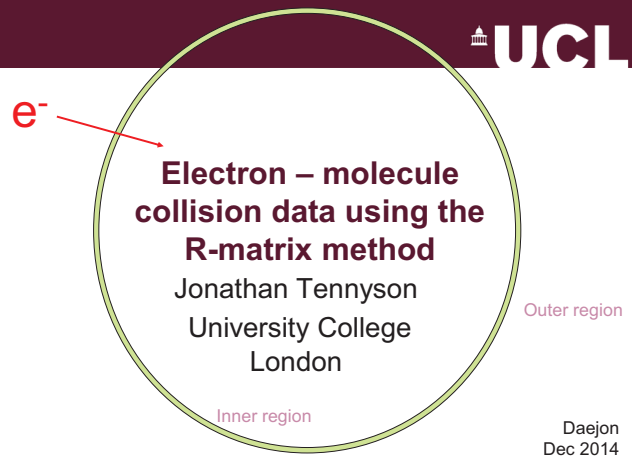
UCL



Electron – molecule collision data using the R-matrix method

Jonathan Tennyson
University College London

Daejon
Dec 2014

Processes at low impact energies

Elastic scattering
$AB + e \rightarrow AB + e$

Rotational excitation
$AB(N'') + e \rightarrow AB(N') + e$

Vibrational excitation
$AB(v''=0) + e \rightarrow AB(v') + e$

Dissociative recombination/Dissociative attachment
$AB + e \rightarrow A + B$

Electronic excitation
$AB + e \rightarrow AB^* + e$

Impact dissociation
$AB + e \rightarrow A + B + e$

Impact ionisation (e,2e)
$AB + e \rightarrow AB^+ + e + e$

Increasing Energy

Why get fusion data from theory not experiment?

1. Unstable species:
   Expt difficult for all but stable (closed shell) species.

2. Difficult atoms:
   Isotopologues: T-bearing species; Be chemistry

3. Vibrational excitation:
   Cross sections different for hot (v > 0) species.

   Eg e + XY(v) → e + X + Y

HD, HT, DT all v
CS Trevisan & J Tennyson 2002 *Plasma Phys. Control. Fusion* **44** 2217

H_2, D_2, T_2 all v
CS Trevisan & J Tennyson 2002 *Plasma Phys. Control. Fusion* **44** 1263

Measurement for H_2(v=0) only.

Uncertainties

- To be (really) useful data requires uncertainties
- Almost entirely lacking from theoretical data

Sources of uncertainty in theoretical calculations of electron – molecule collisions

1. Target model
2. Scattering model
3. The code/theoretical formalism

Target model

1. Dipoles if non-zero (and other target moments)

Rotational excitation,
elastic scattering,
electronic excitaiton

Cross section $\alpha \quad \mu^2$

So uncertainty approx 2 $\Delta\mu / \mu$

Dipole moment of water at equilibrium

.

Contribution	Value (a.u.)	Uncertainty (a.u.)
Nonrelativistic, all electron	0.7310	0.0005
Relativistic correction	−0.0017	0.0001
Vibrational averaging	0.0001	0.0001
Final value for the ground-state dipole	0.7294	0.0006
Experimental value (Clough et al, 1973)	0.7296	0.0002

L. Lodi, R.N. Tolchenov, J. Tennyson, A.~E. Lynas-Gray, S.V. Shirin, N.F. Zobov, O.L. Polyansky, A.G. Csaszar, J. van Stralen & L. Visscher, J. Chem. Phys., 128, 044304 (2008)

Also
L. Lodi, J. Tennyson and O.L. Polyansky, J. Chem. Phys., 135, 034113 (2011)

