Electron Impact Dissociation of Ground and Metastable States of O_2 Molecule

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Inelastic Collisions

$$e^- + O_2(^3\Sigma^-_g) \rightarrow O_2^* + e^-$$

$$e^- + O_2(^1\Delta_g) \rightarrow O_2^* + e^-$$

$$e^- + O_2(^1\Sigma_g) \rightarrow O_2^* + e^-$$

Electron Impact Dissociation

$$e^- + O_2(^3\Sigma^-_g) \rightarrow 2O + e^-$$

$$e^- + O_2(^1\Delta_g) \rightarrow 2O + e^-$$

$$e^- + O_2(^1\Sigma_g) \rightarrow 2O + e^-$$

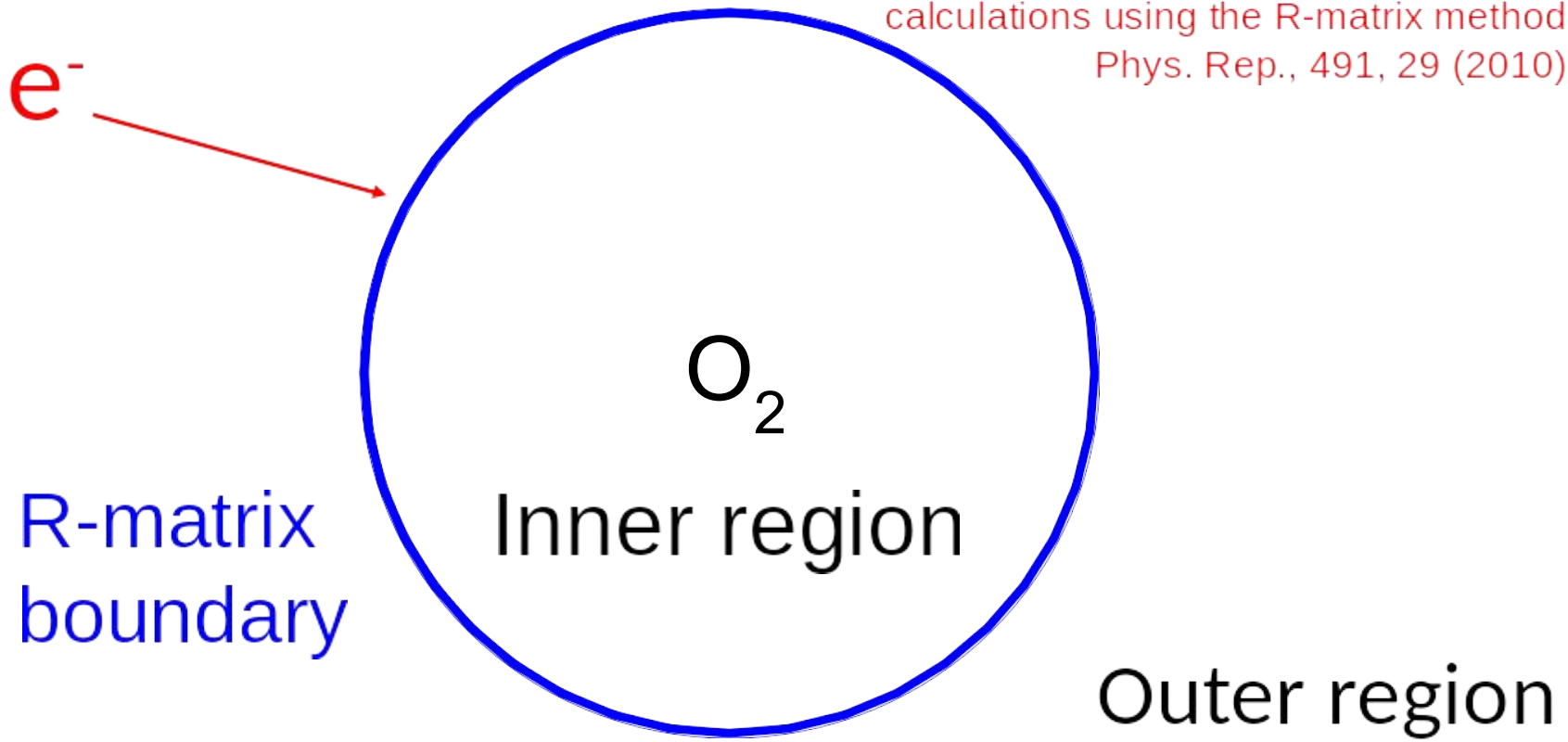
Electron Impact Ionisation

$$e^- + O_2(^1\Sigma_g) \rightarrow O_2^+ + e^-$$

$$e^- + O_2(^1\Delta_g) \rightarrow O_2^+ + e^-$$

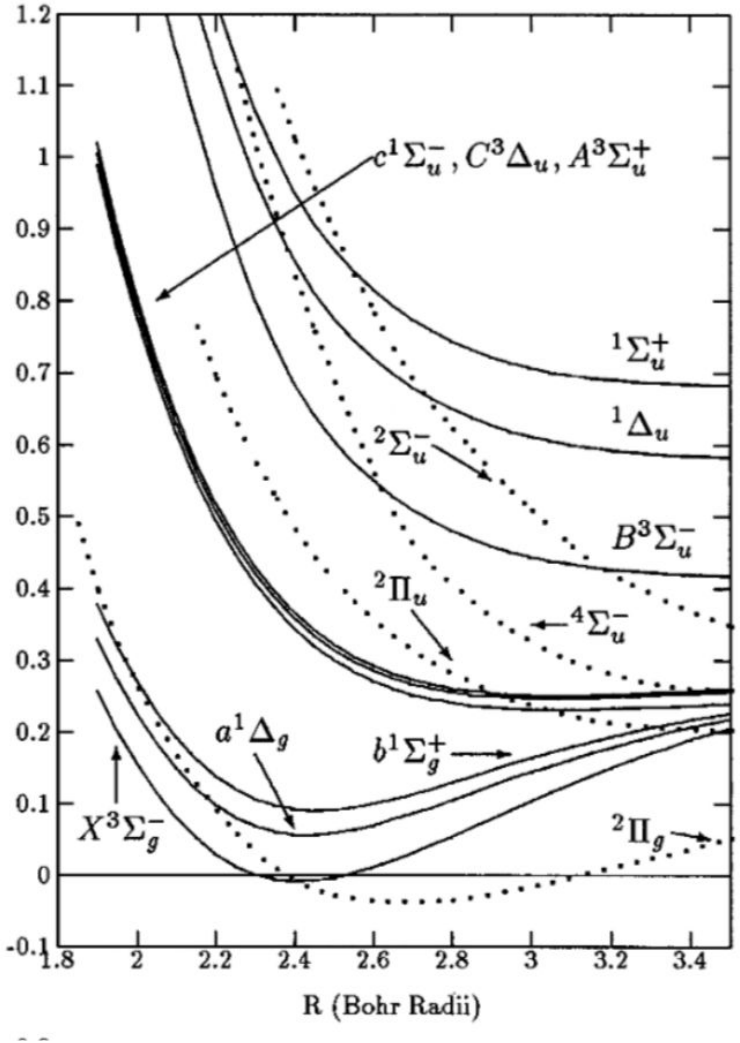
