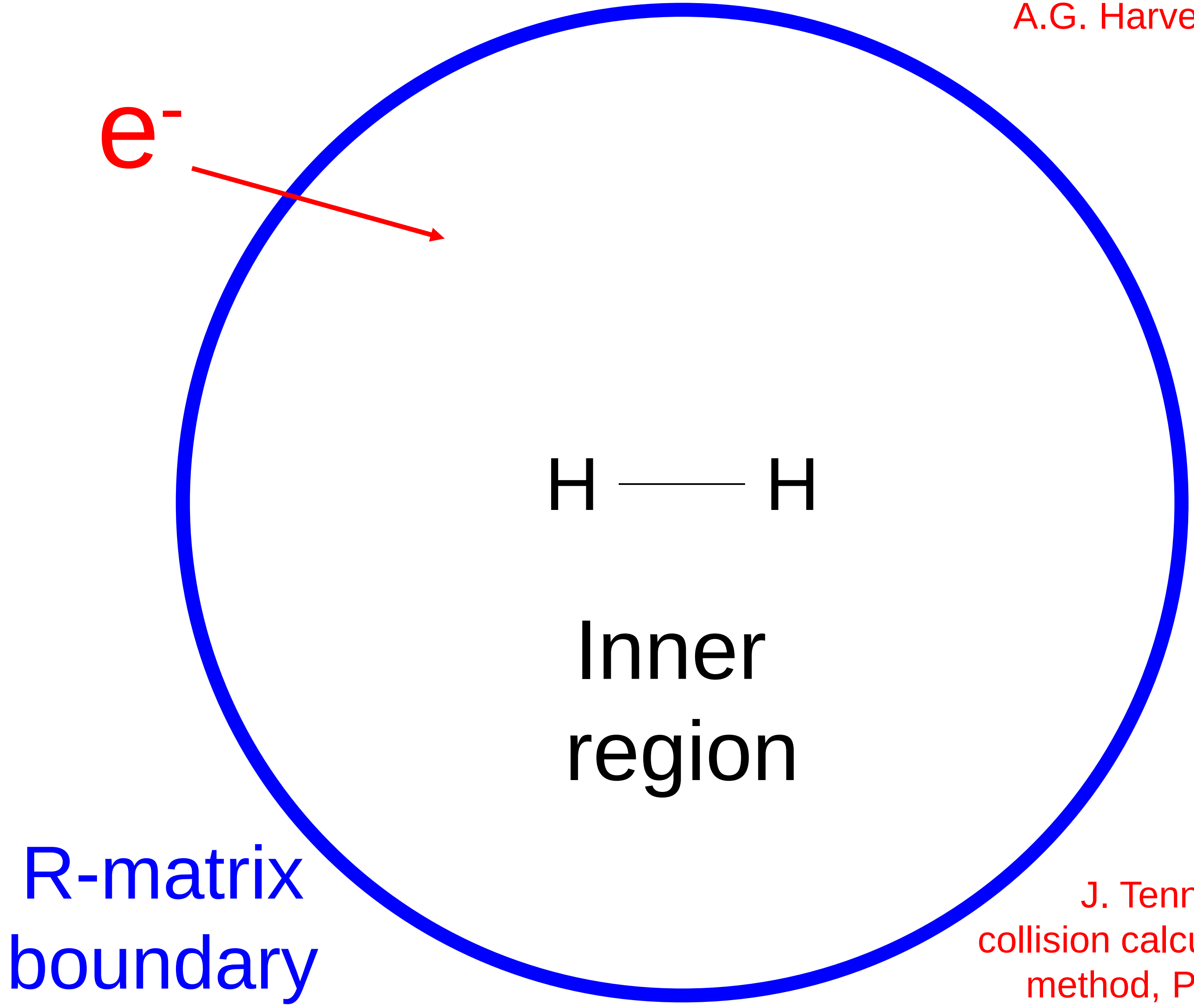
Contents

1. Formalisms:
    (a) the R-matrix method (electron collisions)
    (b) ExoMol (spectroscopic data)
2. Electron collision applications:
    Fusion plasmas: BeH, H_2
    Technological plasmas
    Atmospheric: space craft re-entry
    Astrophysics
3. Conclusions

The R-matrix method: UKRmol+

Z. Masin, J Benda, J.D. Gorfinkiel, A.G. Harvery, J. Tennyson, UKRMol+ Computer Phys. Comms., 249, 107092 (2020)

B-Splines
Large R-matrices

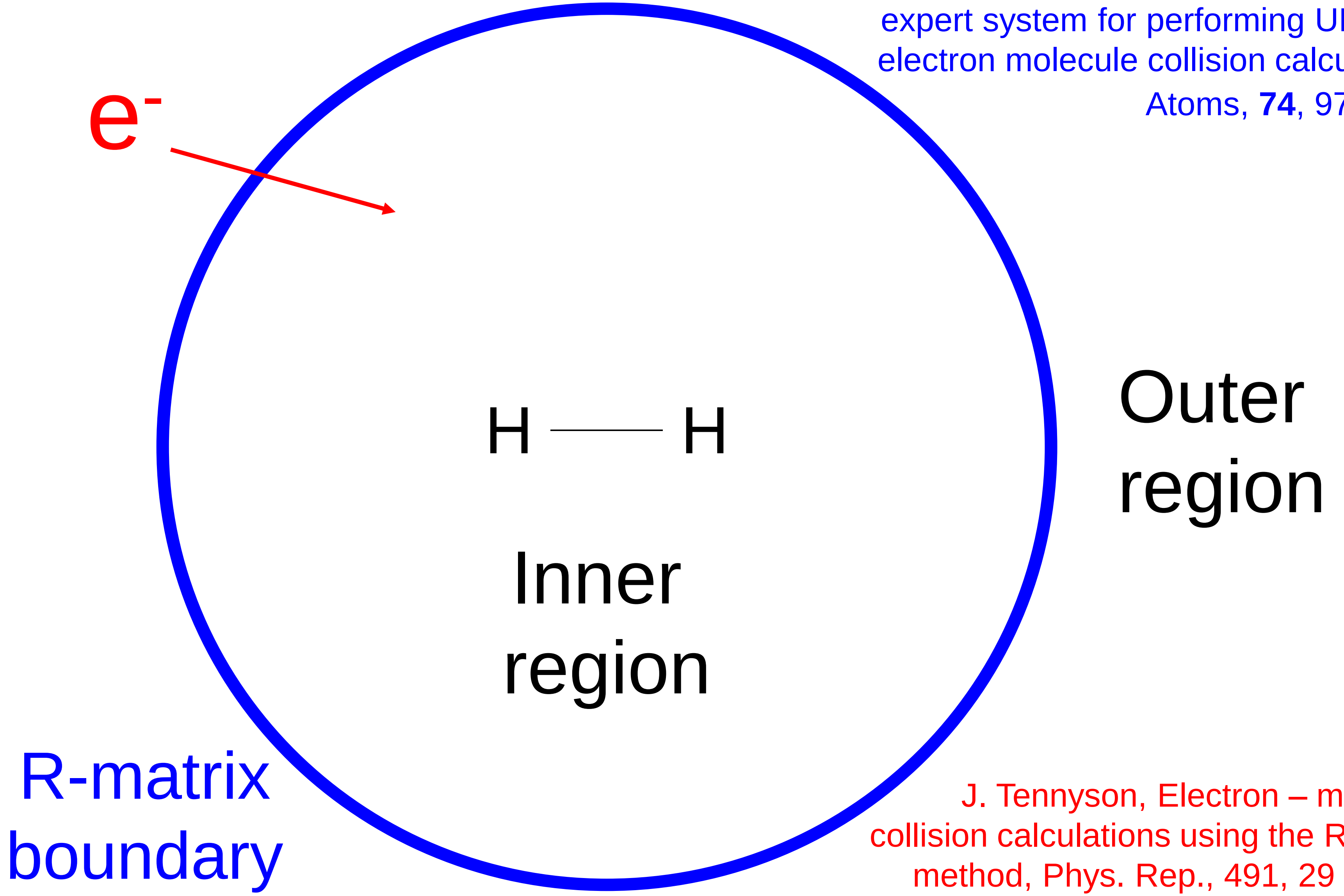


Outer region

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

The R-matrix method:

Cooper et al., Quantemol Electron Collision: an expert system for performing UKRmol+ electron molecule collision calculations, Atoms, **74**, 97 (2019)



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

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

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

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

R-matrix method for electrons: inner region wavefunction

(within the Fixed-Nuclei approximation)

Close-coupling expansion:

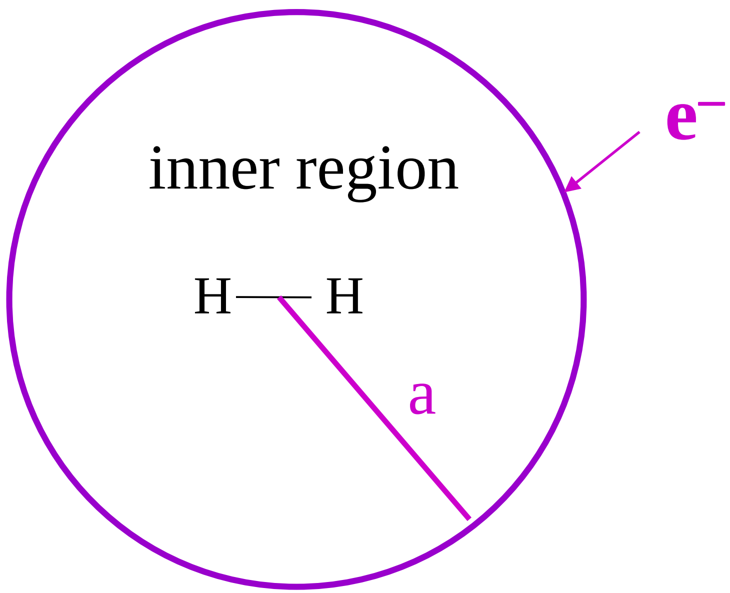
$$\Psi_k = \mathcal{A} \sum_{i,j} a_{i,j,k} \phi_i^N \eta_{i,j} + \sum_i b_{j,k} \phi_j^{N+1}$$

ϕ_i^N = *target states* = CI target built from nuclear centred GTOs

ϕ_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

ExoMol

Hot line lists; 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
XXXVI SH (UV)
XXXVII HCCH
XXXVIII SiO_2
XXXIX CO_2
XL. H_3O^+

XLI: NaOH, KaOH
XLII: NO (UV)

In progress
D_3^+, D_2H^+ O_2, C_3, TiH, NaO, YO, SO, SiO (UV), ZnO, CaOH, AlF, AlCl, HCO^+

Formal data releases:
J. Tennyson *et al*., J. Mol. Spectrosc. **373**, 73 (2016)
and JQSRT **255**, 107228 (2020)

ExoMol: 2011-16
ExomolHD: 2020-25

ExoMolHD

5 year project: 2020-25

Precision spectroscopic data for studies of exoplanets and other hot atmospheres:

1. Line lists with spectroscopic accuracy
2. Spectroscopic line lists for isotopologues
3. Pressure broadening and pressure shifts
4. Photodissociation: Temperature Dependent
5. The ExoMolHD Database

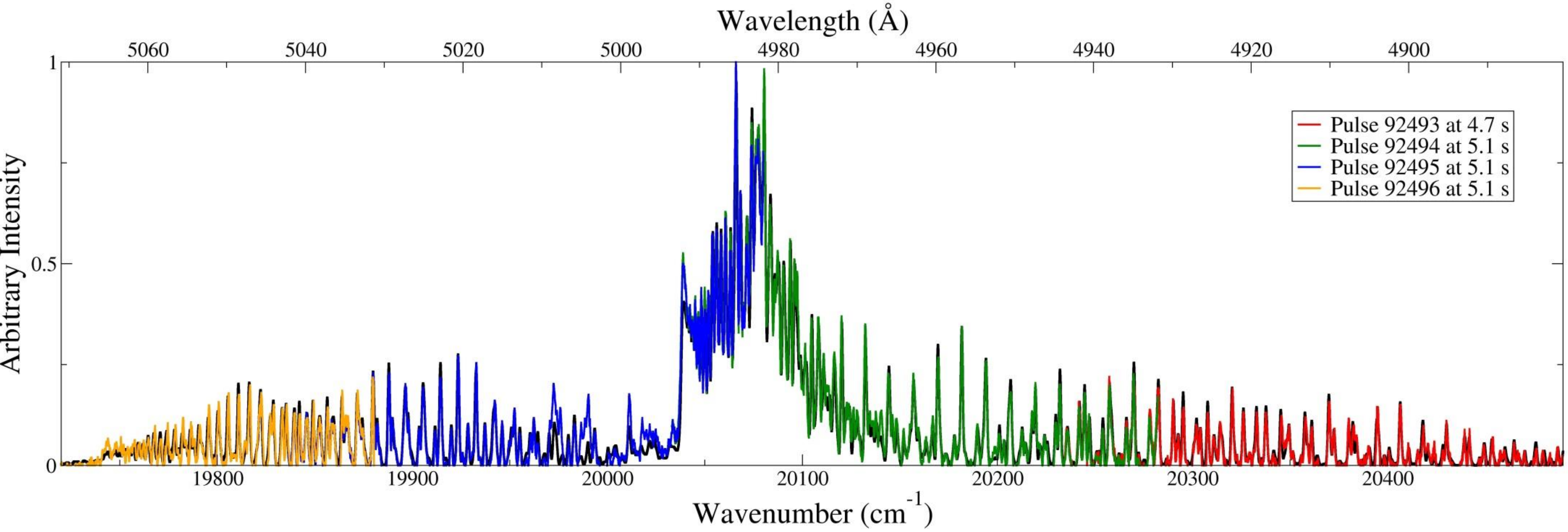
Fusion appications: BeH / BeD / BeT

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

Daniel Darby-Lewis

In collaboration with Kerry Lawson (CCFE)