2. Codes, Formalism, numerical approximations
R-matrix, Schwinger, Kohn, etc

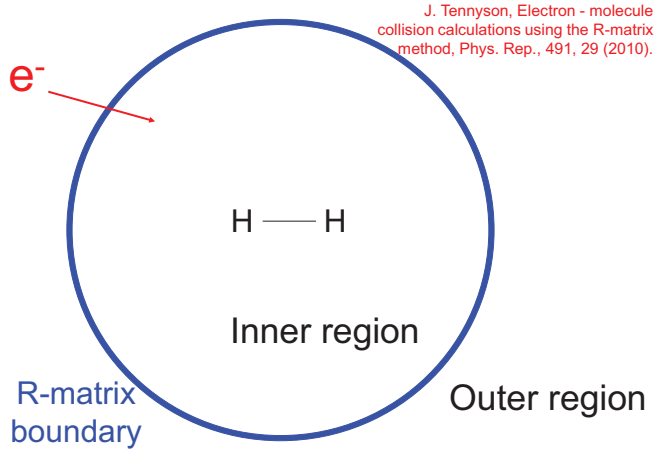
- Code comparisons: generally satisfactory
- Numerical approximations (grids, basis set truncation, etc):
  Generally well-understood and not major source of error

3. Scattering models

- Usually the major source of (unquantified) uncertainty
- Solution?
  Repeat with variety of models?
  Systematic study eg using pseudo-state methodology?
  Benchmark problems: eg N_2 and dipolar system?

The R-matrix method

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



R-matrix method for electrons: inner region wavefunction

(within the Fixed-Nuclei approximation)

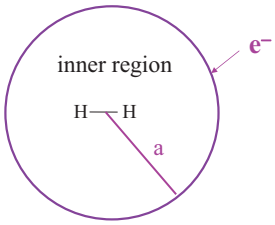
$$\Psi_k = \mathcal{A} \sum_{i,j} a_{i,j,k}\, \phi_i^N\, \eta_{i,j} + \sum_i b_{j,k}\, \phi_j^{N+1}$$

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

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

Target Wavefunctions

$$\phi_i^N = \Sigma_{i,j}\, c_{i,j}\, \zeta_j$$

where

ϕ_i^N N-electron wavefunction of i^{th} target state

ζ_j N-electron configuration state function (CSF) Usually defined using as CAS-CI model.

$c_{i,j}$ variationally determined coefficients

$e - N_2^+$ calculations: Duncan Little

- Dissociative recombination hard to measure
- Rydberg states poorly characterised
- Close – coupling calculation
- Excellent representation of X, A and B states of N_2^+

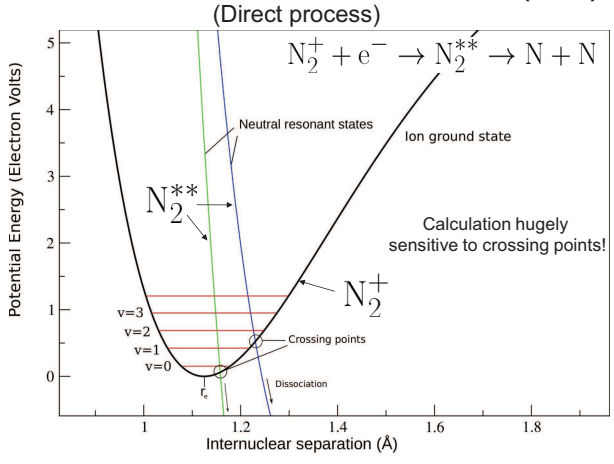
Dissociative recombination (DR)

$$N_2^+ + e^- \rightarrow N_2^{**} \rightarrow N + N$$

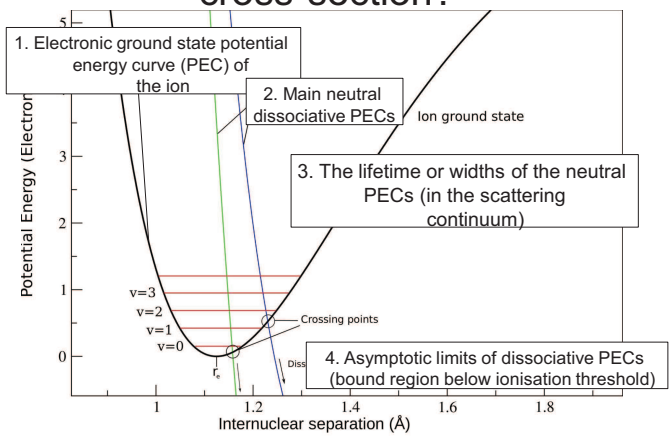
50,000 times heavier!

