Electron scattering from molecular hydrogen

D.V. Fursa[1], M.C. Zammit[1,2], J.S. Savage[1] & I. Bray[1]

[1]Curtin University, Perth, Australia
[2]Los Alamos National Laboratory, Los Alamos, USA

Acknowledgements

Australian Research Council
Curtin University
Los Alamos National Laboratory
Pawsey Supercomputing Centre

Method: H_2 molecule

Born-Oppenheimer approximation $\Phi = \varphi_{Nuclear}(\vec{R})\phi_{Electronic}(\vec{r};\vec{R})$

Fixed-nuclei approximation, R = fixed

Solve for the electronic wave function

Adiabatic-nuclei approximation: perform FN calculations at a number of R, study nuclear motion

- spherical coordinate code: the origin at the midpoint
- spheroidal coordinate code: the best approach for diatomic molecules (nuclear motion)

Target Hamiltonian H_T is diagonalized in a Sturmian (Laguerre) basis

$$f_{n,l}(2/r) \mu (2/r)^{l+1} e^{-/r} L_n^{2l+2}(2/r)$$

modeling of *infinite* number
of bound and continuum states
with a *finite* number of pseudostates

- N-state multi-channel expansion

$$\Psi_i^{(+)}(\mathbf{x}_p,\mathbf{x}_t) = \mathcal{A}\sum_{n=1}^{N} F_n(\mathbf{x}_p)\ \phi_n(\mathbf{x}_t)$$

- The Schrödinger equation is converted to an integral LS equation for the T-matrix

$$T_{fi}(\vec{k}_f,\vec{k}_i) = V_{fi}(\vec{k}_f,\vec{k}_i) + \sum_{n=1}^{N} \int d^3k \frac{V_{fn}(\vec{k}_f,\vec{k})T_{ni}(\vec{k},\vec{k}_i)}{E + i0 - \epsilon_n - k^2/2}$$

- Cross sections

$$Q_{fi}(R) \mu \left|T_{fi}(R)\right|^2$$

Electron scattering from H_2

- Is a benchmark system with a range of applications
- Accurate measurements exist for some major processes
- Theory had not done sufficiently well:

  Previous largest CC calculations use 9-states RM and SMC or 41-states RMPS
- There is room for improvement…

Convergence & accuracy studies

- ✧ Fixed-nuclei calculations at R = 1.448 a.u.
- ✧ Size of projectile partial wave expansion L_{max} ← ABS to speed up p.w. convergence
- ✧ Size of expansion in total M, Π, S
- ✧ Size of close-coupling expansion
  - number of states in close-coupling expansion
  - size of underlying one-electron (Sturmian) basis
    - maximum value of orbital angular momentum l_{max}
    - number of functions N_l for given l
  - Two-electron configuration interaction: choice of configurations, (1sσ,nl), (nl,n'l), n, n' < 2

Largest calculations:

- 491-state, N_l =17-l, l_{max} = 3, projectile p.w. L_{max} = 8

Convergence is established with:

- 427-state, N_l =15-l, l_{max} = 3, projectile p.w. L_{max} = 8
- 259-state, , N_l =15-l, l_{max} = 2, projectile p.w. L_{max} = 6
- 92-state: only negative energy (bound) states from 491 state model
- 9-state: first 9 states of H_2

Accuracy of the target structure

Two-electron energies (a.u.) at R=1.4 a.u.		
State	Present	Ref.
$X\ ^1\Sigma^+_g$	-1.162	-1.174[a]
$b\ ^3\Sigma^+_u$	-0.770	-0.784[b]
$a\ ^3\Sigma^+_g$	-0.710	-0.714[c]
$c\ ^3\Pi_u$	-0.701	-0.707[d]
$B\ ^1\Sigma^+_u$	-0.697	-0.706[e]
$E,F\ ^1\Sigma^+_g$	-0.687	-0.692[e]
$C\ ^1\Pi_u$	-0.683	-0.689[f]
$e\ ^3\Sigma^+_u$	-0.683	-0.689[g]
$h\ ^3\Sigma^+_g$	-0.640	-0.644[h]
$B'\ ^1\Sigma^+_u$	-0.625	-0.629[i]
$D\ ^1\Pi^+_u$	-0.621	-0.624[f]
$B''\ ^1\Sigma^+_u$	-0.600	-0.602[e]
$D'\ ^1\Pi^+_u$	-0.598	-0.600[h]

[a]Kolos etal, J. Chem. Phys. 84 (1986) 3278
[b]Kolos & Wolniewicz, J. Chem. Phys. 43 (1965) 2429
[c]Kolos & Wolniewicz, J. Chem. Phys. 48 (1968) 3672
[d]Kolos & Rychlewski, J. Mol. Spectrosc. 66 (1977) 428
[e]Liu & Hagstrom, Phys. Rev. A 48 (1993) 1966
[f]Wolniewicz & Dressler, J. Chem. Phys. 143 (1988) 386
[g]Kolos & Rychlewski, J. Mol. Spectrosc. 13 (1990) 237
[h]Sharp, At. Data Nucl. Data Tables 2 (1971) 119
[i]Wolniewicz, Chemical Physics Letters 31 (1975) 248

OOS (length) at R=1.4 a.u.		
transition	Present	Ref.[a]
$X\ ^1\Sigma^+_g \rightarrow B\ ^1\Sigma^+_u$	0.2769	0.2995
$X\ ^1\Sigma^+_g \rightarrow C\ ^1\Pi_u$	0.3368	0.3508
$X\ ^1\Sigma^+_g \rightarrow B'\ ^1\Sigma^+_u$	0.0578	0.0603
$X\ ^1\Sigma^+_g \rightarrow D\ ^1\Pi^+_u$	0.0832	0.0913
$X\ ^1\Sigma^+_g \rightarrow B''\ ^1\Sigma^+_u$	0.0221	0.0353
$X\ ^1\Sigma^+_g \rightarrow D'\ ^1\Pi^+_u$	0.0344	0.0534

[a]Branchett and Tennyson J. Phys. B 25, 2017 (1992)

Static dipole polarizability (a.u.) at R=1.4 a.u.			
	$\alpha_\parallel$	$\alpha_\perp$	α
CCC	6.43	4.64	5.23
Ref.[a]	6.38	4.58	5.18

[a]Kolos and L. Wolniewicz, J. Chem. Phys. 46, 1426 (1967)