BeD spectra measured in JET



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

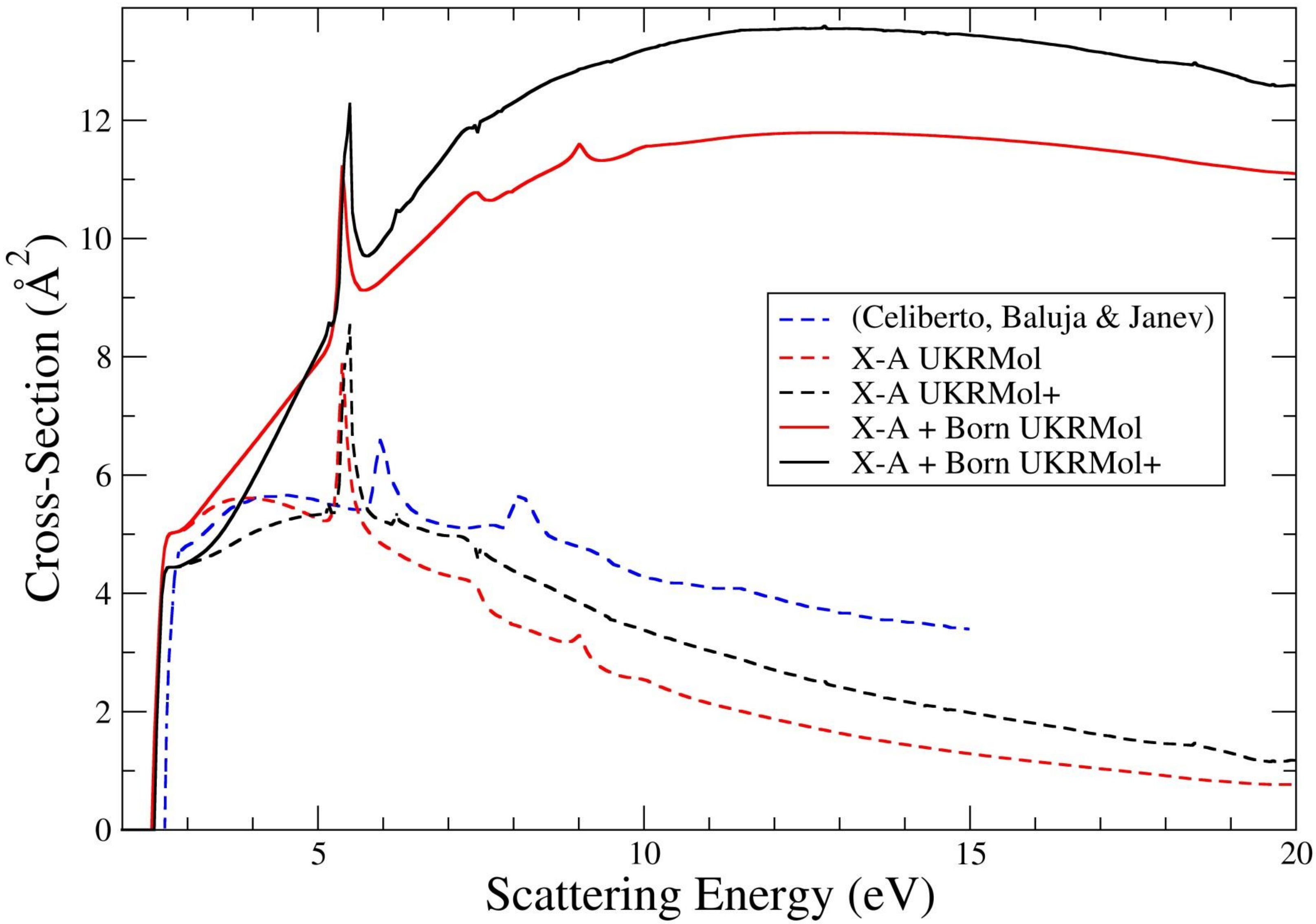
D. Darby-Lewis, J. Tennyson, K.D. Lawson, S.N. Yurchenko, M.F. Stamp, A. Shaw, S. Brezinsek and JET Contributor, Synthetic spectra of BeH, BeD and BeT for emission modelling in JET plasmas, *J. Phys. B: At. Mol. Opt. Phys.*, 51, 185701 (2018)

Interpretation requires collisional-radiative model

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

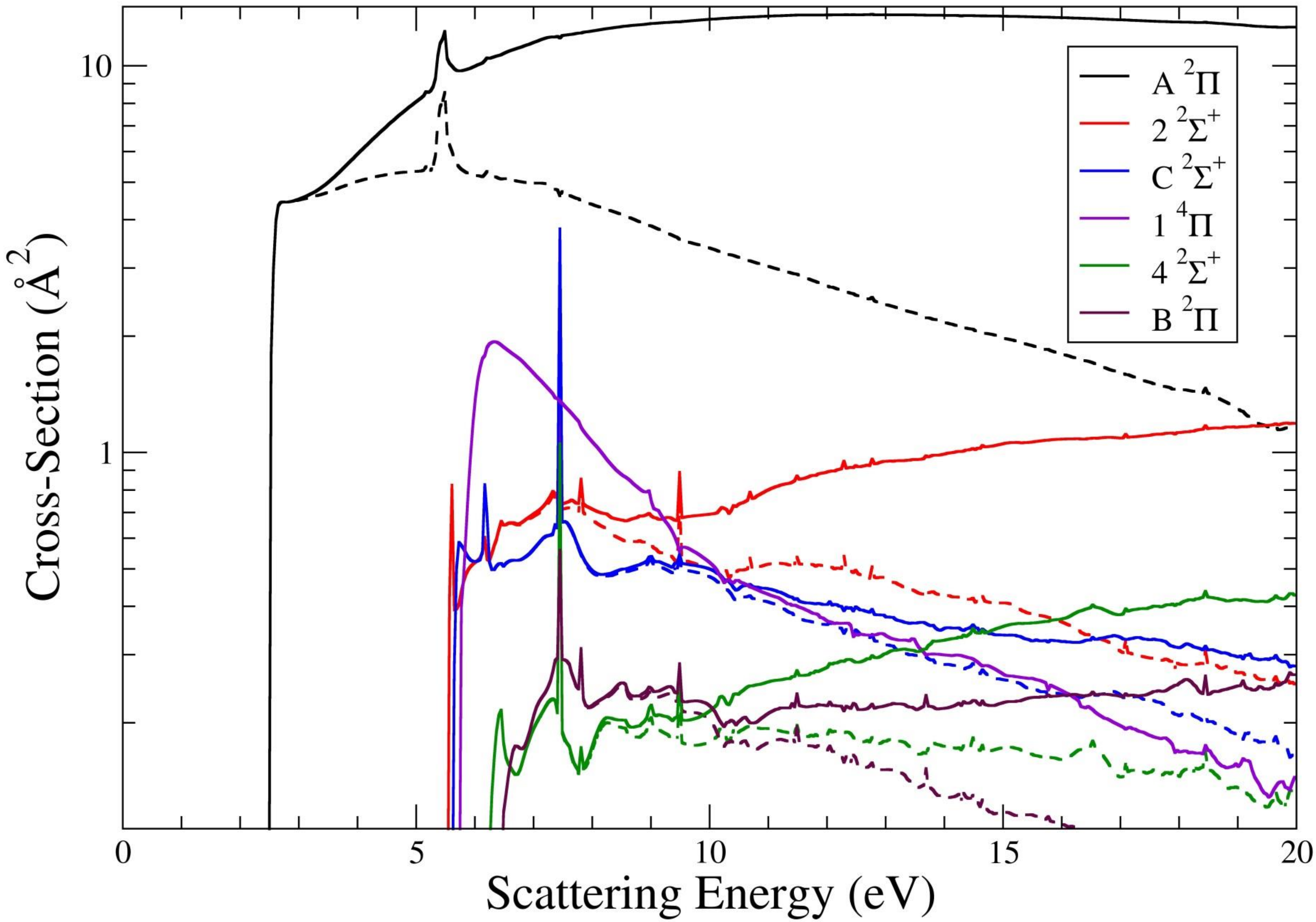
Step 2 $BeH\ (A\ ^2\Pi, v', J') \rightarrow BeH\ (X\ ^2\Sigma^+, v'', J'') + h\nu$

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



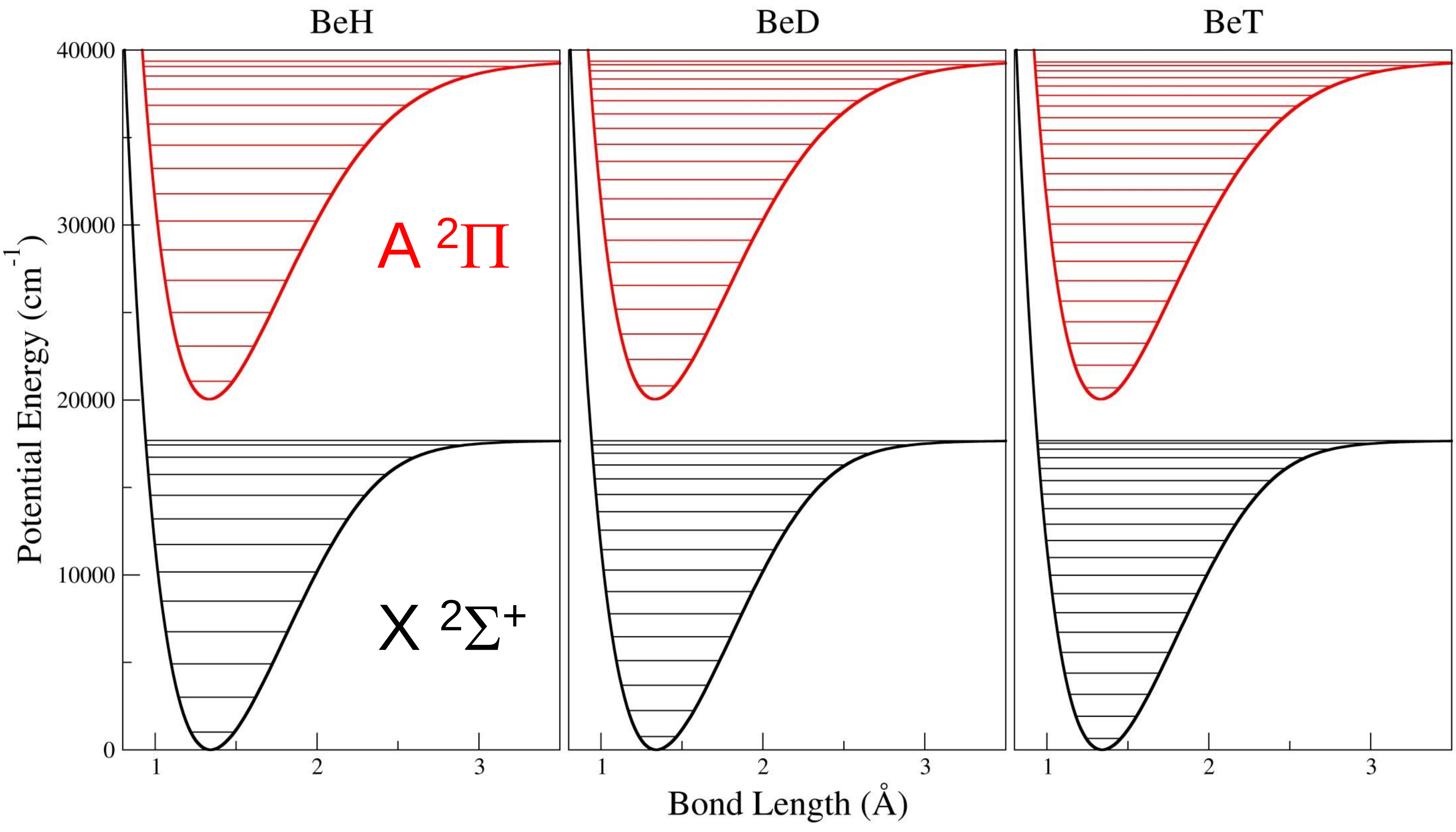
D. Darby-Lewis, Z. Masin & J. Tennyson, *J. Phys. B: At. Mol. Opt. Phys*, **50**, 175201 (2017).

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).

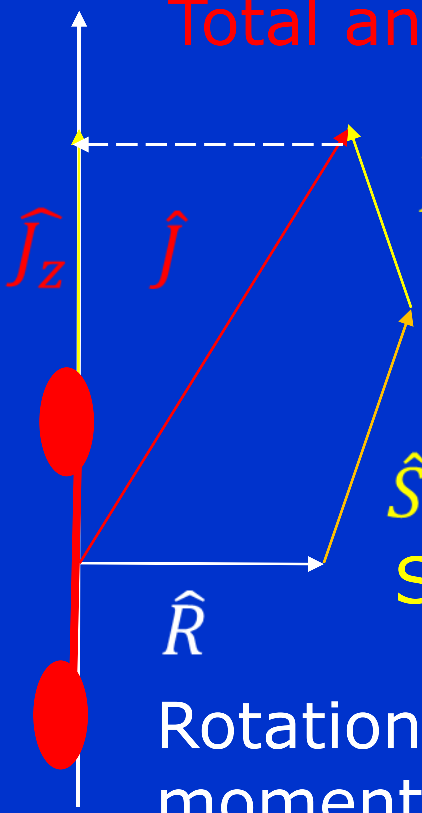
Spectroscopic model for BeH/BeD/BeT



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).