Dissociative recombination (DR)

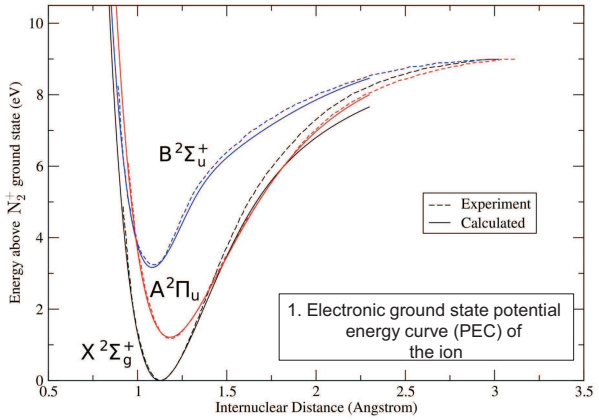
(Direct process)



What do we need to calculate a DR cross-section?

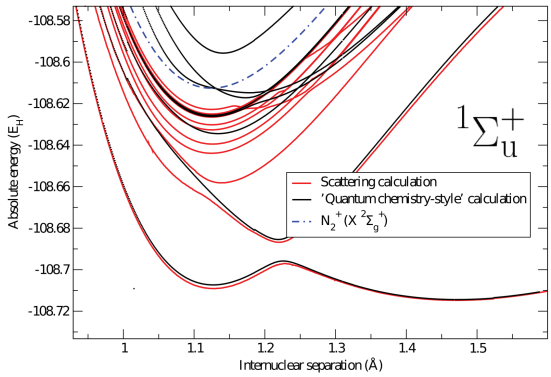


Target electronic states compared with experiment (Lofthus, 1977)

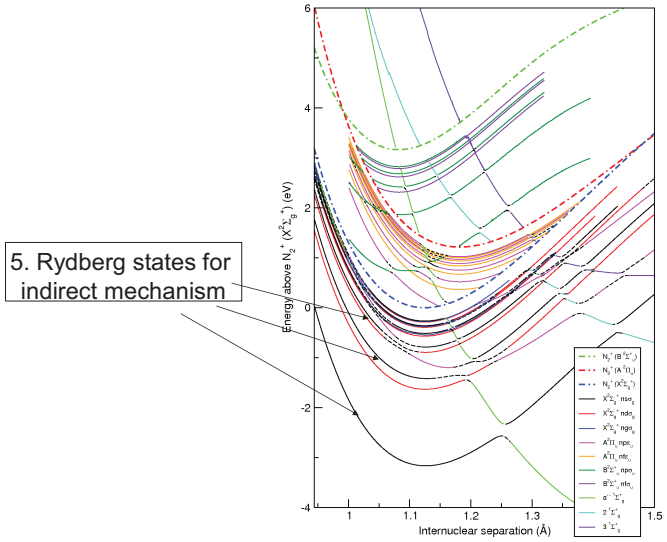


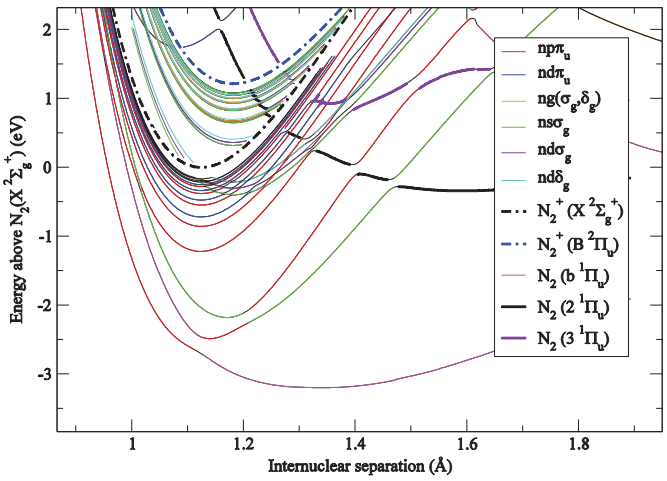
A. Lofthus and P.H. Krupenie J. Phys. Chem. Ref. Data **6**, 1 (1977)