Accuracy due to the structure is about 9%

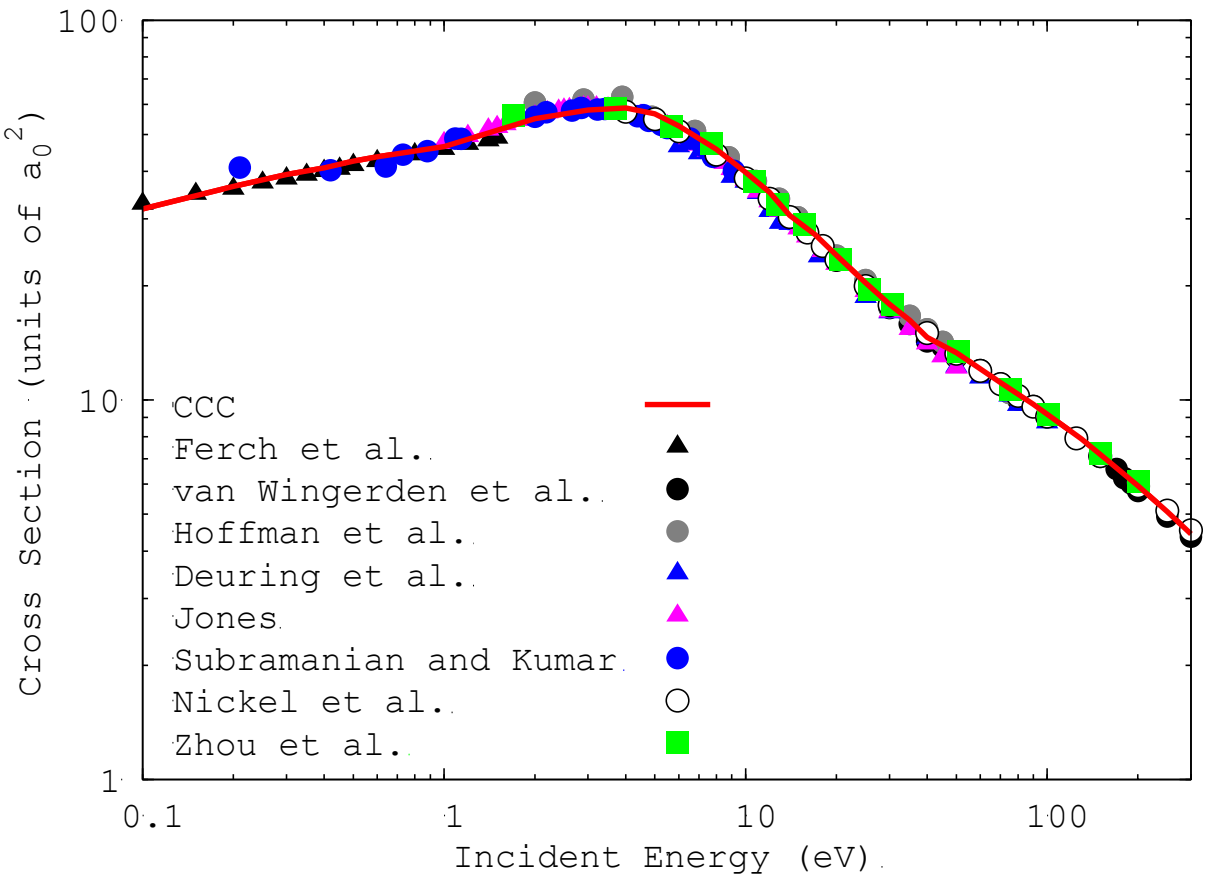
Electron scattering from H_2

The best estimate of CCC cross sections is produced for energies from 0.1 to 300 eV for

- total cross section
- total ionization cross section
- elastic scattering (ICS, DCS)
- excitation cross sections (ICS, DCS) for
  - b $^3\Sigma_u^+$, a $^3\Sigma_g^+$, c $^3\Pi_u$, e $^3\Sigma_u^+$, h $^3\Sigma_g^+$
  - B $^1\Sigma_g^+$, C $^1\Pi_u$, E,F $^1\Sigma_g^+$, B' $^1\Sigma_g^+$, D $^1\Pi_u$, B'' $^1\Sigma_g^+$, D' $^1\Pi_u$
  - more transitions are available on request

e^--H_2 recommended cross sections of Yoon et al. *J. Phys. Chem. Ref. Data 37(2008)913* are all derived from experimental data

e^--H_2 total cross section

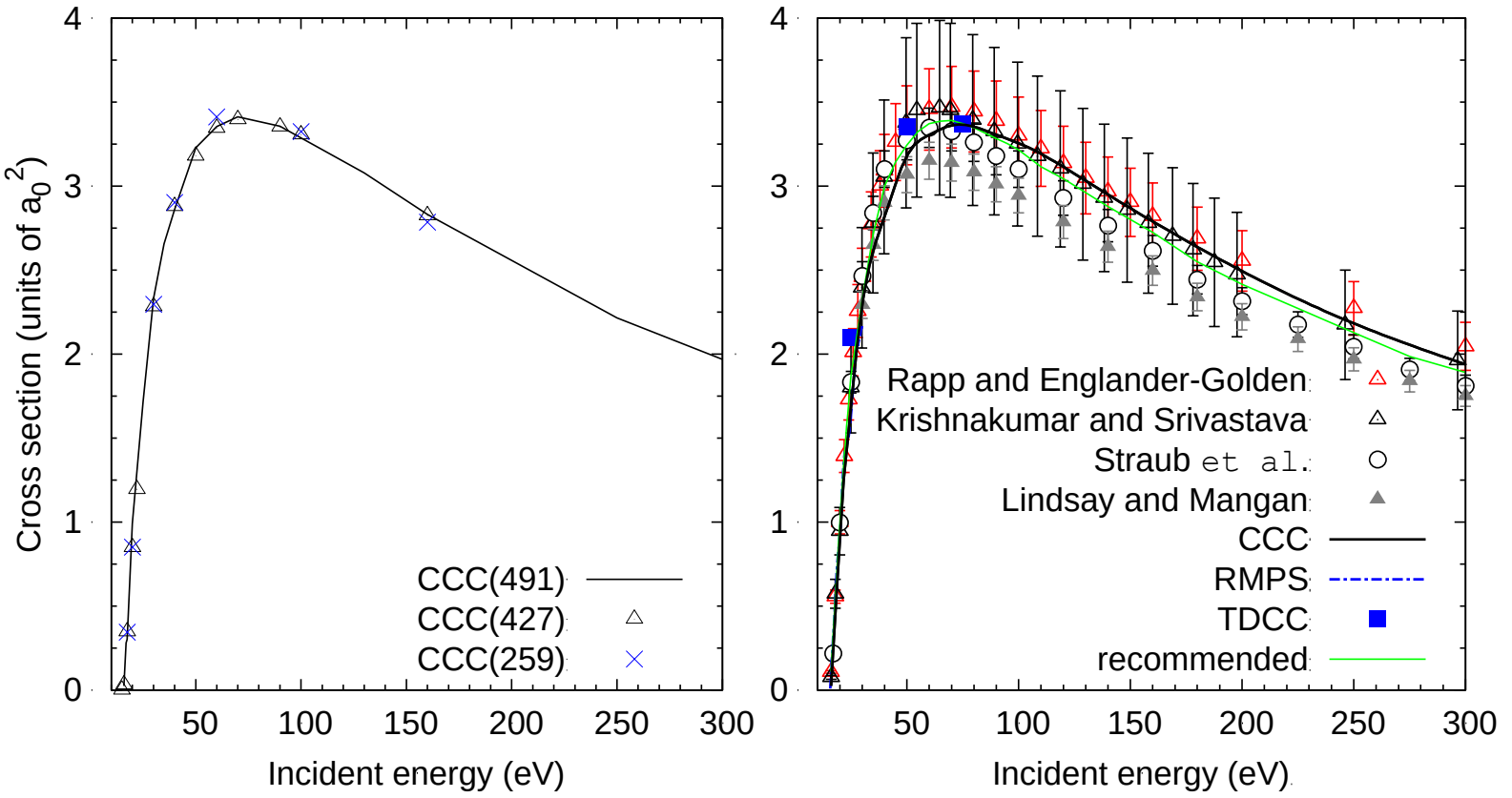


All major scattering processes are accounted for correctly:

- elastic scattering
- excitations
- ionization

Zammit, Savage, Fursa & Bray, Phys. Rev. Lett. 16 (2016) 233201

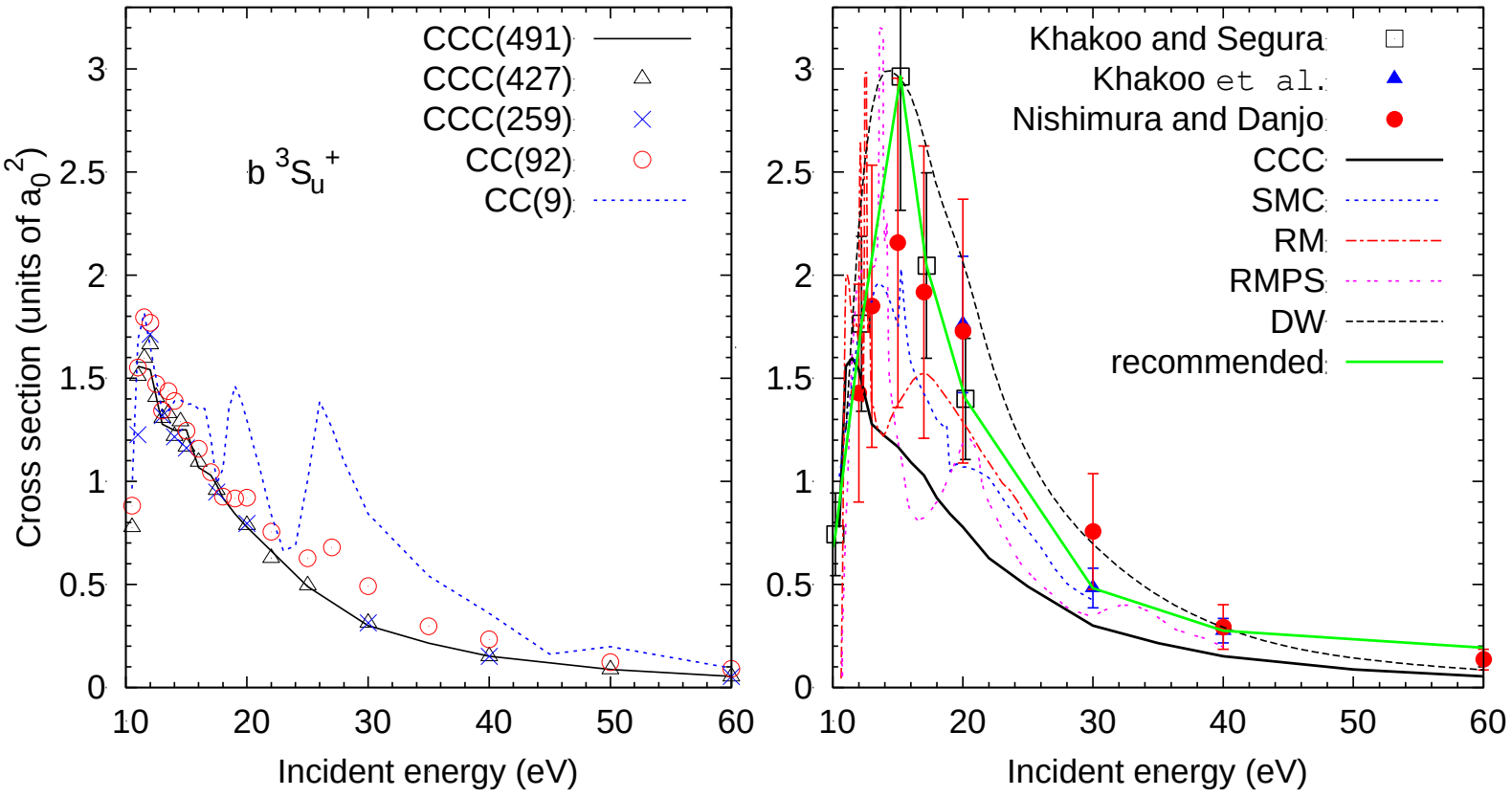
e^--H_2 total ionization cross section



Zammit, Savage, Fursa & Bray, Phys. Rev. Lett. 16 (2016) 233201

recommended cross sections are due to Yoon *et al.* J.Phys.Chem.Ref.Data 37(2008)913

e^--H_2 excitation ICS & DCS: b $^3\Sigma_u^+$

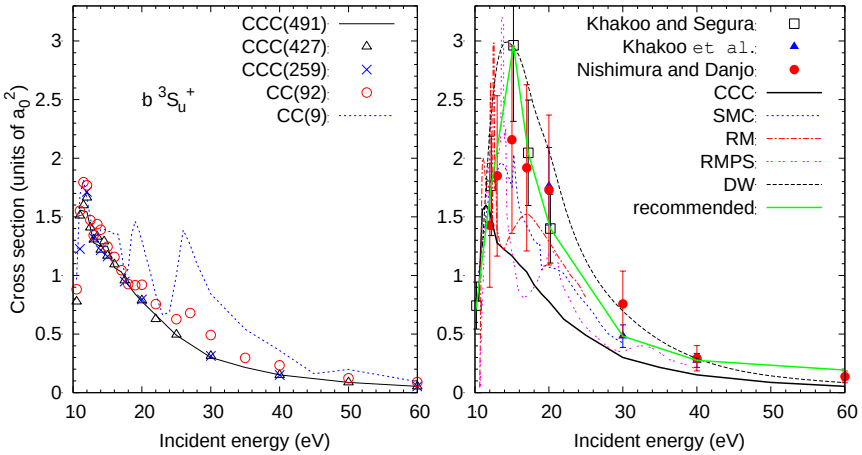


Zammit, Savage, Fursa & Bray,
submitted to PRA

SMC, RM ~ 9-state
recommended cross sections are due to Yoon *et al.*
J.Phys.Chem.Ref.Data 37(2008)913

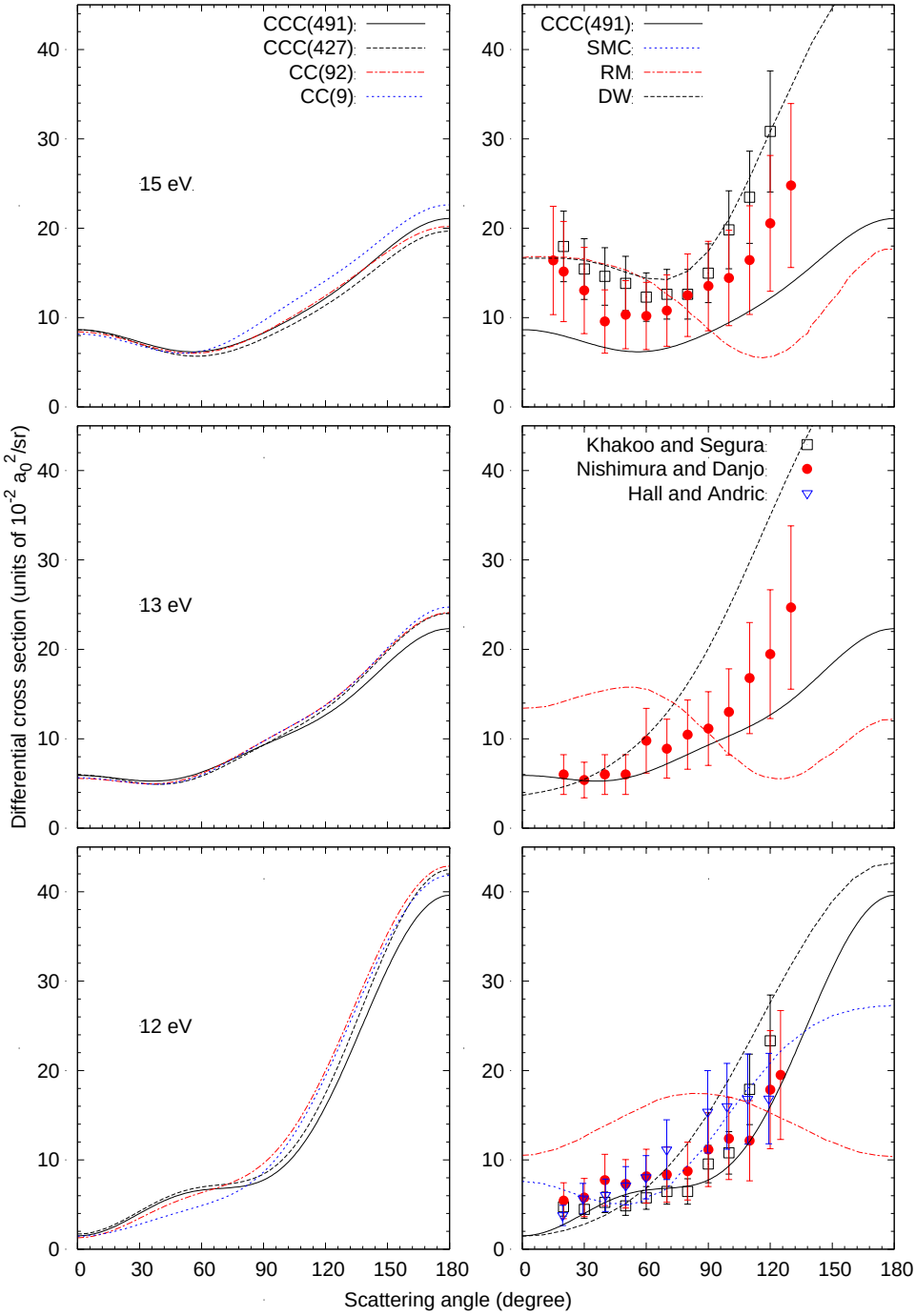
e^--H_2 excitation ICS & DCS:

b $^3\Sigma_u^+$

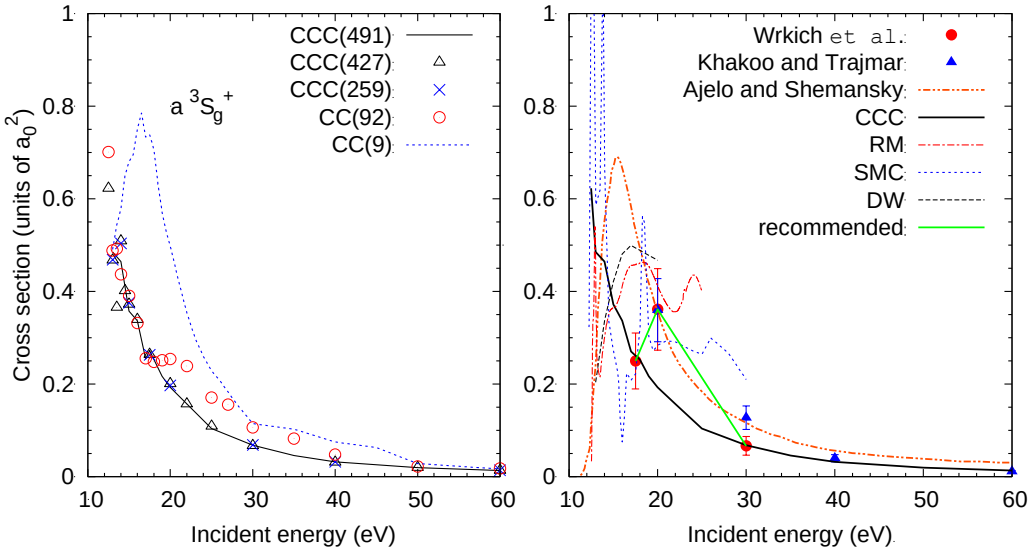


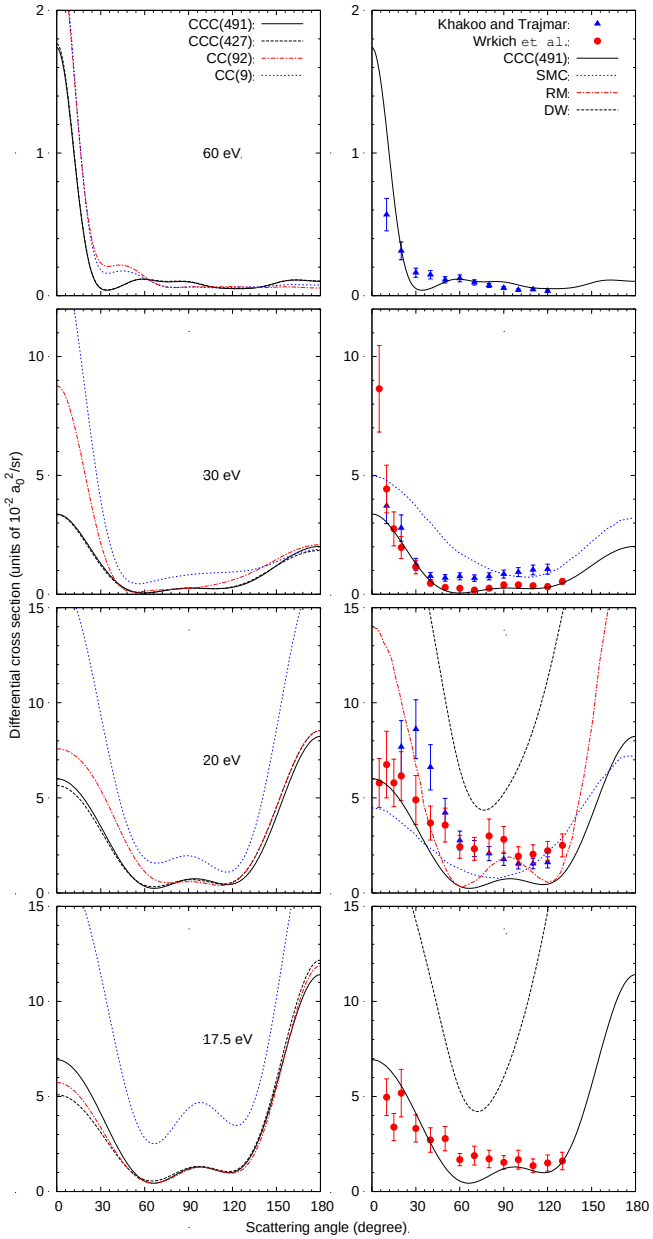
SMC, RM ~ 9-state
recommended cross sections are due to Yoon *et al.*
J.Phys.Chem.Ref.Data 37(2008)913

Zammit, Savage, Fursa & Bray,
submitted to PRA



e^--H_2 excitation ICS & DCS: a $^3\Sigma_g^+$

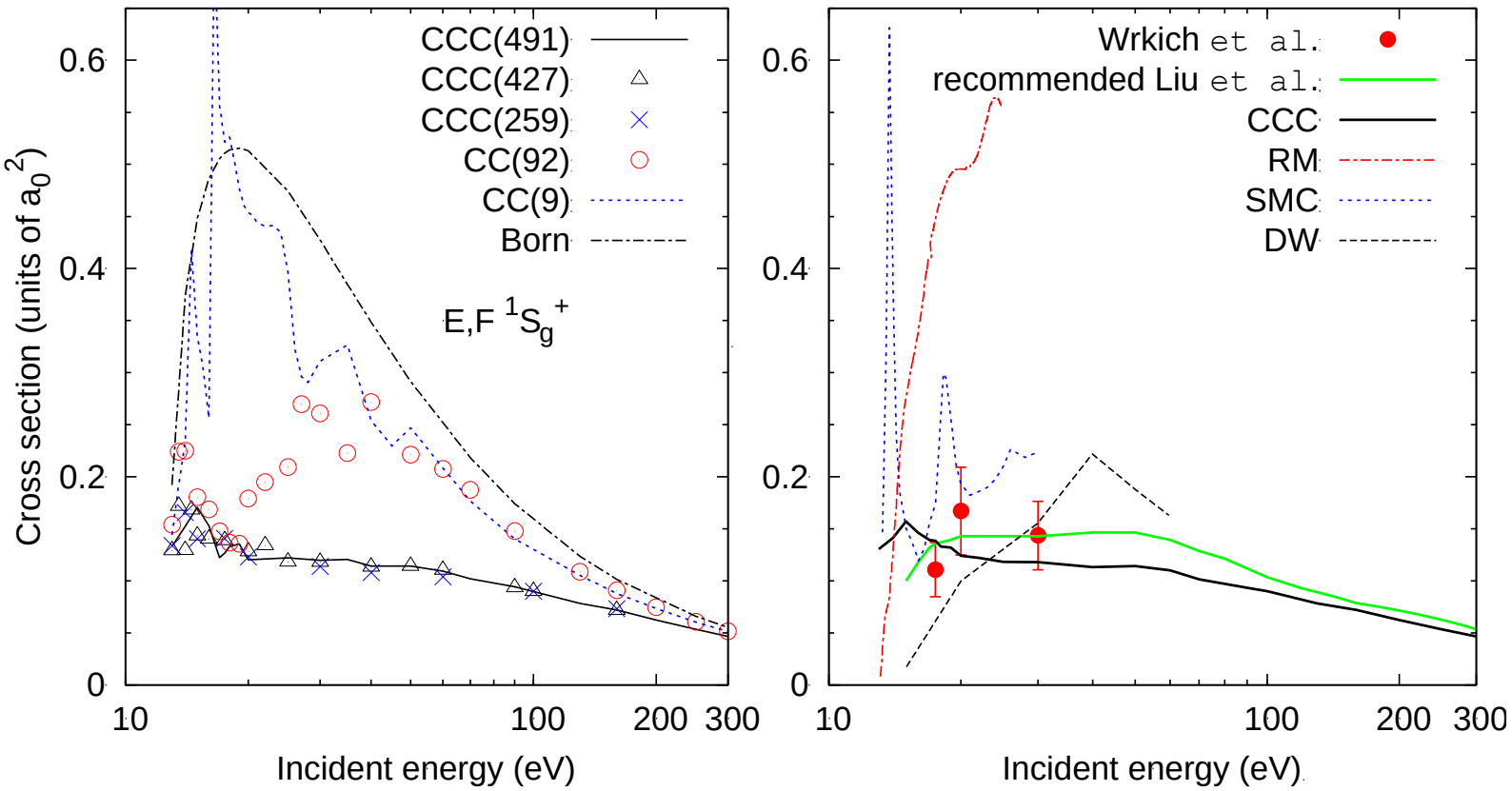




SMC, RM ~ 9-state
recommended cross sections are due to Yoon *et al.*
J.Phys.Chem.Ref.Data 37(2008)913