Total angular momentum

$\hat{L}$ Electronic angular momentum

$\hat{S}$ Spin

$\hat{R}$ Rotational angular momentum

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

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

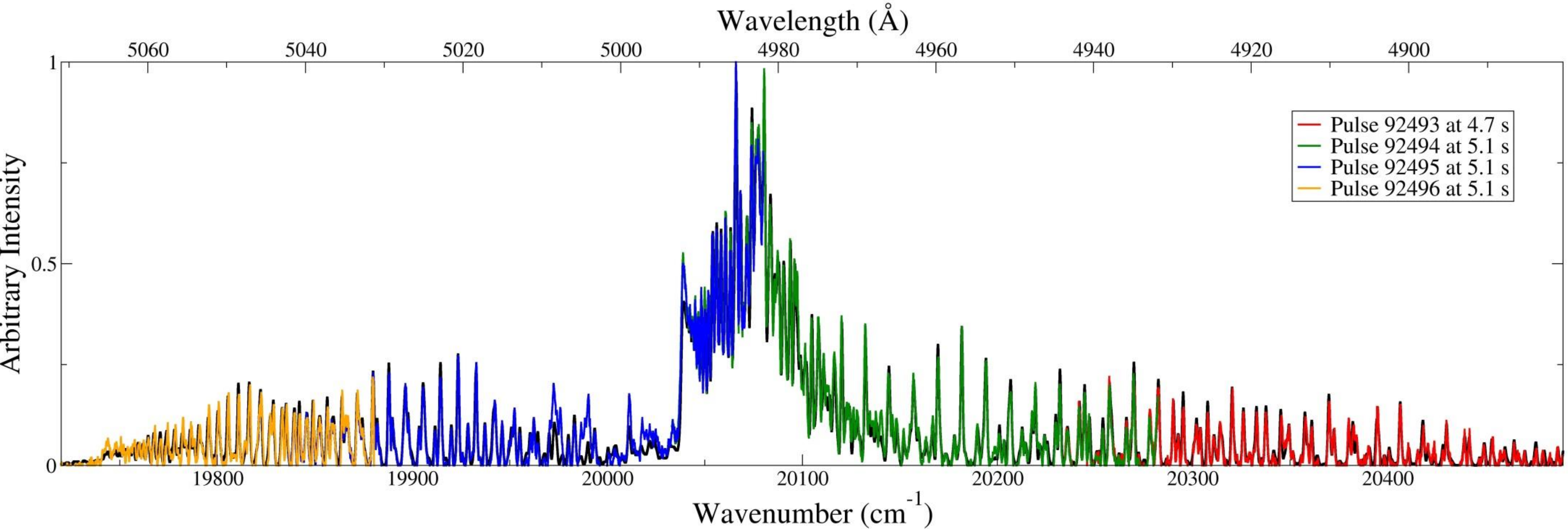
Variational basis set
Hund's case (a)

Vibrational Spin

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

Rotational Electronic

BeD spectra measured in JET

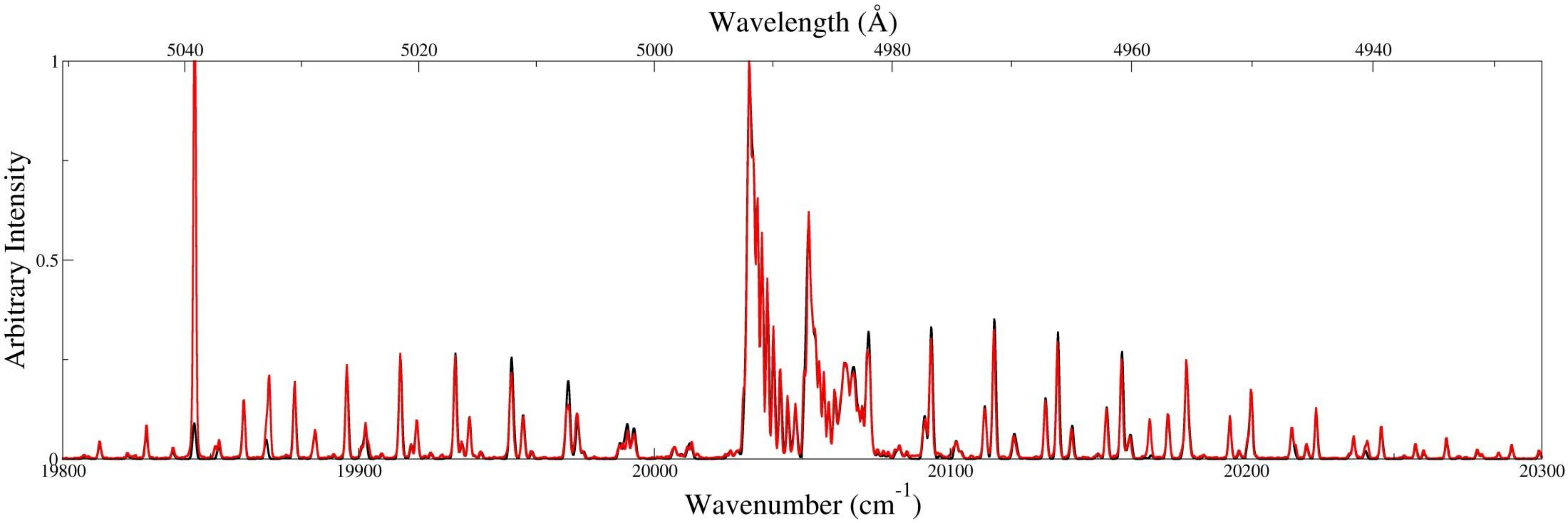


Red, green, blue and orange regions are different pulses.

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 $e + BeH (X\ ^2\Sigma^+, v', J') \rightarrow e + BeH (A\ ^2\Pi, v'', J'')$

Step 2 $BeH (A\ ^2\Pi, v', J') \rightarrow BeH (X\ ^2\Sigma^+, v'', J'') + h\nu$

Interpretation requires collisional-radiative model

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

D. Darby-Lewis, J. Tennyson, S.N. Yurchenko and K. D. Lawson, Vibrational resolved electron impact electronic excitation of BeH, *J. Phys. B: At. Mol. Opt. Phys*., **53**, 135202 (2020).

Data in the AMDIS database (Christian Hill, IAEA)

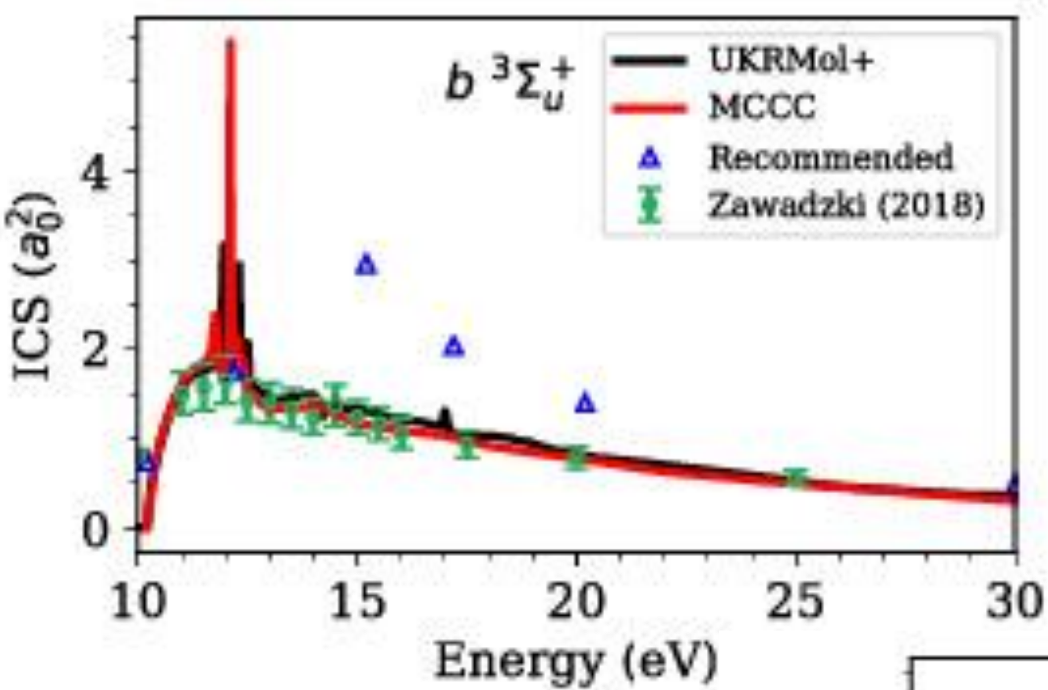
Step 2 BeH (A $^2\Pi$, *v*',*J*') → BeH (X $^2\Sigma^+$,*v*'',*J*'') + hν

Fusion appications?: H_2/ D_2 /T_2 etc

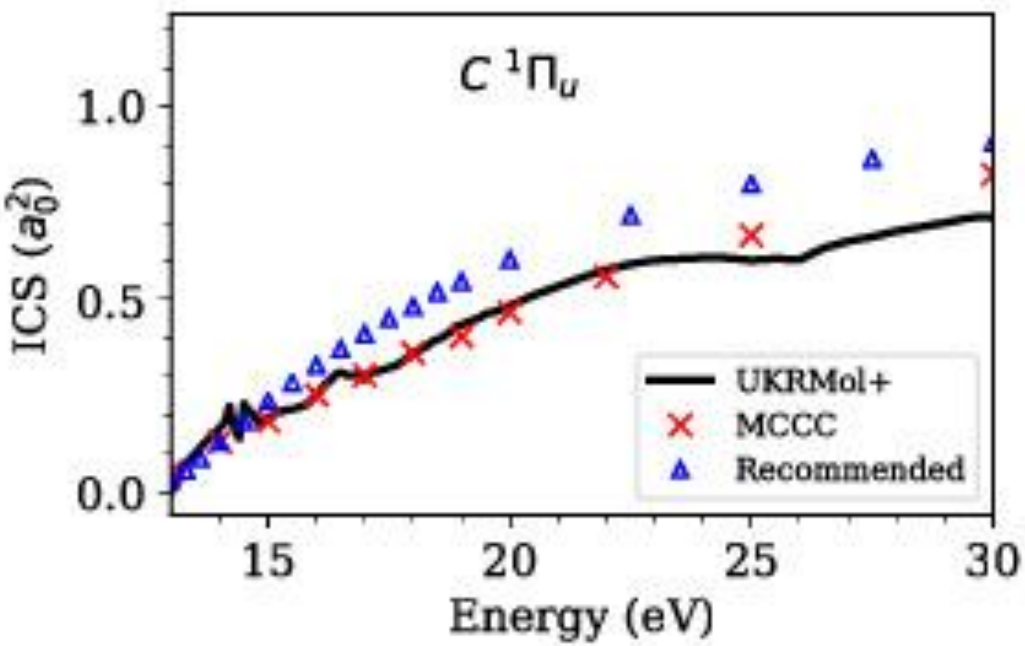
- New UKRmol+ allows study of diffuse targets
- Considering collisions going up H(n=3) states
- R-matrix sphere with a = 100 a.u. !
- Consider collisions from excited states

Tom Meltzer

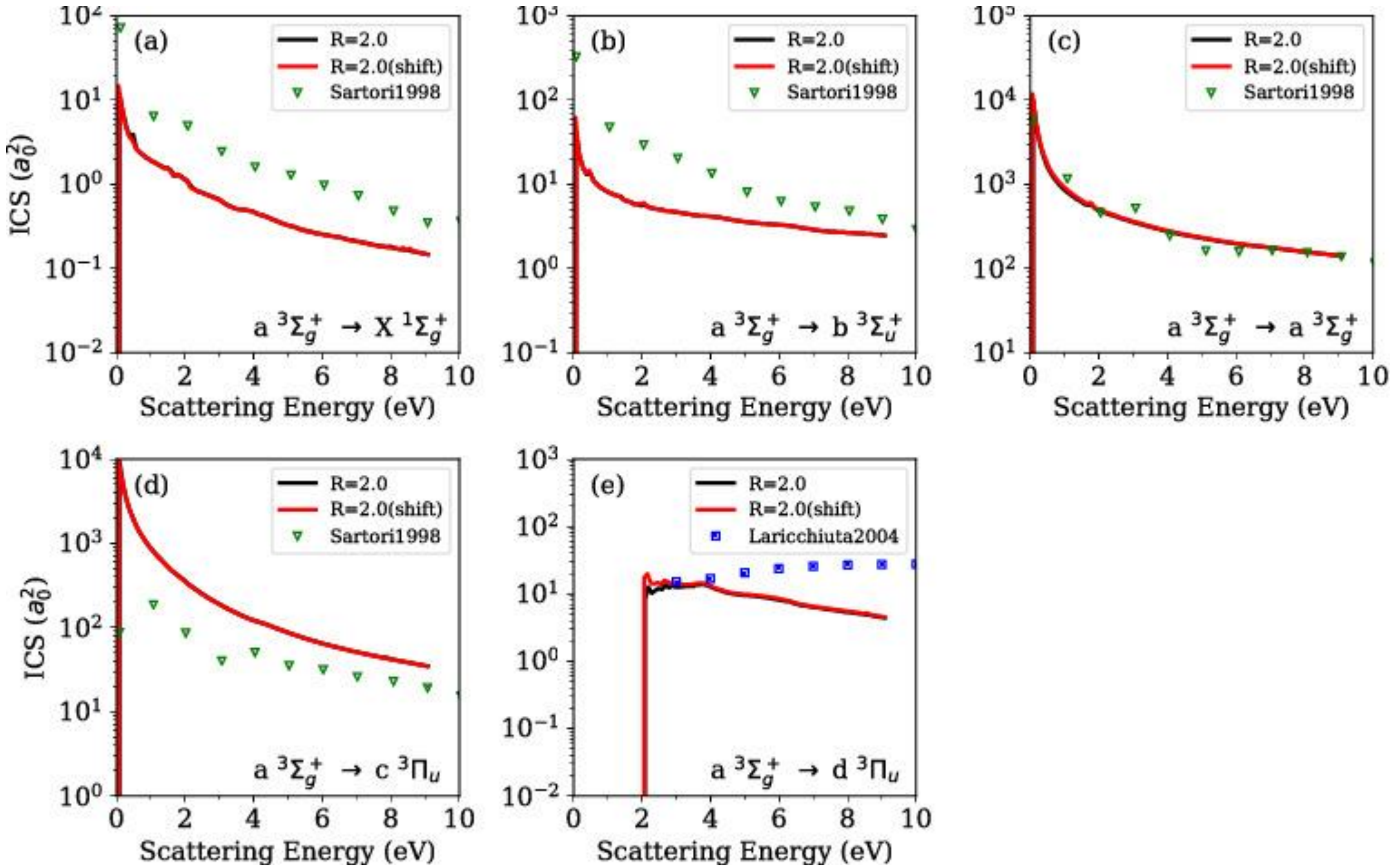
H_2 electronic excitation cross sections from X state



T. Meltzer et al. Benchmark Calculations of Electron Impact Electronic Excitation of the Hydrogen Molecule, *J. Phys. B: At. Mol. Opt. Phys*., **53**, 145204 (2020).