Bound states, solve for negative scattering energies



For more details see: D. A. Little and J. Tennyson, J. Phys. B. **46** 145102 (2013)



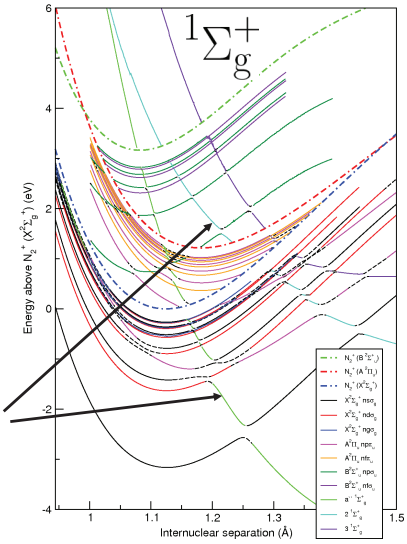


Need to find **bound states** and **resonances**

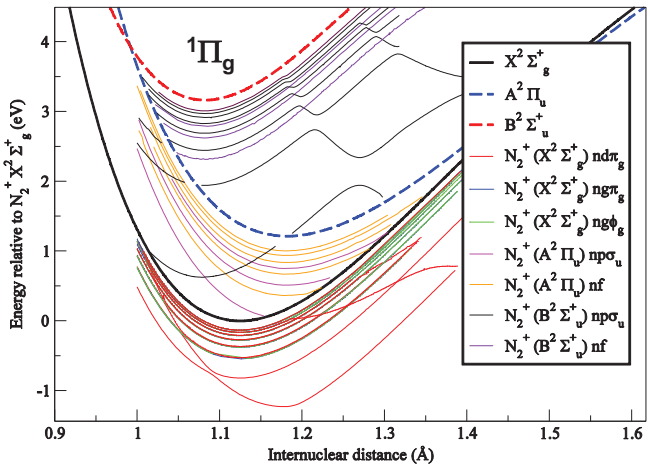
Bound state finding:

1. **Standard quantum chemistry code eg Molpro**
2. **Scattering-style quantum chemistry calculation (No R-matrix)**
3. **Negative energy scattering (bound state finder)**

In reality Rydberg states complicate things..



Dissociating ionic states

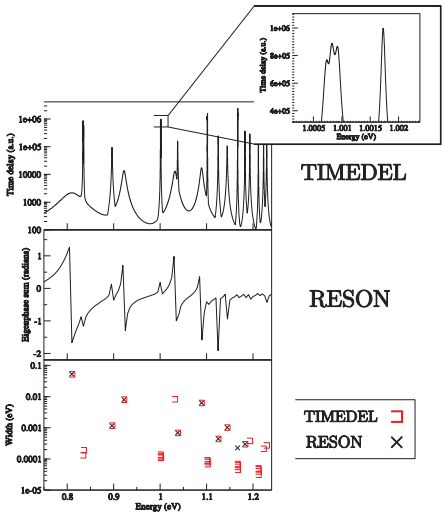


DA Little & J Tennyson, An ab initio study of singlet and triplet Rydberg states of N_2, J Phys B, 46, 145102 (2013)