Zammit, Savage, Fursa & Bray,
submitted to PRA

e^--H_2 excitation ICS & DCS: E,F $^1\Sigma_g^+$

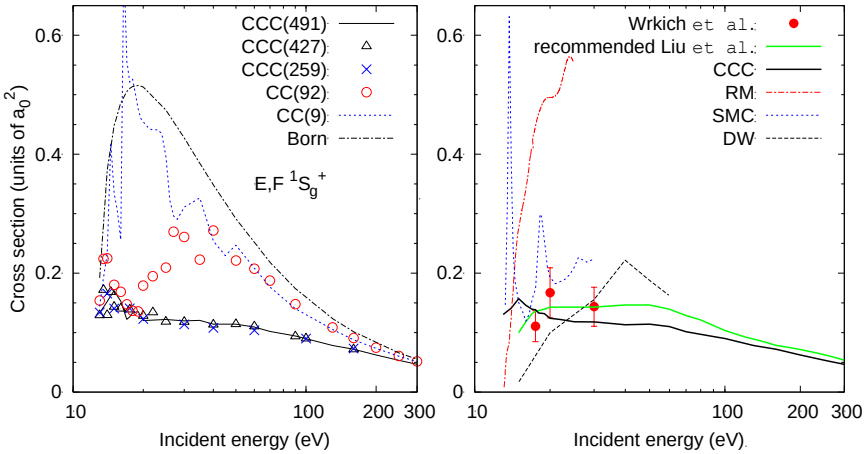


Zammit, Savage, Fursa & Bray,
submitted to PRA

SMC, RM ~ 9-state
recommended cross sections are due to Yoon *et al.*
J.Phys.Chem.Ref.Data 37(2008)913

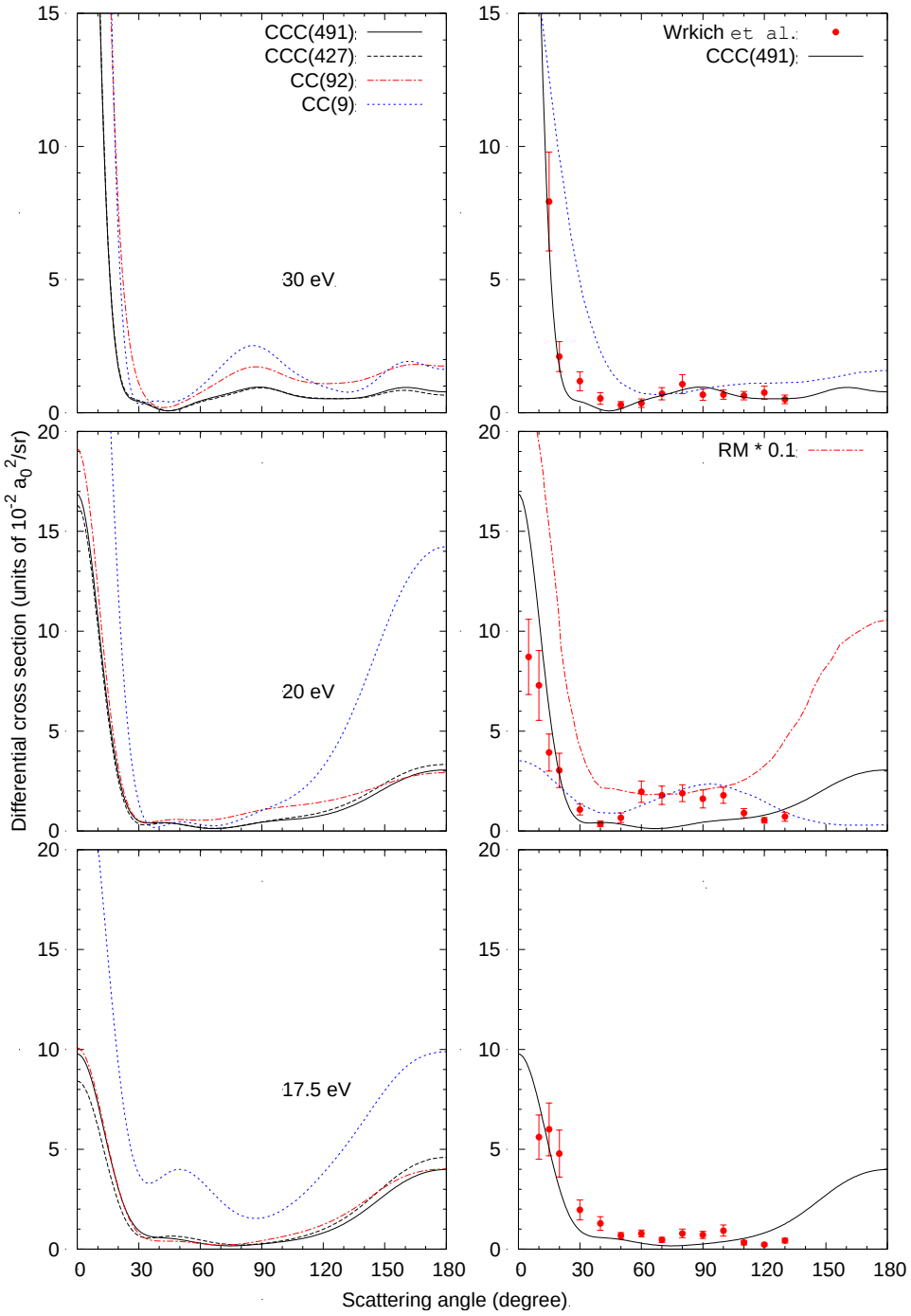
e^--H_2 excitation ICS & DCS:

E,F $^1\Sigma_g^+$



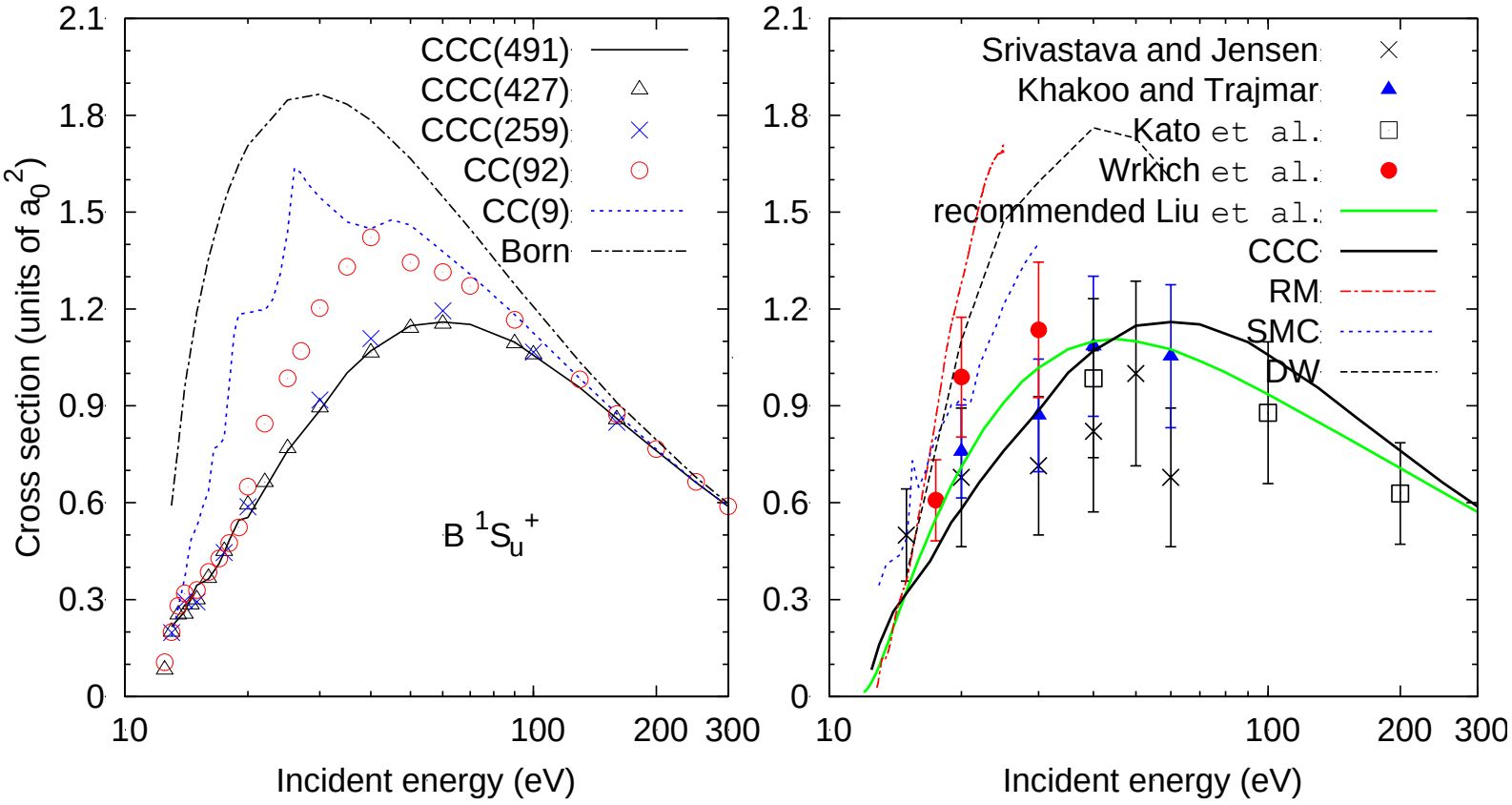
SMC, RM ~ 9-state
recommended cross sections are due to Yoon *et al.*
J.Phys.Chem.Ref.Data 37(2008)913