The R-matrix method

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



Inelastic Collisions

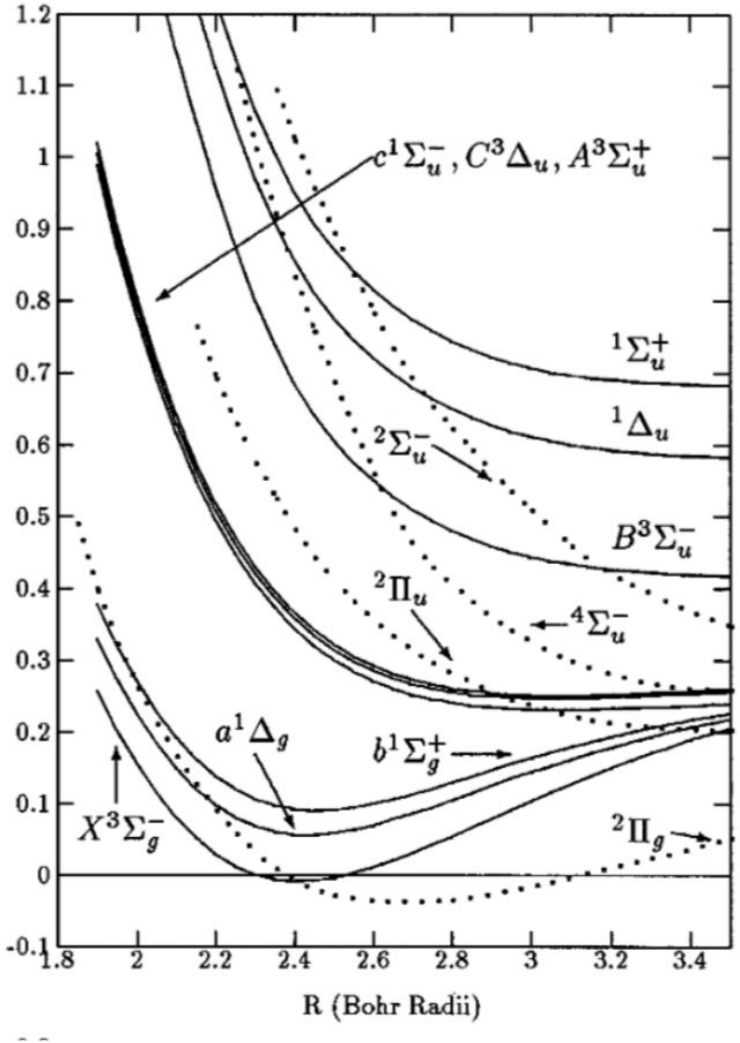
Electronic Excitation



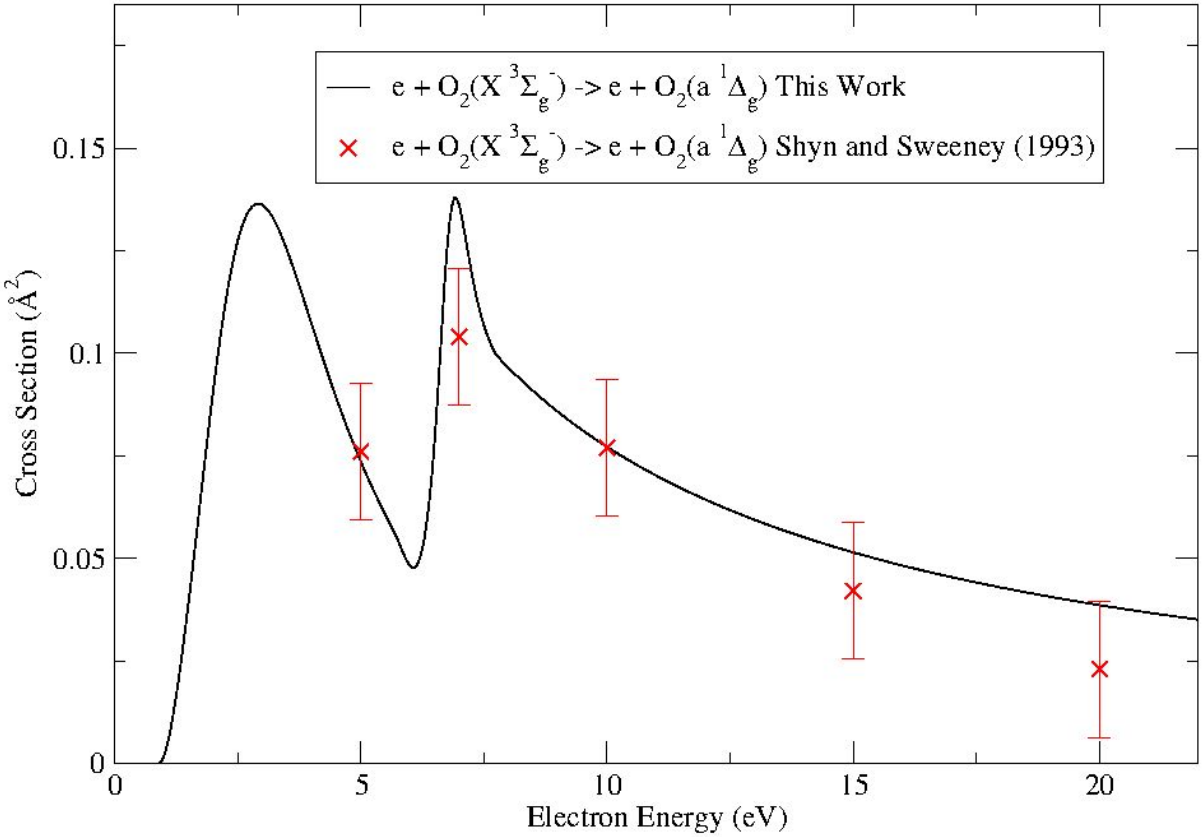
Resonant Mechanisms in the Vibrational Excitation States of Ground State O_2
Noble et. al. Physical Review Letters, 76, 19, 1996