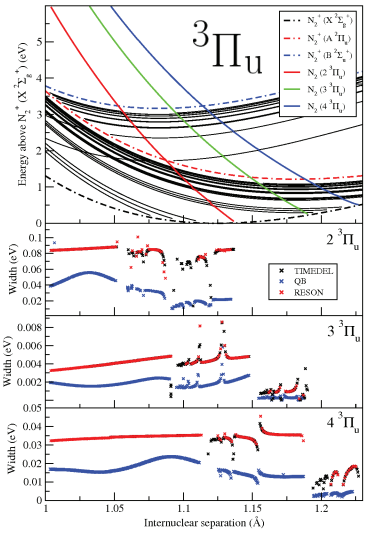
Need to find **bound states** and **resonances**

Resonance finding (position and width):

1. **Eigenphase fitting: Breit-Wigner form. RESON**
2. **Time-delay method, TIMEDEL**
3. **QB method: quasi-analytic R-matrix specific method**

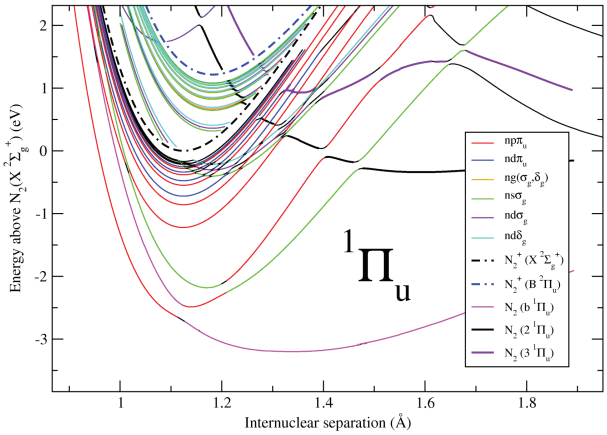


2. Main neutral dissociative PECs



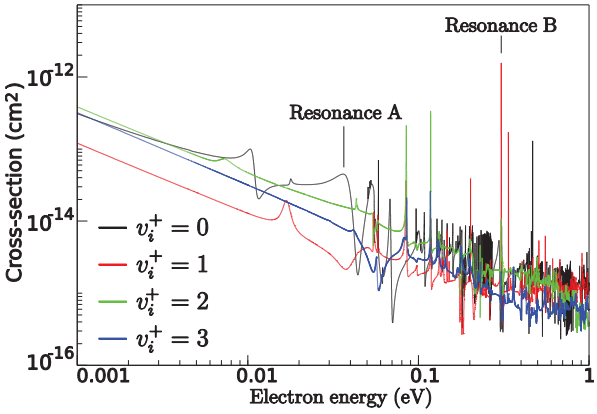
3. The lifetime or widths of the neutral PECs (in the scattering continuum)

Combine bound and continuum for complete description:



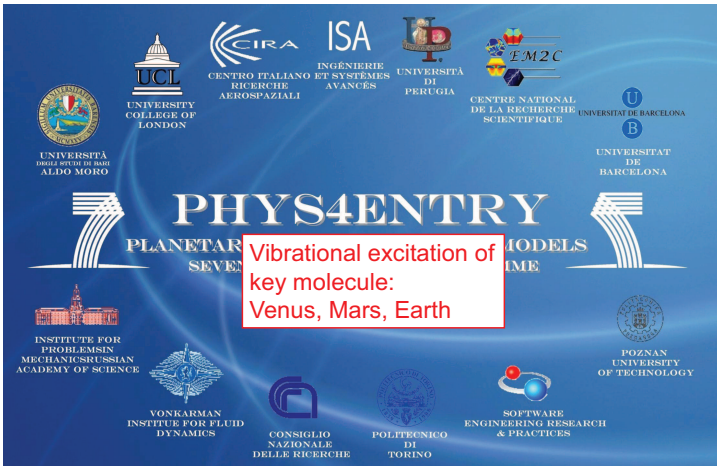
For more details see: D. A. Little and J. Tennyson, J. Phys. B. 47, 105204 (2014)