Zammit, Savage, Fursa & Bray,
submitted to PRA



Curtin University

e^--H_2 excitation ICS & DCS: B $^1\Sigma_g^+$



SMC, RM ~ 9-state
recommended cross sections are due to Yoon *et al.*

J.Phys.Chem.Ref.Data 37(2008)913

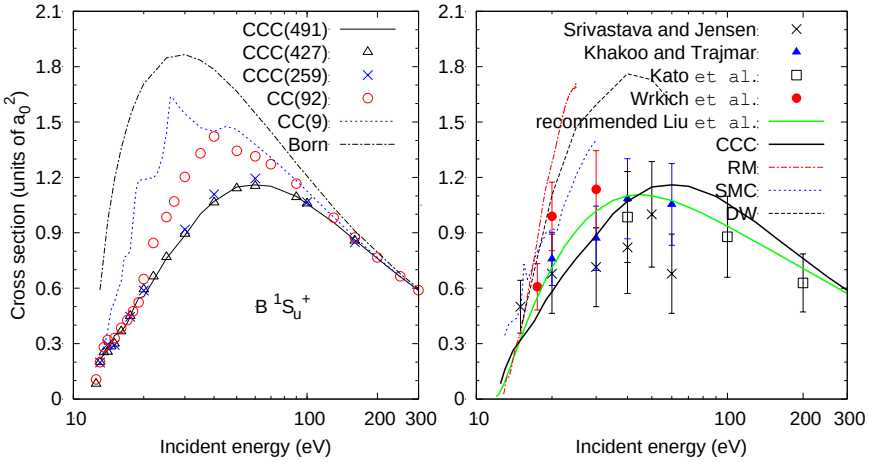
Zammit, Savage, Fursa & Bray,
submitted to PRA

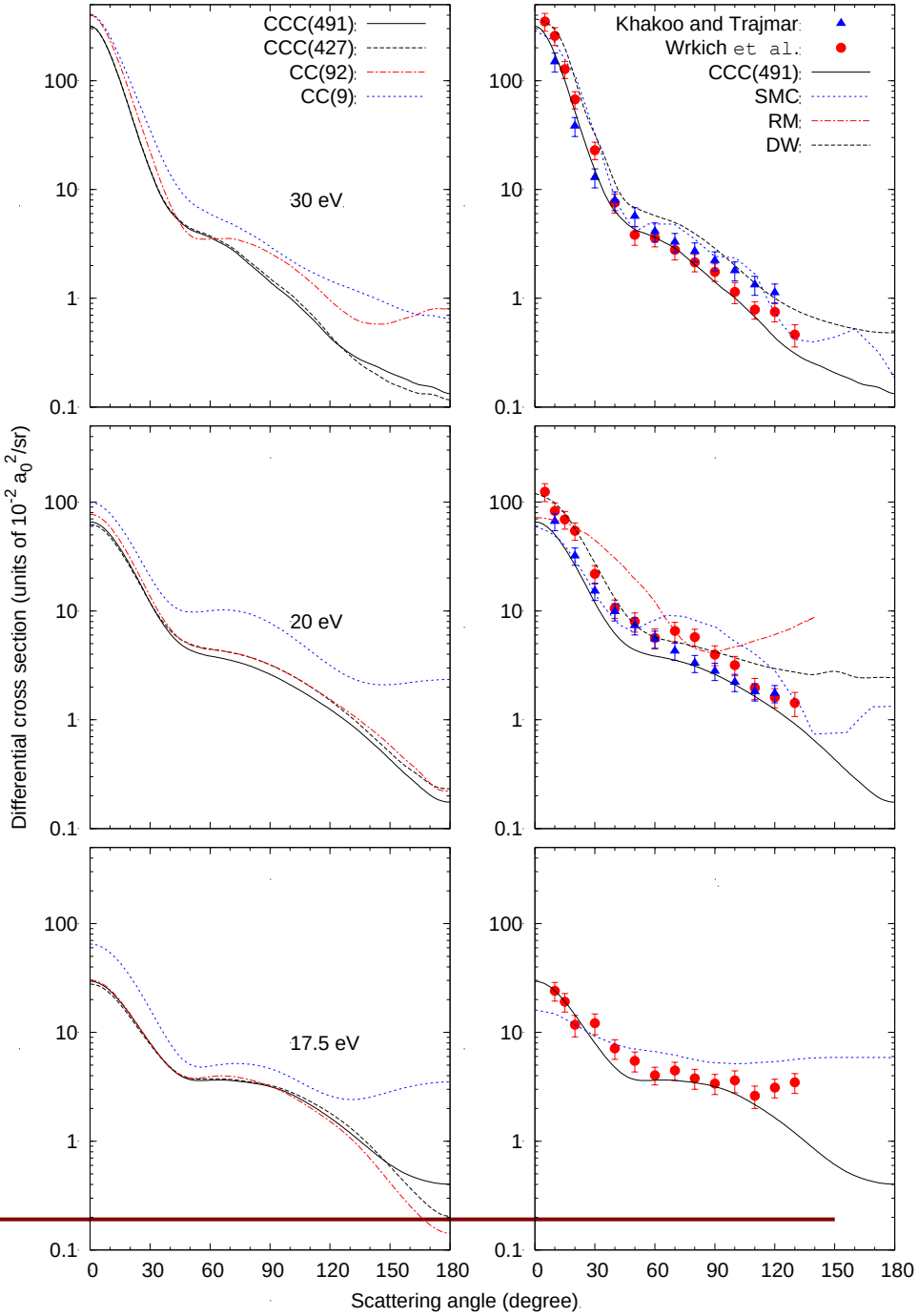
Oscillator Strength

Accurate theory	**0.274**	Phys. Rev. A 60, 1226 (1999)
Fixed-nuclei CCC	0.288	
Kato (measured)	0.241 ± 0.048	Phys. Rev. A 77, 062708 (2008)

e^--H_2 excitation ICS & DCS:

B $^1\Sigma_g^+$



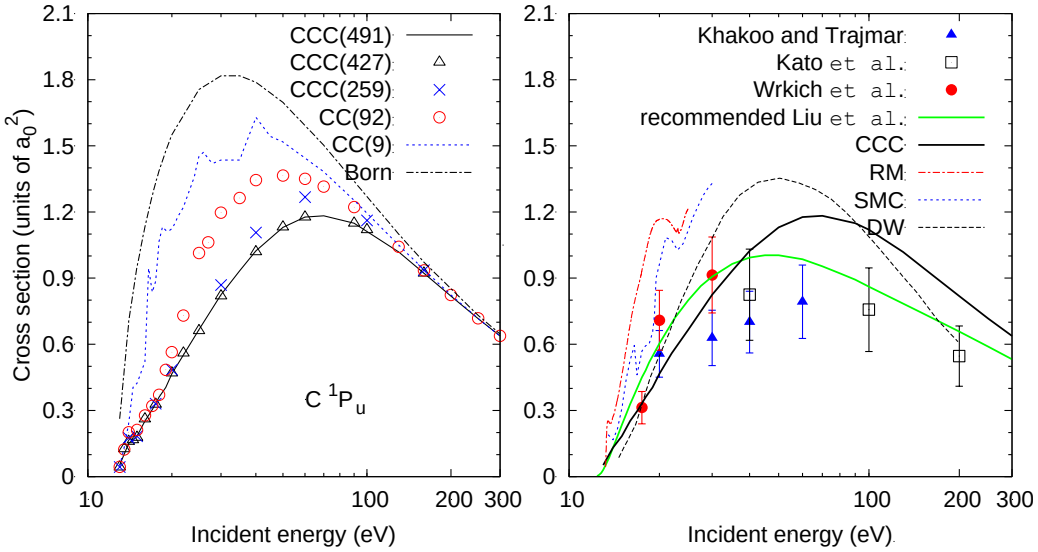


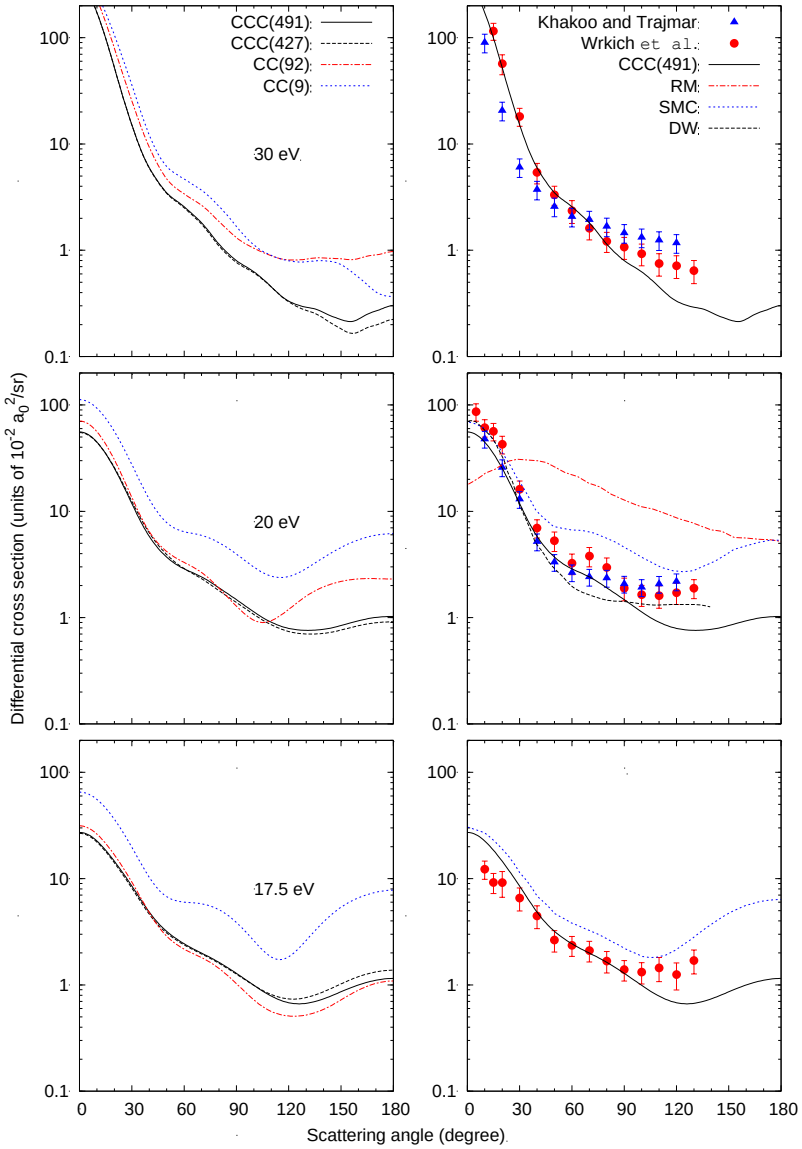
SMC, RM ~ 9-state
recommended cross sections are due to Yoon *et al.*

J.Phys.Chem.Ref.Data 37(2008)913

Zammit, Savage, Fursa & Bray,
submitted to PRA

e^--H_2 excitation ICS & DCS: C $^1\Pi_u$





Oscillator Strength

Accurate theory	**0.351**	Phys. Rev. A 60, 1226 (1999)
Fixed-nuclei CCC	0.342	
Kato (measured)	0.226± 0.045	Phys. Rev. A 77, 062708 (2008)

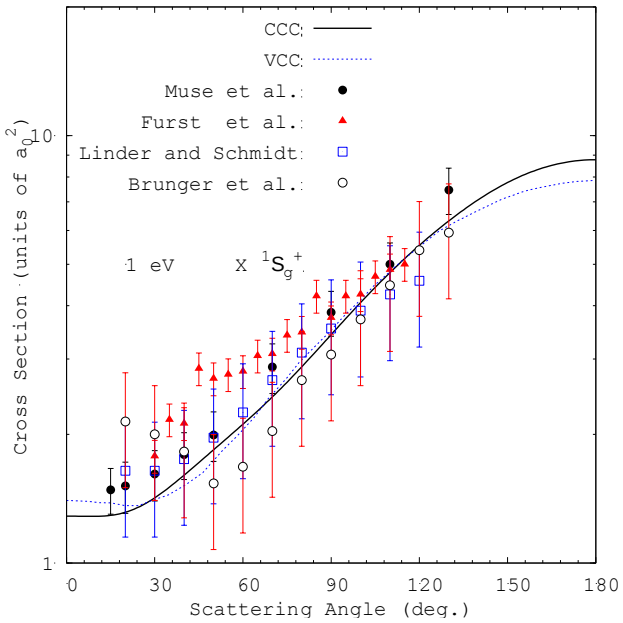
SMC, RM ~ 9-state

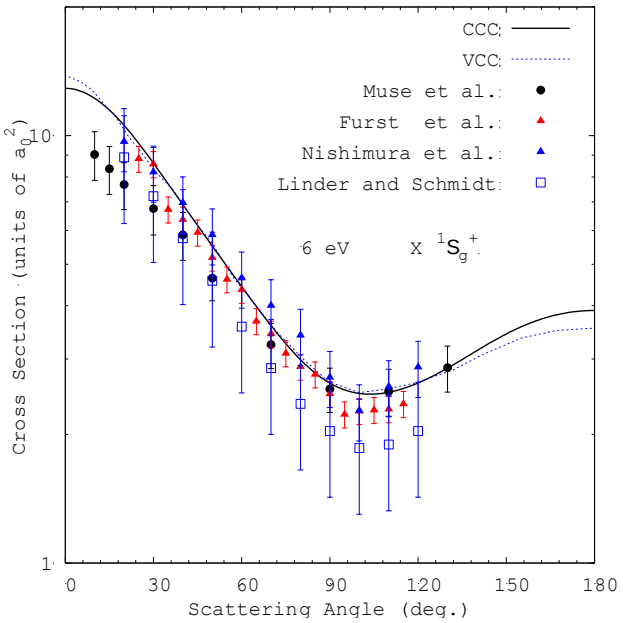
recommended cross sections are due to Yoon *et al.*

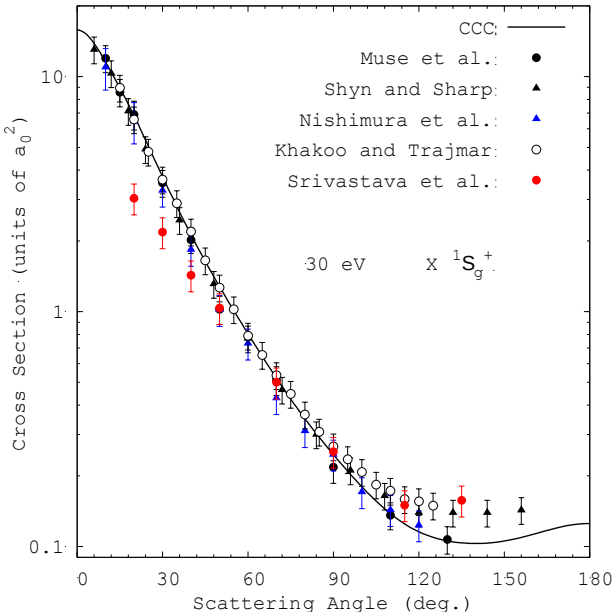
J.Phys.Chem.Ref.Data 37(2008)913

Zammit, Savage, Fursa & Bray,
submitted to PRA

e^--H_2 elastic DCS at 1, 6, and 30 eV







Conclusions

- First large-scale close-coupling calculations for H_2
- First comprehensive theoretical dataset of e-H_2 excitation cross sections
- Uncertainties:
  - ✧ structure: < 9%
  - ✧ close-coupling: < 5%
  - ✧ total: < 10%, better than 5% for most transitions
- Future work
  - scattering from H_2 excited states: electronic and vibrational
  - vibrational and rotational excitations of H_2
  - isotopologues D_2, T_2, HD, HT, DT
  - scattering from HeH^+, He_2^+
  - hydrates (LiH, OH, …) and other diatomics (O_2, N_2, …)

Conclusions

Thank you

- All cross sections are available at access-free databases

LXcat: http://fr.lxcat.net/home/

SCATTERING CROSS SECTIONS

Species: e + **H {10}** , H2 [3], He(s1S) [20], **D2⁺ {15}** , **DT⁺ {16}** , **H2⁺ {11}** « H2⁺(1sSg,v=0) [4], H2⁺(1sSg,v=1) [4], H2⁺(1sSg,v=2) [4], H2⁺(1sSg,v=3) [4], H2⁺(1sSg,v=4) [4], H2⁺(1sSg,v=5) [4], H2⁺(1sSg,v=6) [4], H2⁺(1sSg,v=7) [4], H2⁺(1sSg,v=8) [4], H2⁺(1sSg,v=9) [4], H2⁺(1sSg,v=FC) [4] », **HD⁺ {12}** , **HT⁺ {13}** , **T2⁺ {19}**