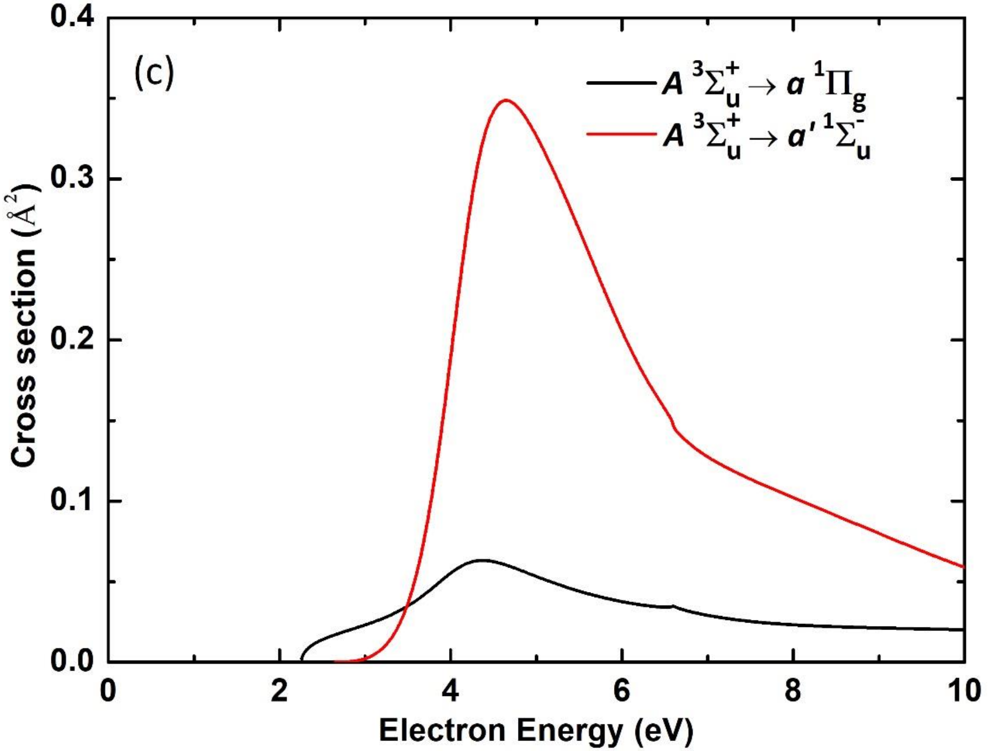


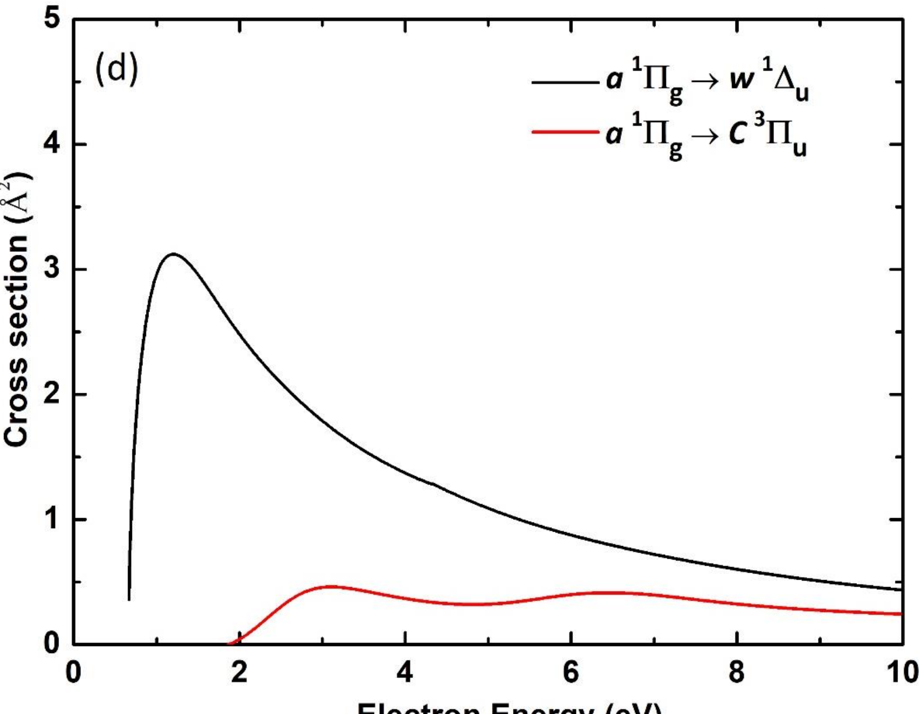
H_2 electronic excitation from excited states



T. Meltzer and J. Tennyson, Electron Collisions with Molecular Hydrogen from Electronically Excited States Using the R-matrix Method, *J. Phys. B: At. Mol. Opt. Phys.*, **53**, 245203 (2020).

N_2 electronic excitation from excited states





He Su, X. Cheng, H. Zhang & J. Tennyson, J. Phys. B (under review)

Future projects:

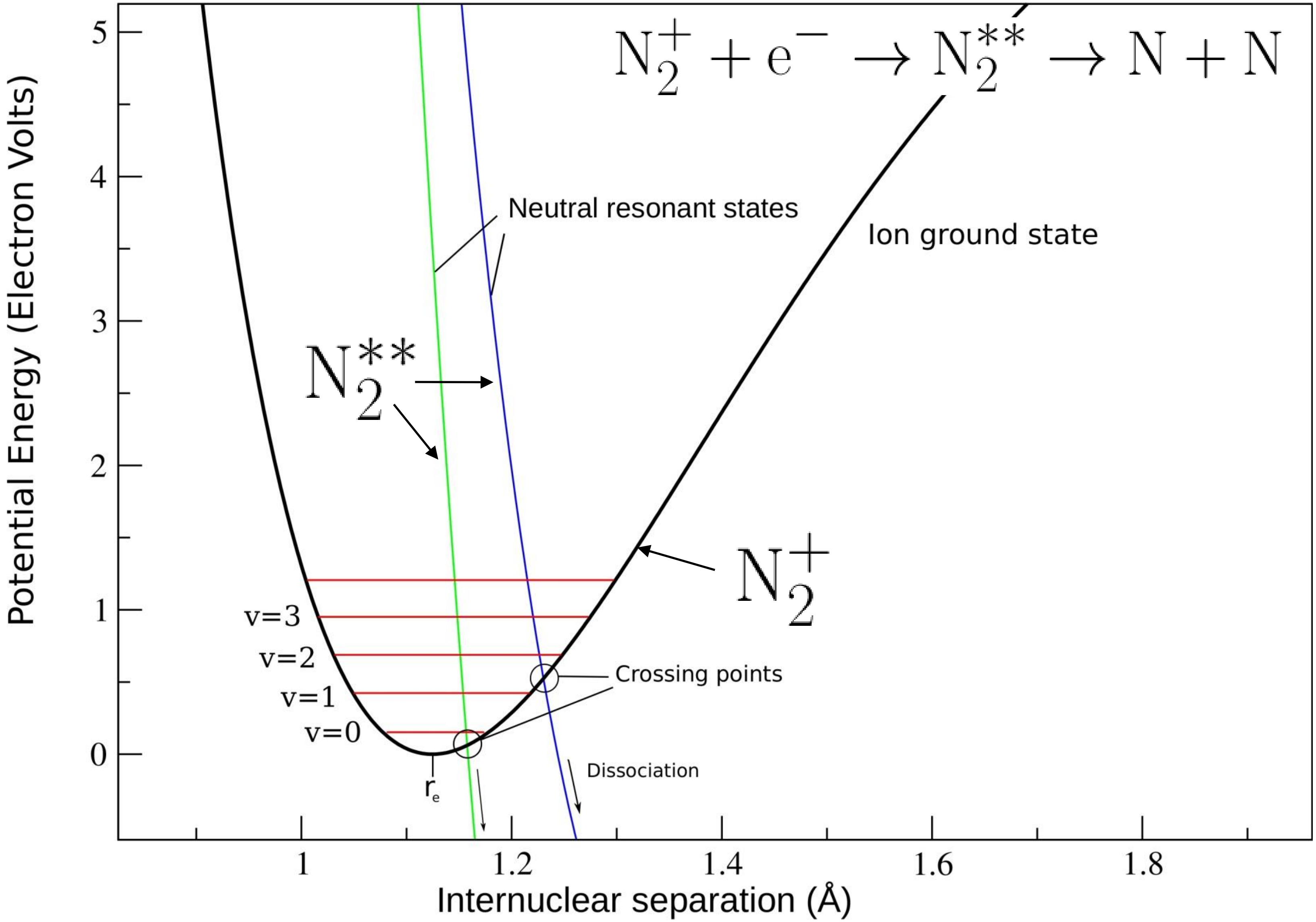
BeH_2 ?

Other systems (eg N_2) ?

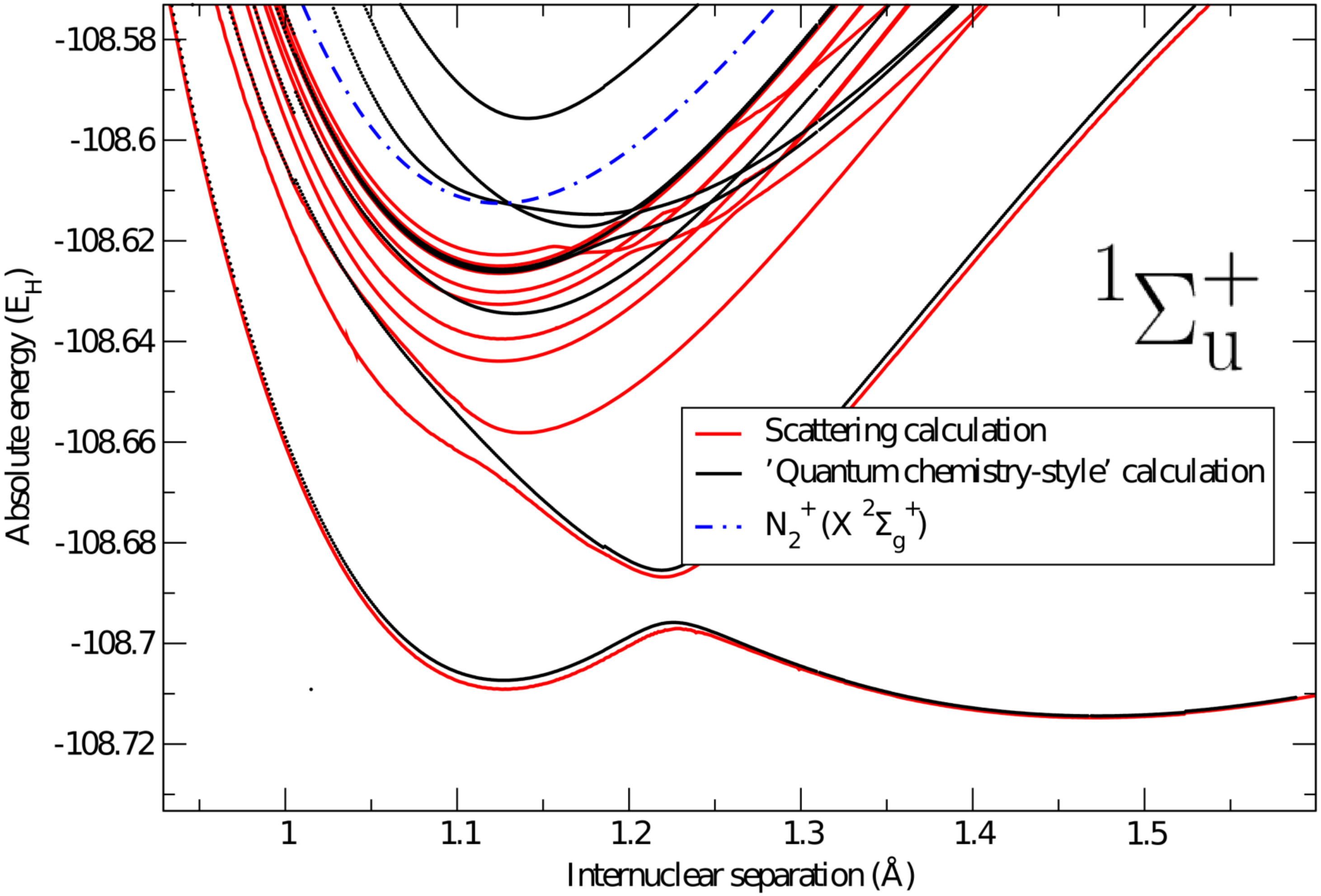
WH?