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

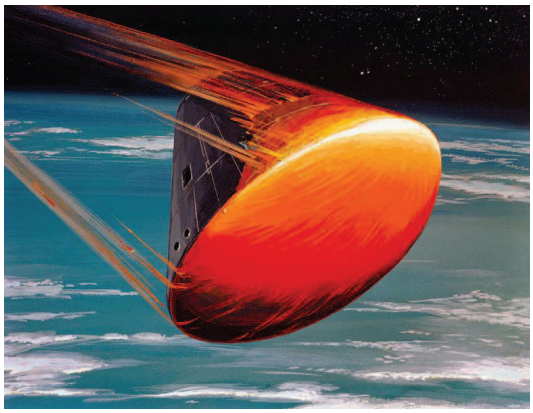


See: D. A. Little, K. Chakrabarti, J. Zs. Mezei, I. F. Schneider & J. Tennyson, Phys. Rev. A, 90, 052705 (2014)

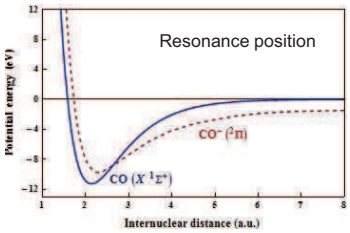
Re-entry physics:
plasmas created on spacecraft (rocket) re-entry

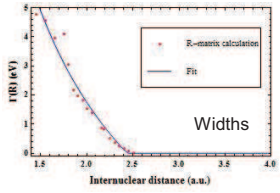


Vibrational excitation of key molecule: Venus, Mars, Earth



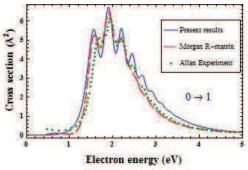
Electron – CO: $^2\Pi$ resonance



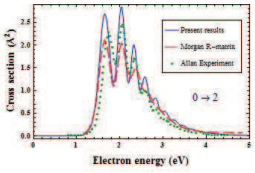


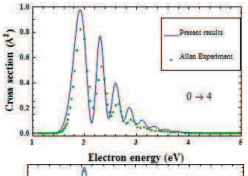
R-matrix resonance positions and widths

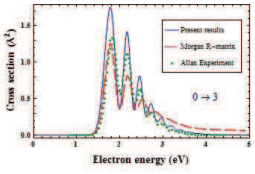
Static exchange plus polarisation (SEP) model

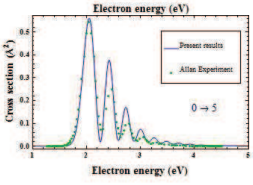


Electron – CO:
resonance enhanced vibrational excitation 0 → v'





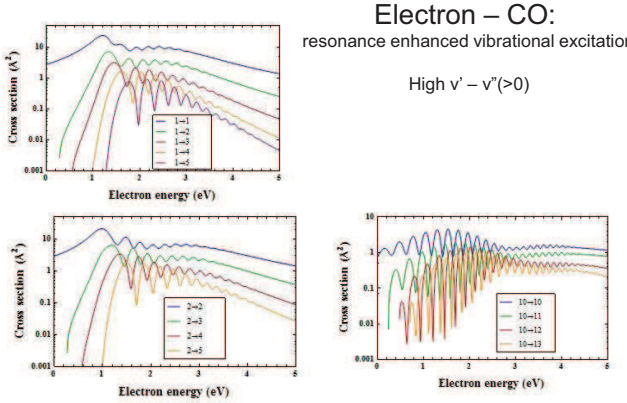




Electron – CO:

resonance enhanced vibrational excitation

High v' – v"(>0)



V Laporte, CM Cassidy, J Tennyson & R Celliberto,
Plasma Sources Science and Technology 21, 045005 (2012)

Calculations being extended to:

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

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

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

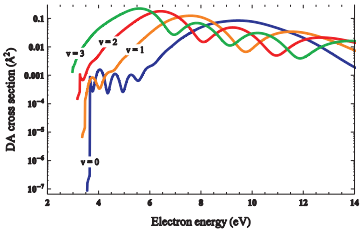
V. Laporta, R. Celiberto & J. Tennyson, Plasma Sources Sci. Technol., 22, 025001 (2013)

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

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

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

Dissociative attachment of O_2



Vincenzo Laporta