Updates: 2011-06-09 … 2016-06-07

Downloads: 949 times from 2011-11-04

DIFFERENTIAL SCATTERING CROSS SECTIONS

Species: e + H2 [7]

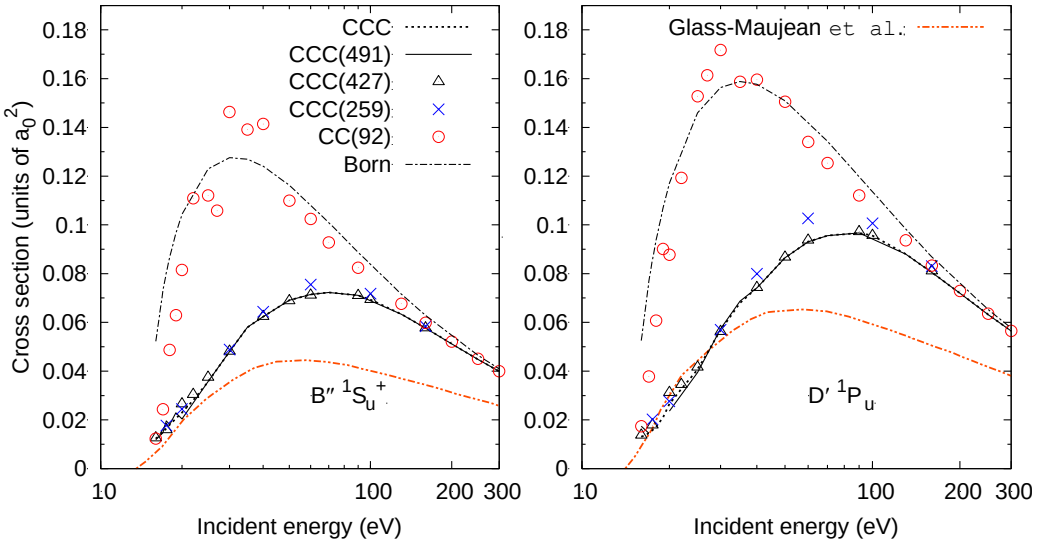
Updates: 2016-06-15 … 2016-06-15

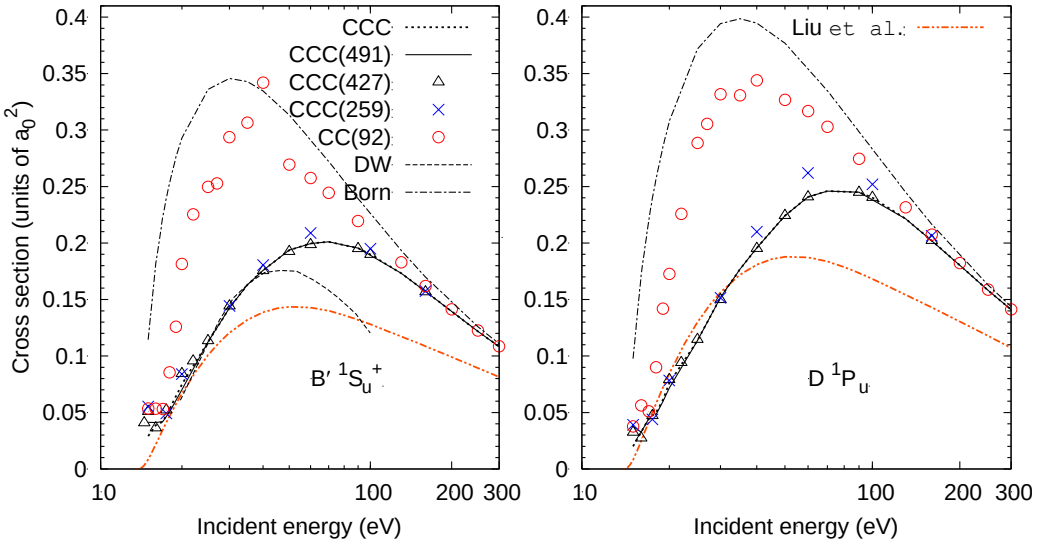
Downloads: 17 times from 2016-06-15

ALADDIN: https://www-amdis.iaea.org/infoaladdin.php

1	2	3	4	Reactants	Products	7	Comment	Authors	Year	Publication	Validity Limits in eV	
☐	DIS		THE	e, T_2^+ *[1s Sigma$_g$ v=FC]*	e, T, T^+	TAB1D	comment	M. C. Zammit, D. V.	2014	Phys. Rev. A 90, 022711 (2014)	1.00000e+01	1.00000e+03 (E_P)
☐	DIS		THE	e, T_2^+ *[1s Sigma$_g$ v=17]*	e, T, T^+	TAB1D	comment	M. C. Zammit, D. V.	2014	Phys. Rev. A 90, 022711 (2014)	1.00000e+01	1.00000e+03 (E_P)
☐	DIS		THE	e, T_2^+ *[1s Sigma$_g$ v=16]*	e, T, T^+	TAB1D	comment	M. C. Zammit, D. V.	2014	Phys. Rev. A 90, 022711 (2014)	1.00000e+01	1.00000e+03 (E_P)
☐	DIS		THE	e, T_2^+ *[1s Sigma$_g$ v=15]*	e, T, T^+	TAB1D	comment	M. C. Zammit, D. V.	2014	Phys. Rev. A 90, 022711 (2014)	1.00000e+01	1.00000e+03 (E_P)
☐	DIS		THE	e, T_2^+ *[1s Sigma$_g$ v=14]*	e, T, T^+	TAB1D	comment	M. C. Zammit, D. V.	2014	Phys. Rev. A 90, 022711 (2014)	1.00000e+01	1.00000e+03 (E_P)
☐	DIS		THE	e, T_2^+ *[1s Sigma$_g$ v=13]*	e, T, T^+	TAB1D	comment	M. C. Zammit, D. V.	2014	Phys. Rev. A 90, 022711 (2014)	1.00000e+01	1.00000e+03 (E_P)

e^--H_2 excitation ICS: B' $^1\Sigma_g^+$, D $^1\Pi_u$, B" $^1\Sigma_g^+$, D' $^1\Pi_u$





Zammit, Savage, Fursa & Bray, submitted to PRA

Accuracy of the target structure

Present accurate = large CI in spheroidal coordinates

Two-electron energies (a.u.) at R=1.448 a.u.		
State	Present	Present accurate
$X\ ^1\Sigma^+_g$	-1.161	-1.173
$b\ ^3\Sigma^+_u$	-0.782	-0.797
$a\ ^3\Sigma^+_g$	-0.715	-0.719
$c\ ^3\Pi_u$	-0.707	-0.713
$B\ ^1\Sigma^+_u$	-0.704	-0.713
$E,F\ ^1\Sigma^+_g$	-0.693	-0.698
$C\ ^1\Pi_u$	-0.690	-0.695
$e\ ^3\Sigma^+_u$	-0.647	-0.651
$h\ ^3\Sigma^+_g$	-0.634	-0.637
$d\ ^3\Pi_u$	-0.63234	-0.635
$B'\ ^1\Sigma^+_u$	-0.631	-0.635
$D\ ^1\Pi^+_u$	-0.628	-0.630
$B''\ ^1\Sigma^+_u$	-0.606	-0.609
$D'\ ^1\Pi^+_u$	-0.604	-0.607

OOS (length) at R=1.448 a.u.		
transition	Present	Present accurate
$X\ ^1\Sigma^+_g \rightarrow B\ ^1\Sigma^+_u$	0.2881	0.3129
$X\ ^1\Sigma^+_g \rightarrow C\ ^1\Pi_u$	0.3420	0.3636
$X\ ^1\Sigma^+_g \rightarrow B'\ ^1\Sigma^+_u$	0.0593	0.0580
$X\ ^1\Sigma^+_g \rightarrow D\ ^1\Pi^+_u$	0.0843	0.0852
$X\ ^1\Sigma^+_g \rightarrow B''\ ^1\Sigma^+_u$	0.0225	0.0210
$X\ ^1\Sigma^+_g \rightarrow D'\ ^1\Pi^+_u$	0.0349	0.0336

Accuracy due to the structure is about 9% for the $B\ ^1\Sigma^+_u$ OOS and better than 9% for other transitions