Dissociative recombination (DR)

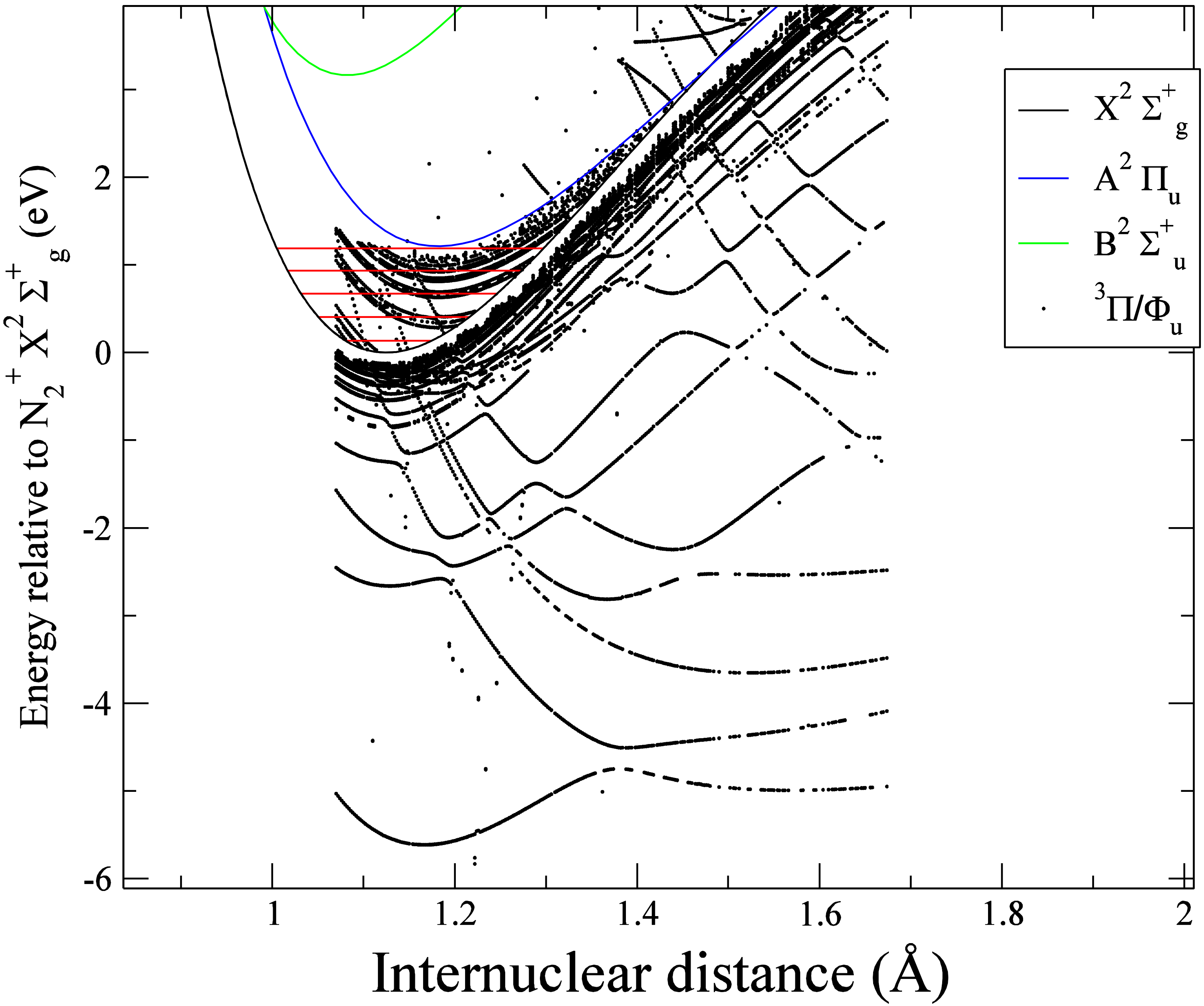
(Direct process)



Bound states, solve for negative scattering energies



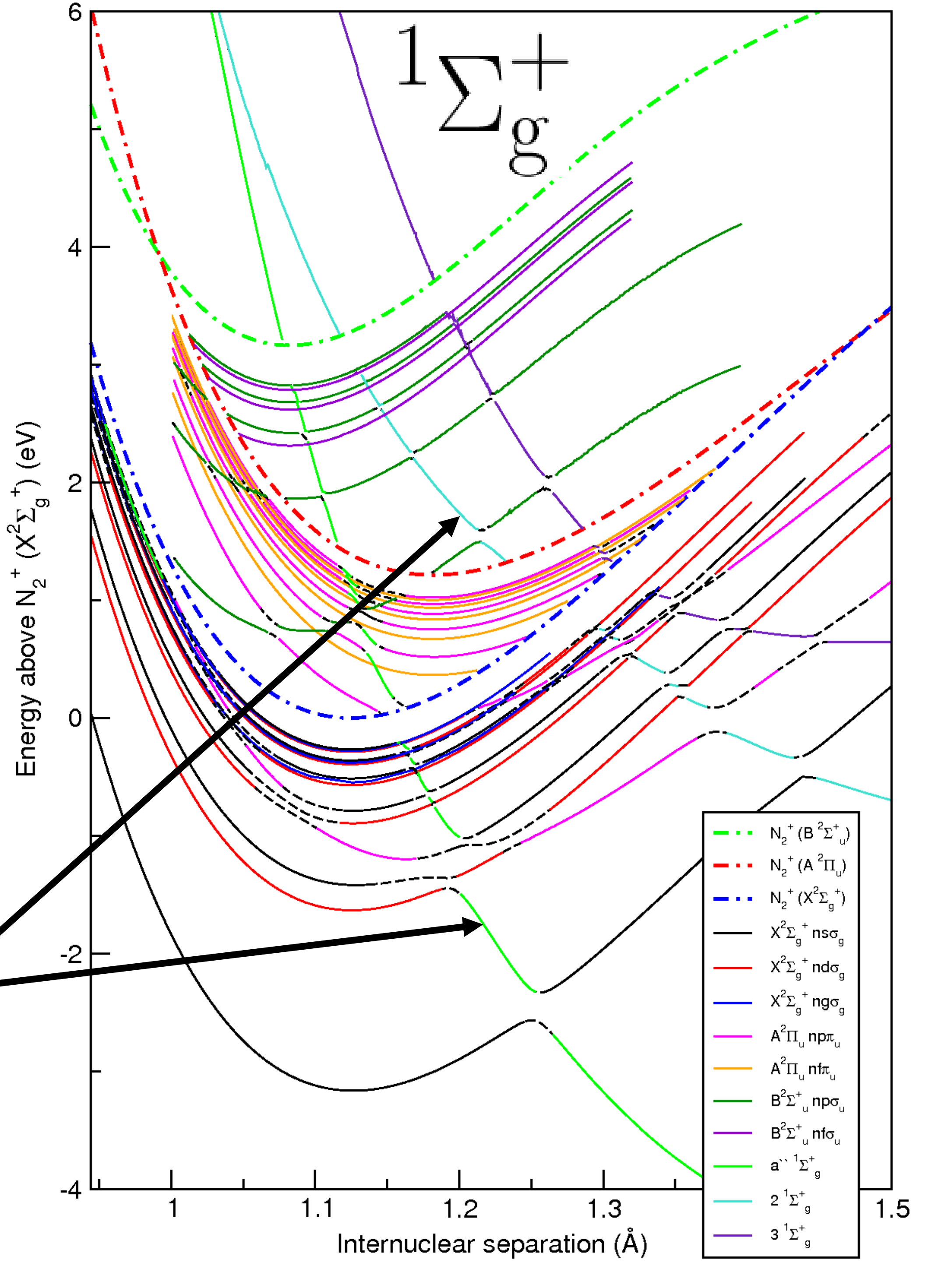
D. A. Little and J. Tennyson, J. Phys. B. **46** 145102 (2013)



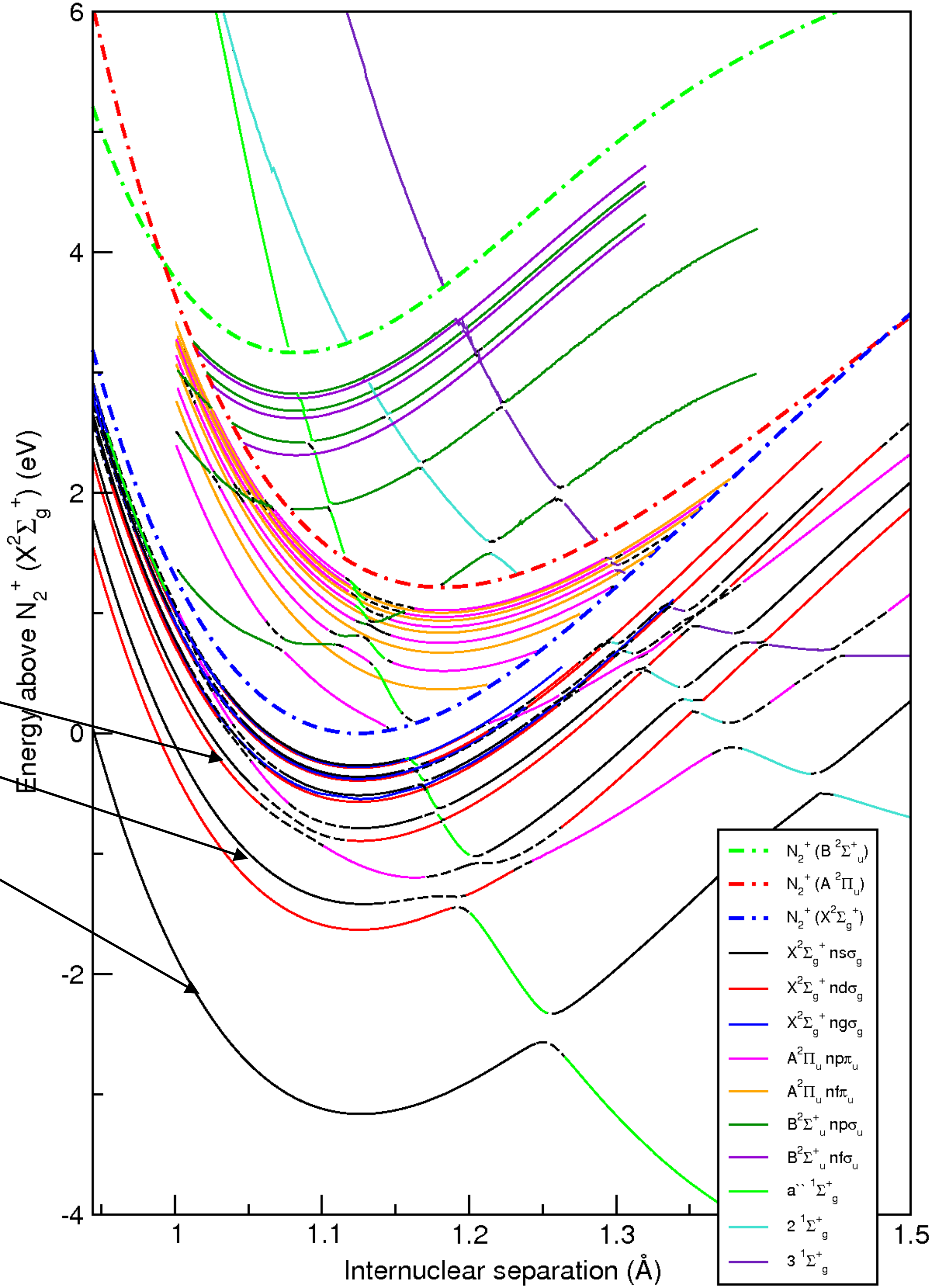
Energy relative to N2+ X2Σ+g (eV)
Internuclear distance (Å)
X2Σ+g
A2Πu
B2Σ+u
3Π/Φu
-6
-4
-2
0
2
1
1.2
1.4
1.6
1.8
2

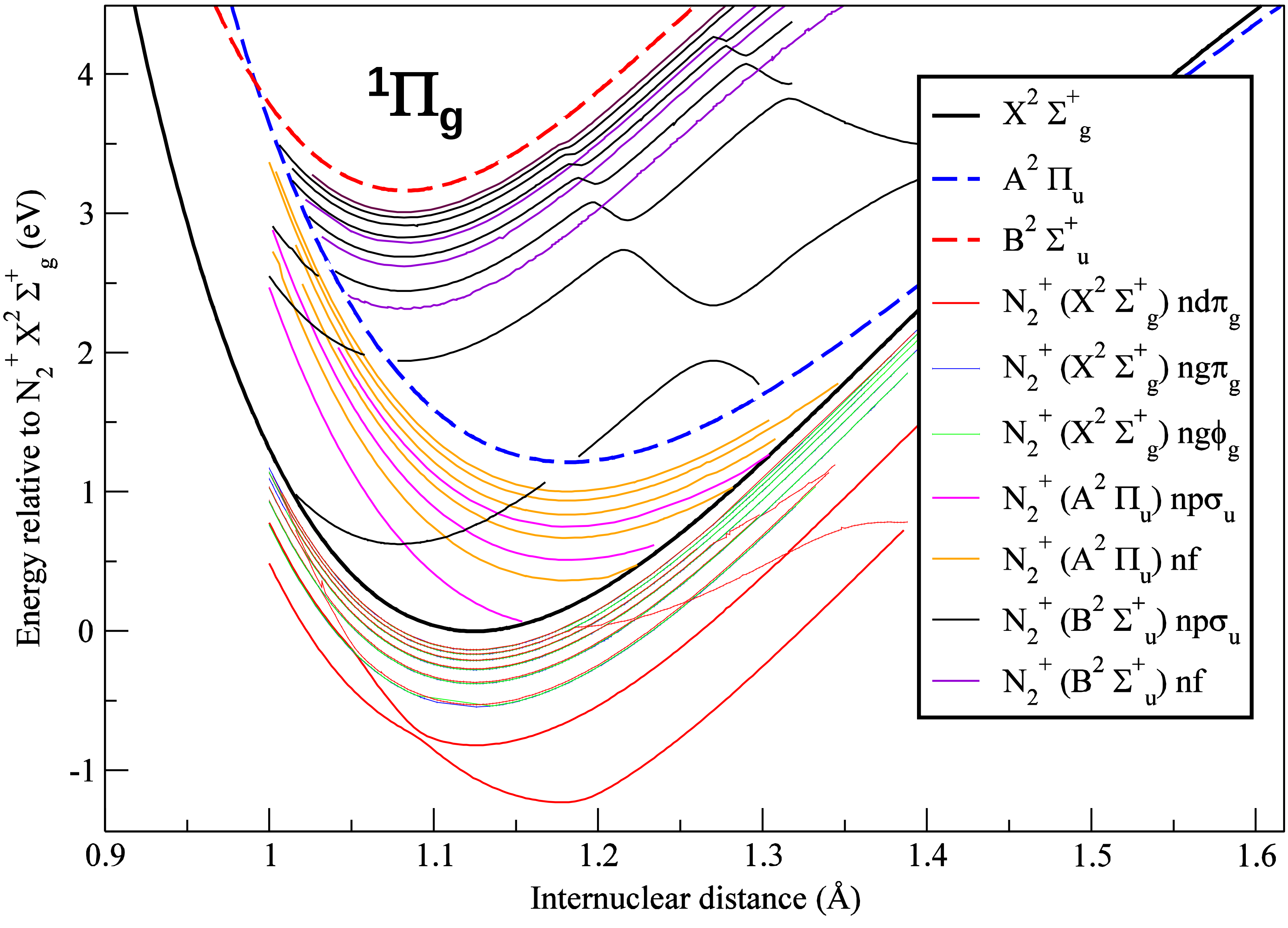
In reality Rydberg states complicate things..

Dissociating ionic states



5. Rydberg states for indirect mechanism

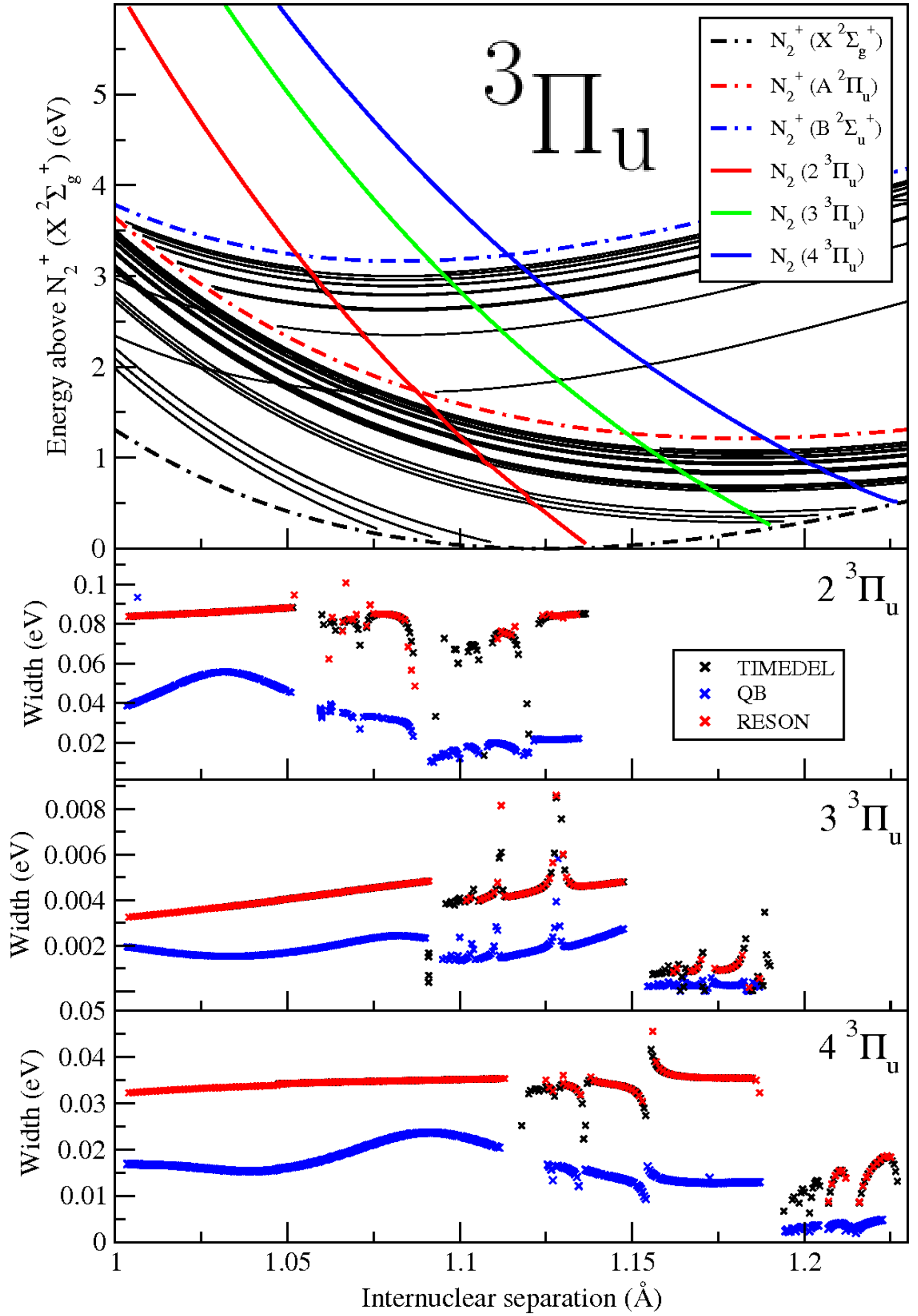




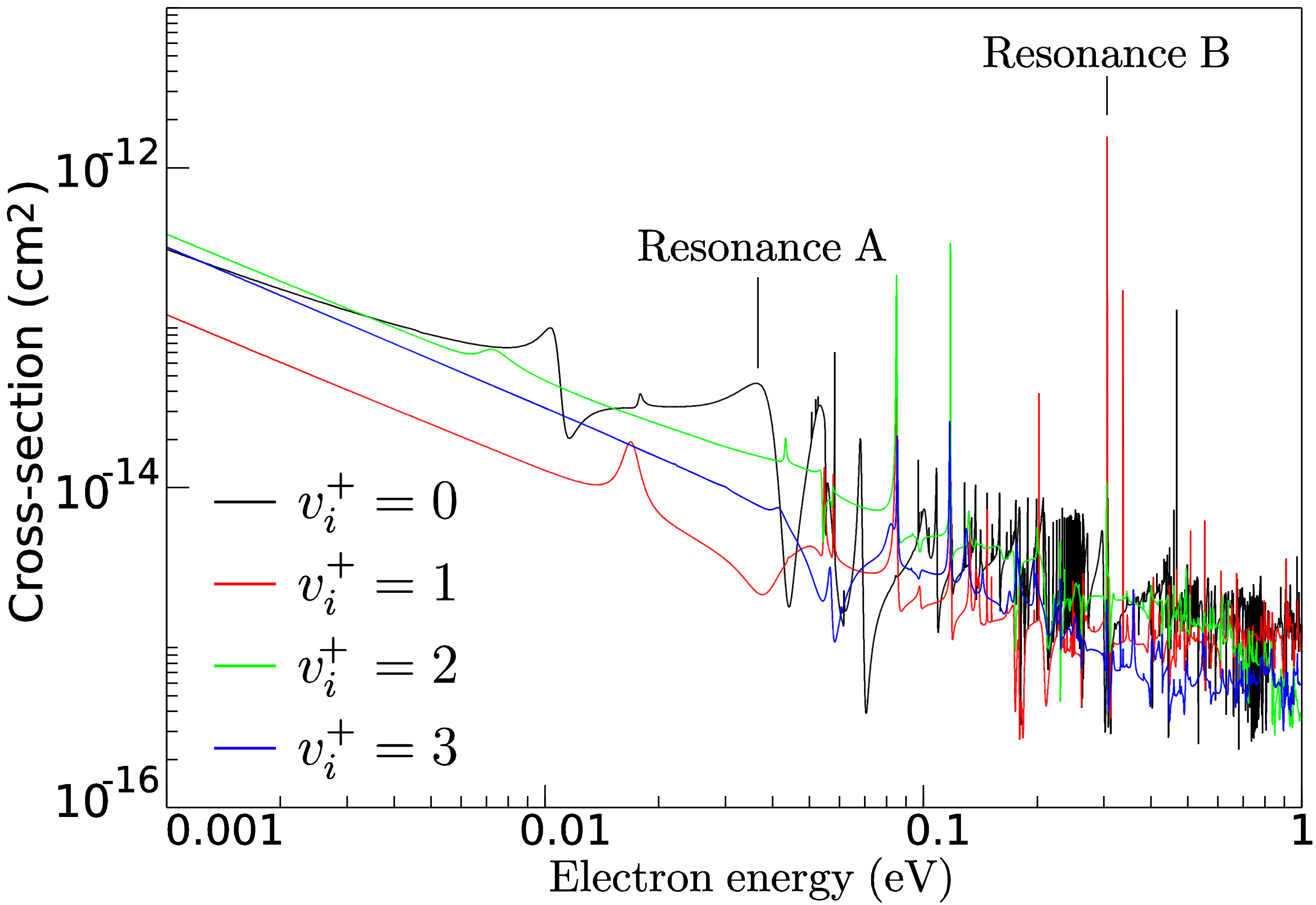
DA Little & J Tennyson, An ab initio study of singlet and triplet Rydberg states of N_2, J Phys B, 46, 145102 (2013)

2. Main neutral dissociative PECs

3. The lifetime or widths of the neutral PECs (in the scattering continuum)

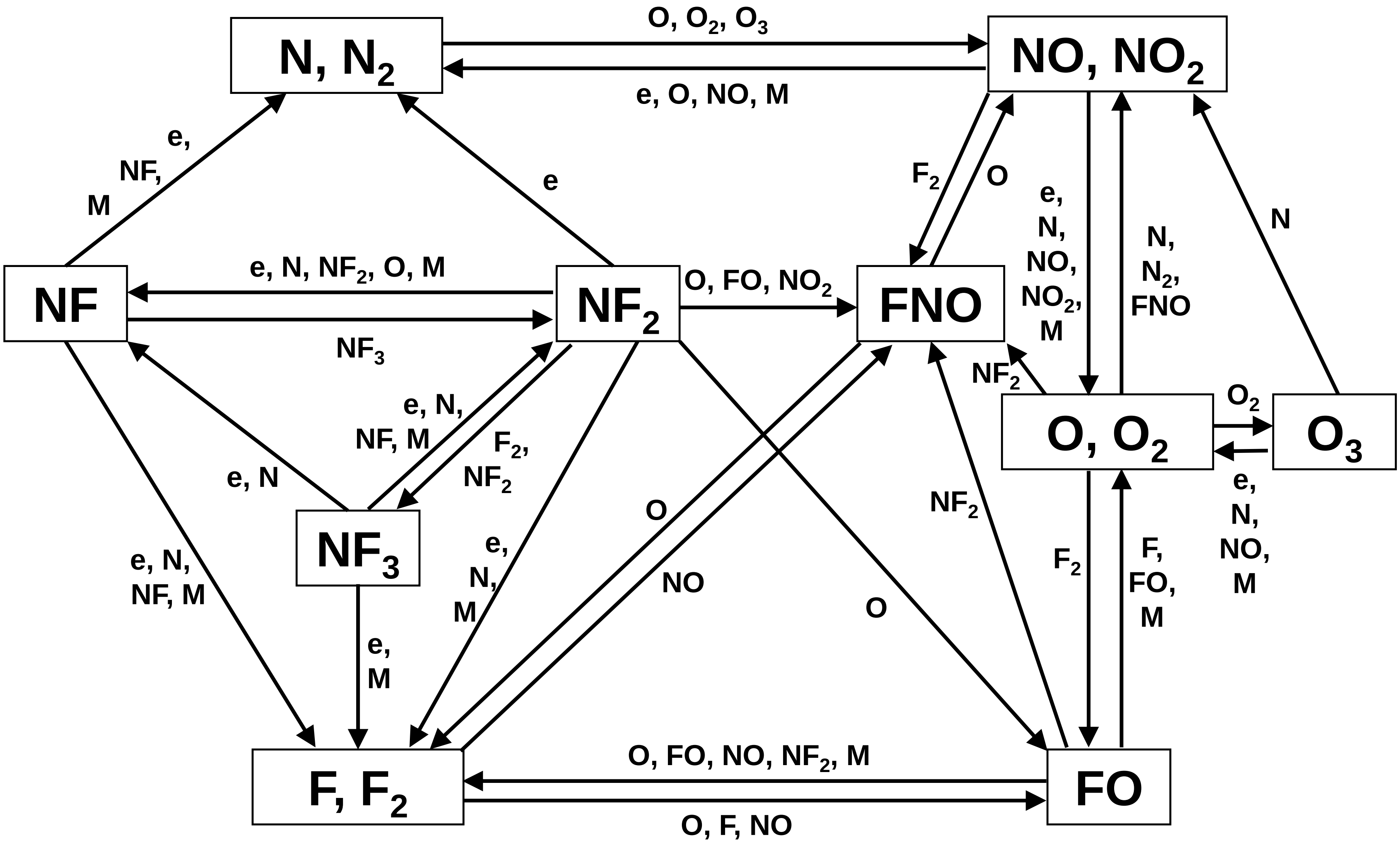


Dissociative recombination of N_2^+: N_2^+ (v) + e --> N + N



D. A. Little, K. Chakrabarti, J. Zs. Mezei, I. F. Schneider & J. Tennyson,
Phys. Rev. A, 90, 052705 (2014)

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

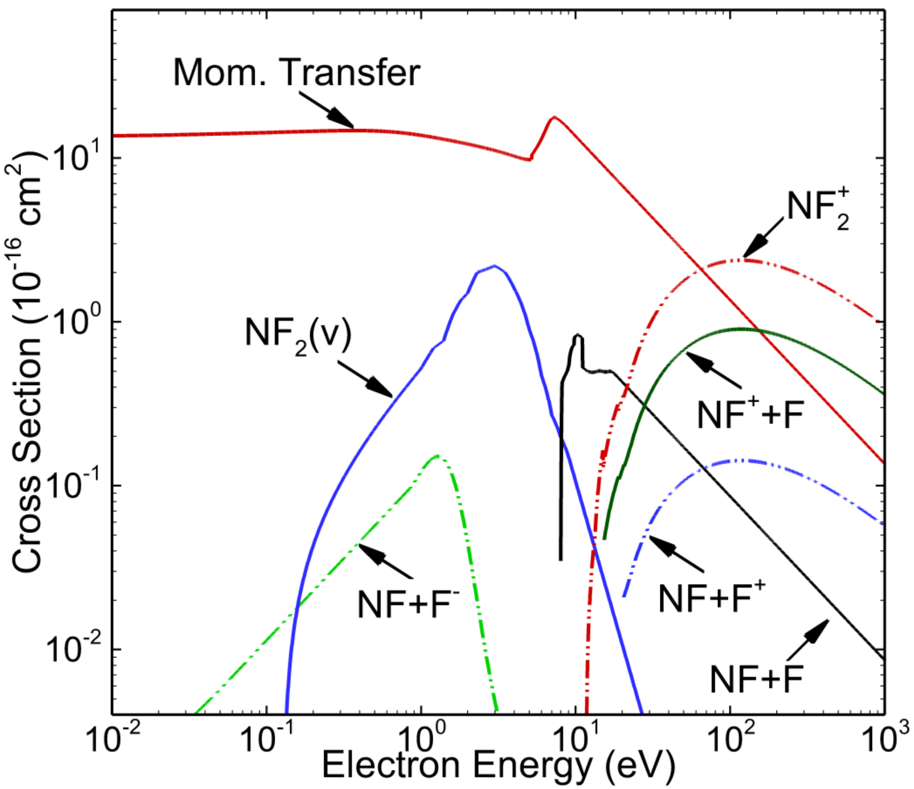
Eg NF_3/O_2 mixture

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.**

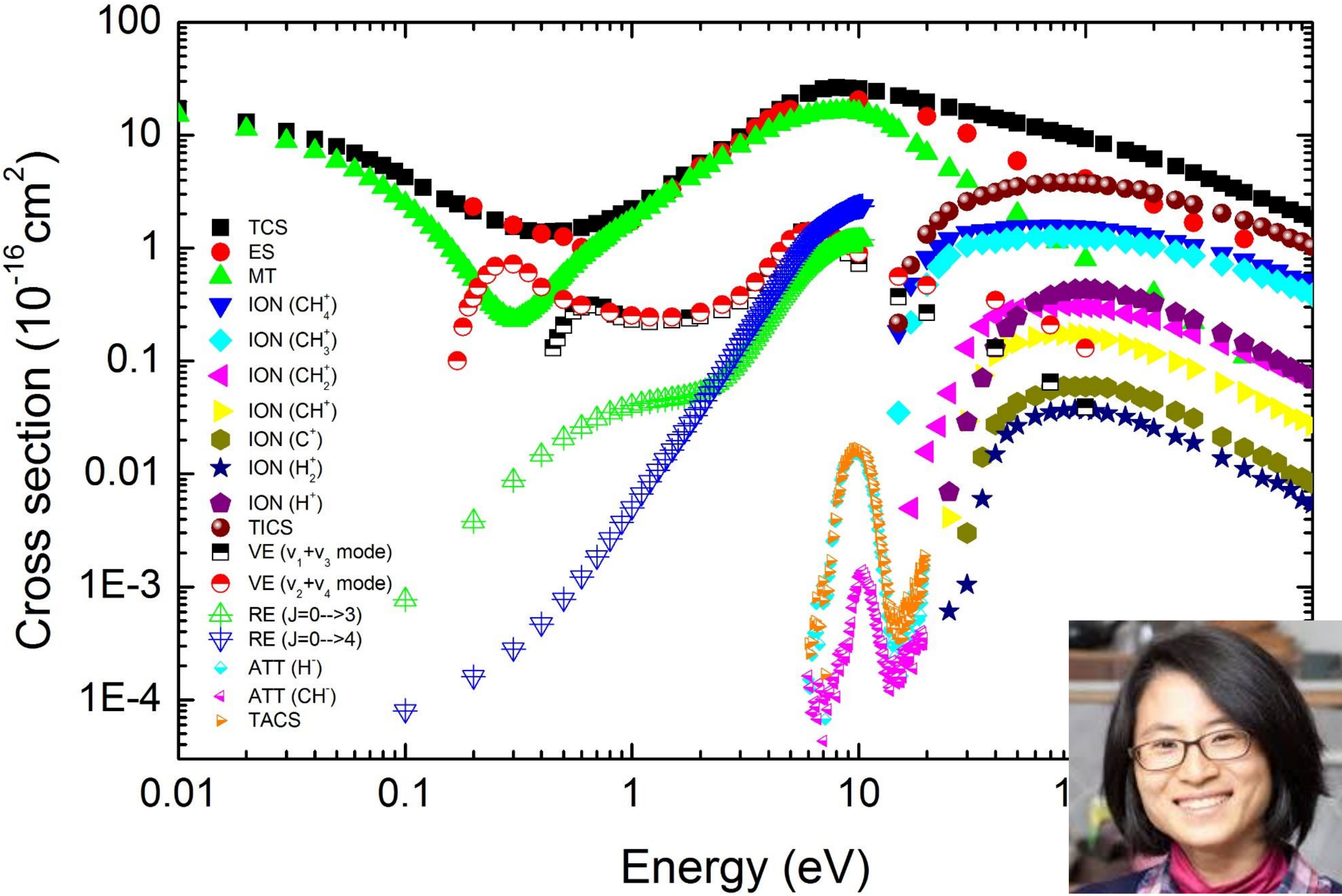


NF_2 cross sections obtained using R-matrix method.

James Hamilton

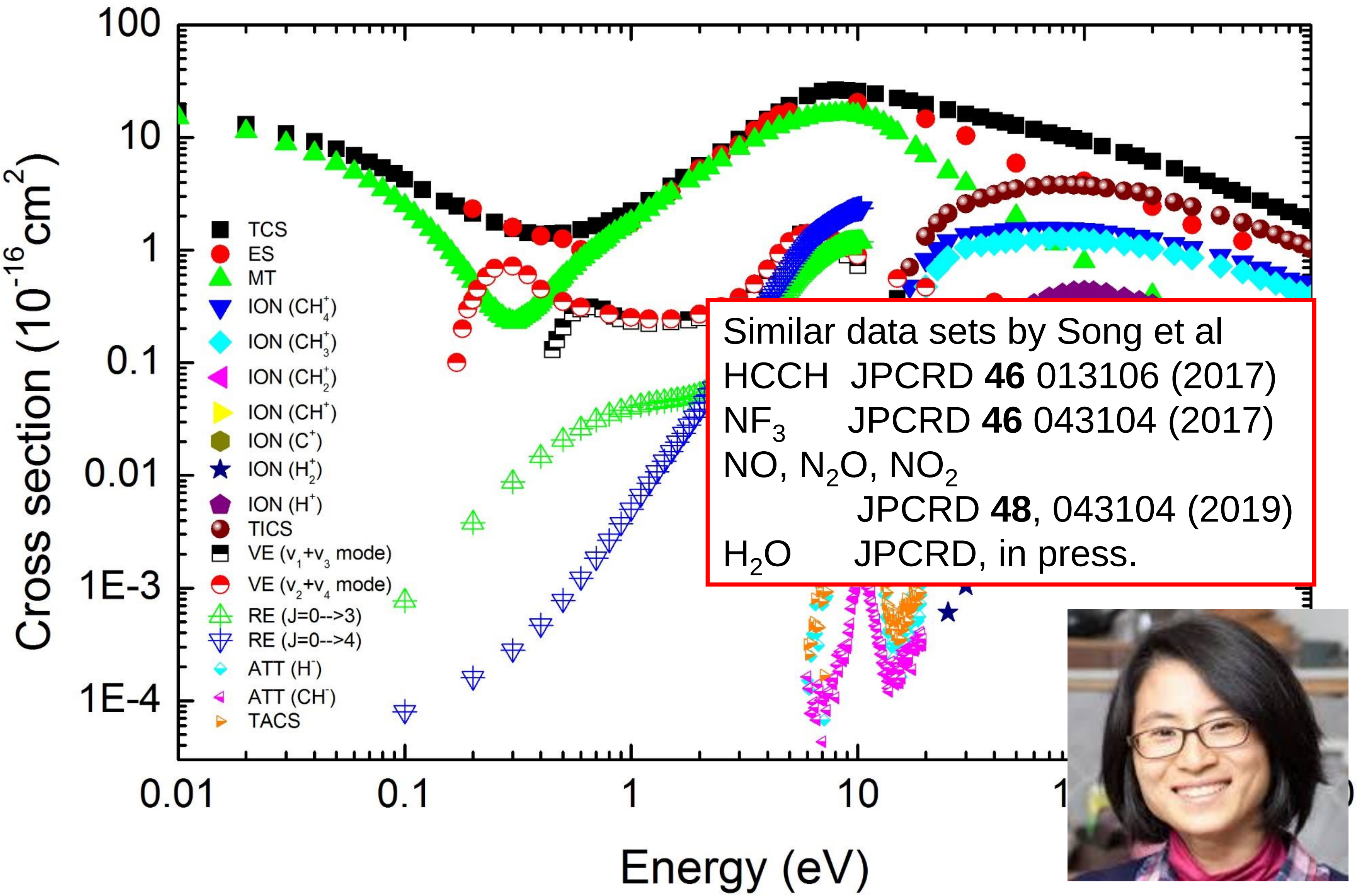
J.R. Hamilton, J. Tennyson, S. Huang and M.J. Kushner, Calculated cross sections for electron collisions with NF_3, NF_2 and NF, Plasma Sources Sci. Technol, 26, 065010 (2017).

Cross sections for electron collisions with methane



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)

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 **48**, 043104 (2019)

H_2O JPCRD, in press.

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)

PHYS4ENTRY

PLANETARY ENTRY INTEGRATED MODELS

SEVENTH FRAMEWORK PROGRAMME

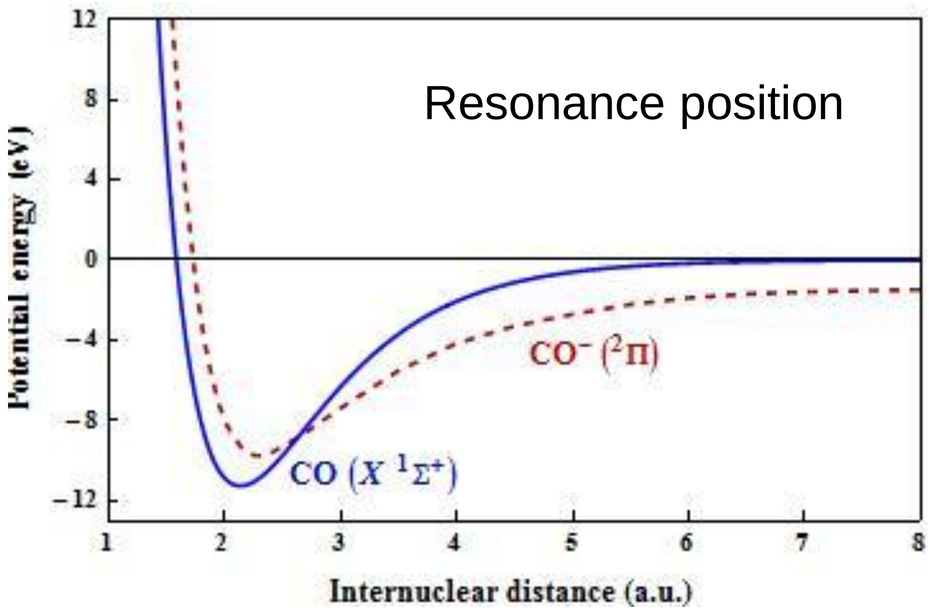
plasmas created on spacecraft (rocket) re-entry

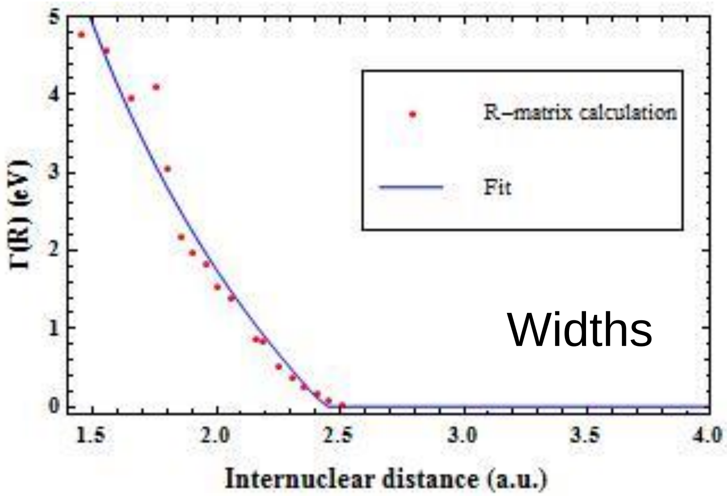
Vibrational excitation of key molecule: Venus, Mars, Earth

Vincenzo Laporta

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

Electron – CO: $^2\Pi$ resonance



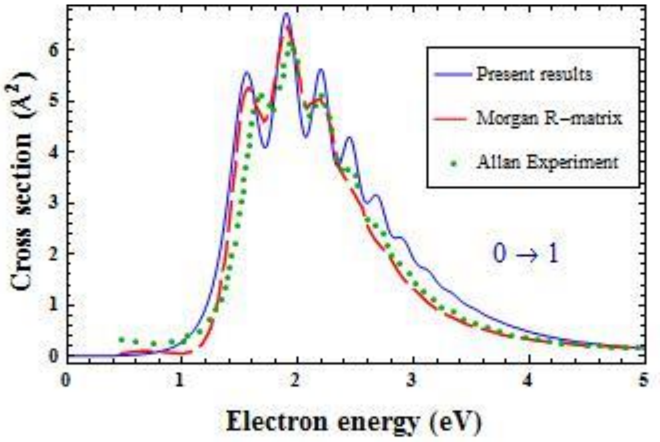


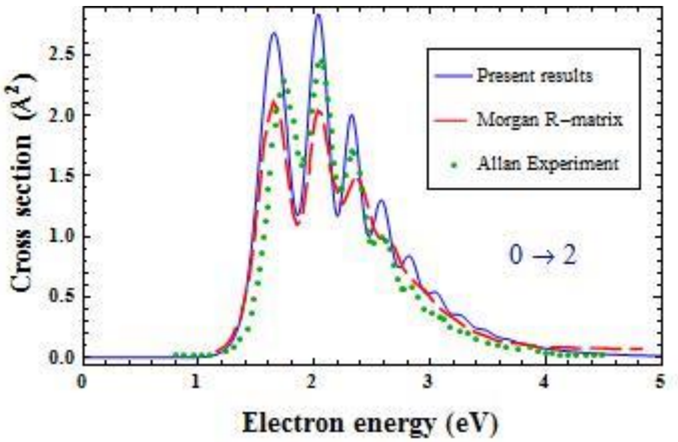
R-matrix resonance positions and widths

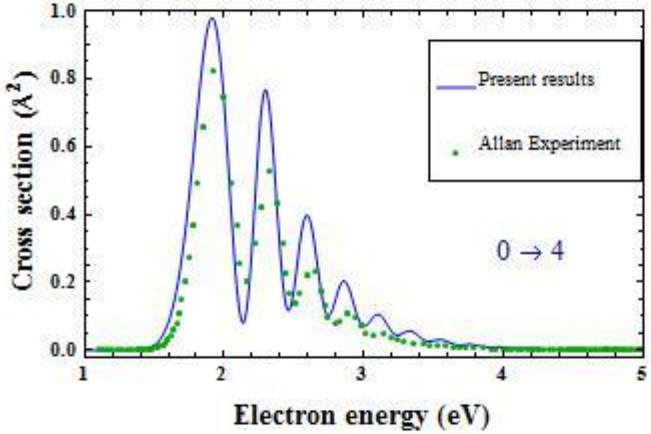
Static exchange plus polarisation (SEP) model

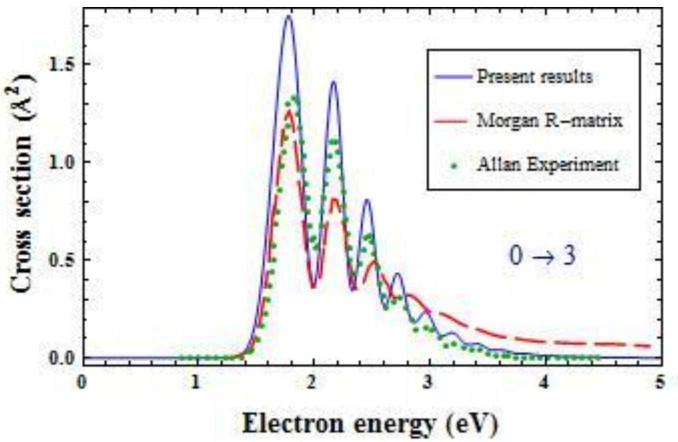
Electron – CO:

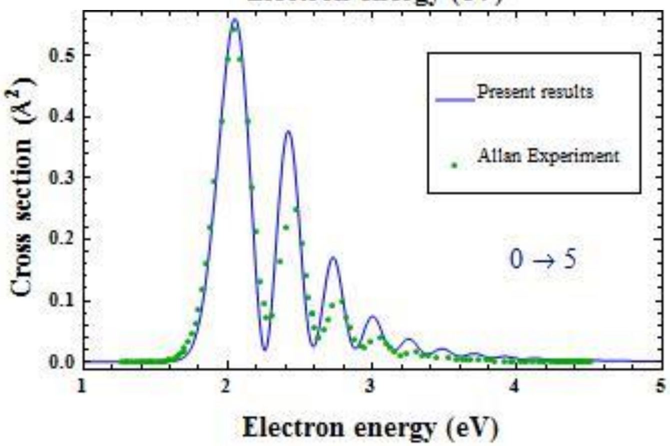
resonance enhanced vibrational excitation 0 → v’







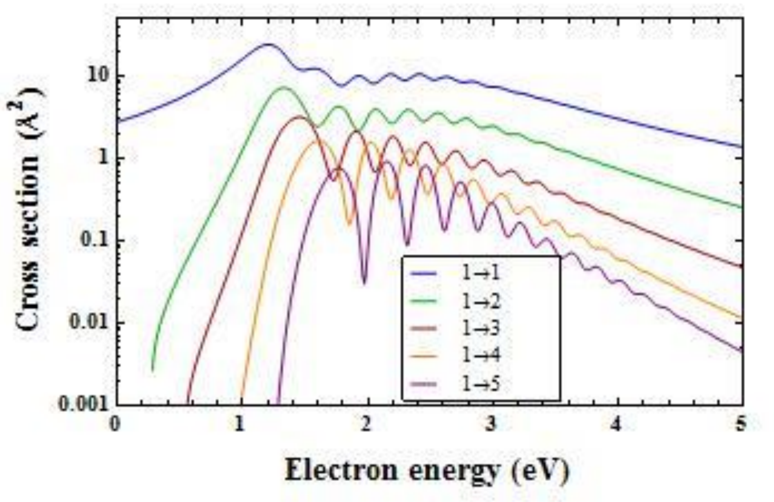


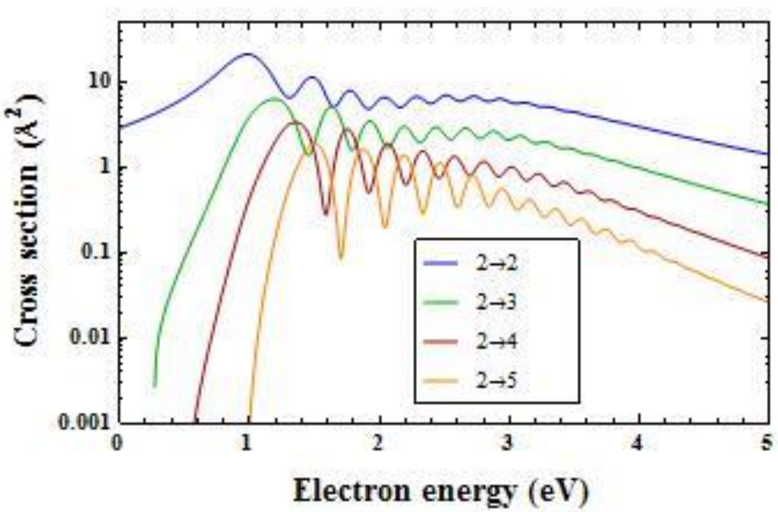


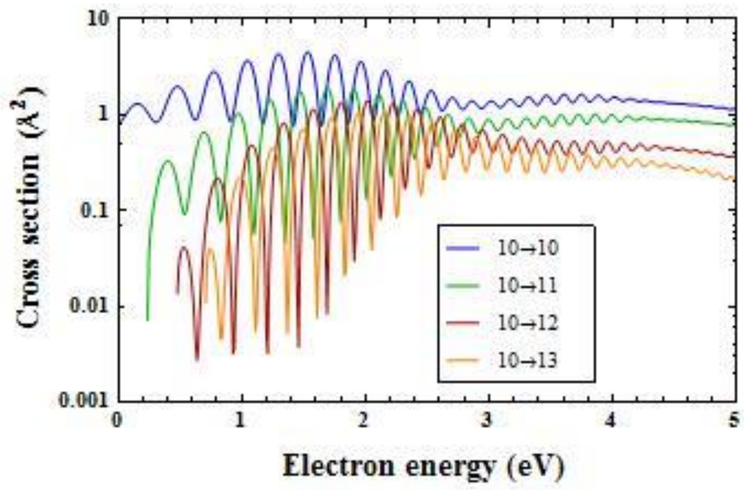
Electron – CO:

resonance enhanced vibrational excitation

High v’ – v”(>0)





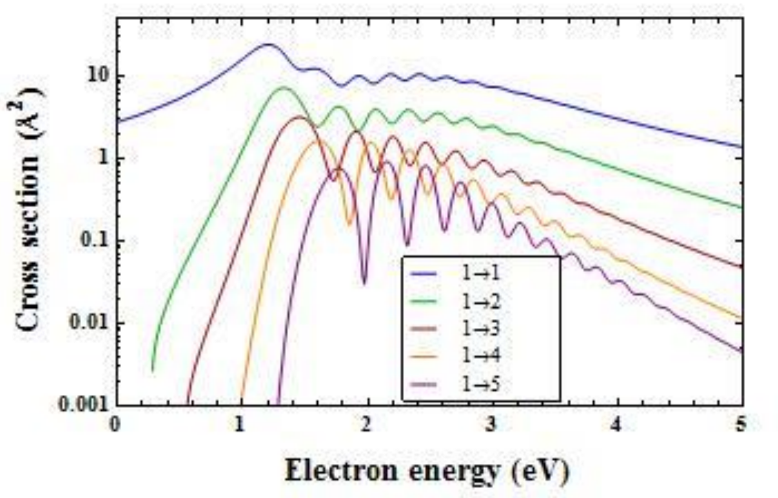


V Laporte, CM Cassidy, J Tennyson & R Celliberto, Plasma Sources Sci. Technol. **21**, 045005 (2012)

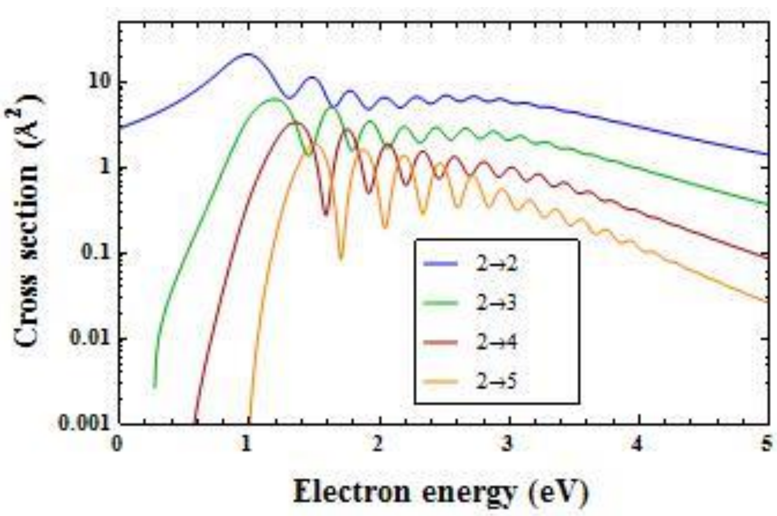
Electron – CO:

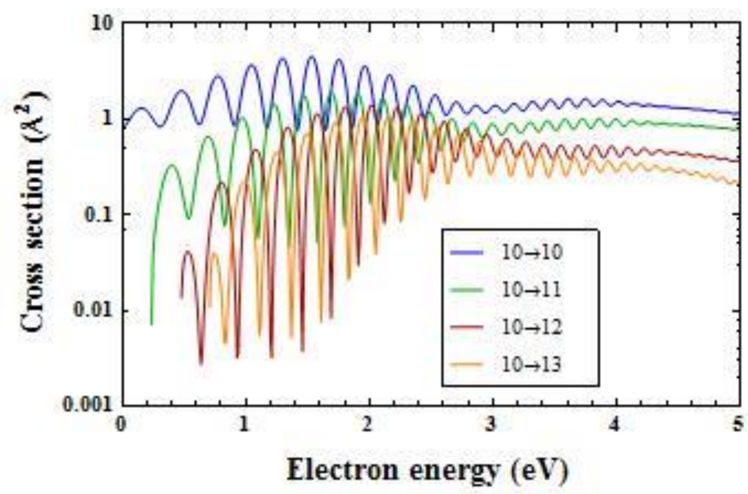
resonance enhanced vibrational excitation

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 et al., PSST **22**, 025001 (2013) and **29**, 225293 (2020)

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

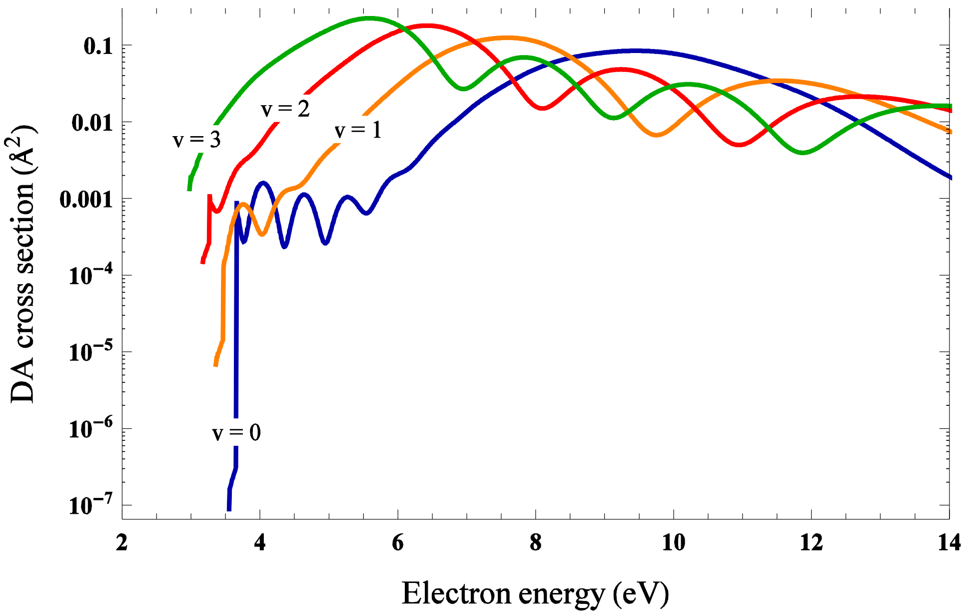
$e + N_2(v'') \rightarrow e + N_2(v')$

V. Laporta, D.A. Little, R. Celiberto & J. Tennyson, PSST, **23**, 065002 (2014)

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

V. Laporta, J. Tennyson & R. Celiberto, PSST, **25**, 06LT02 (2016).

Dissociative attachment of O_2



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

$e + OH(v'') \rightarrow e + O(^2P,^1D) + H$

And other cross sections

K. Chakrabarti et al., PSST **28**, 085013 (2019))

Conclusions

1. Theory can provide a wealth of data important for plasma models;
2. Particular important for where experiment can’t reach:
   a. Radicals and transient species;
   b. Excited states (and high temperatures)
   c. Isotopologues (ie isotopic substitution)
3. Uncertainty quantification: work in progress