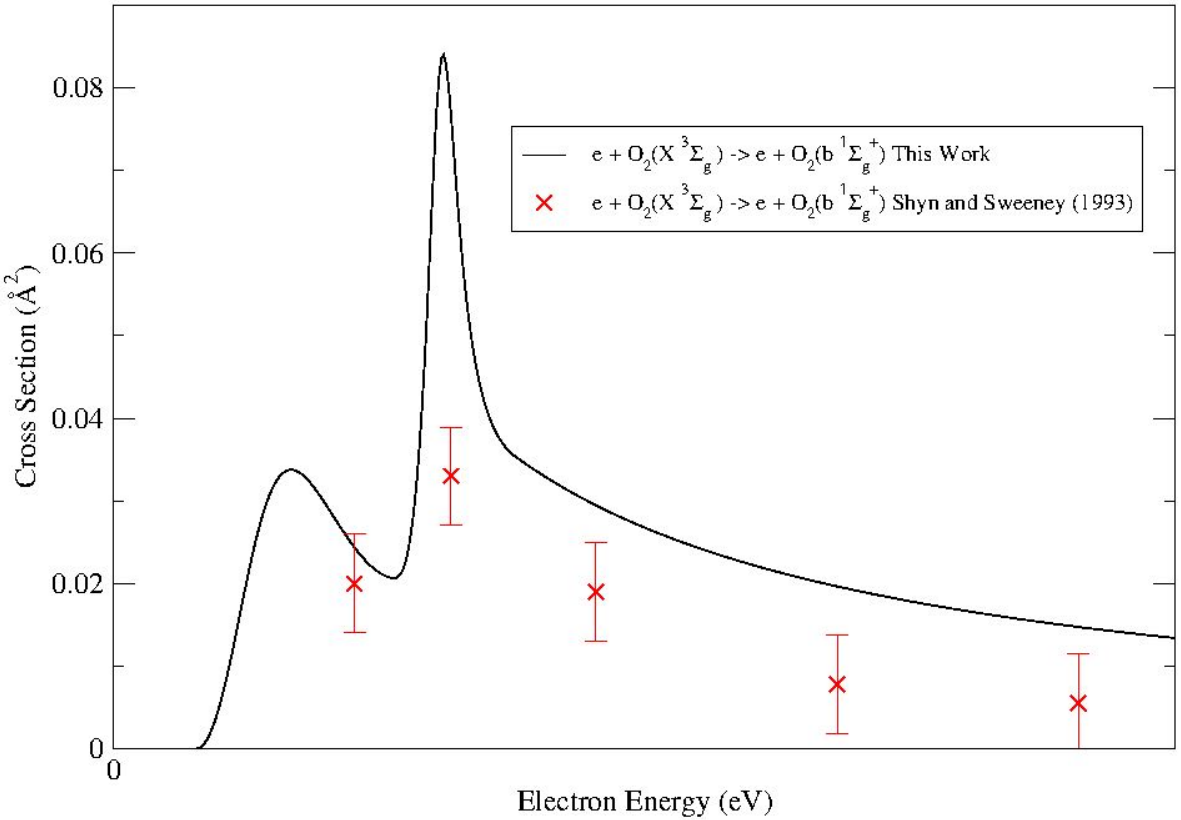
State	cc-pVTZ CAS(6,9)	aug-cc-pVTZ CAS(6,9)	Liu *et. al.* Theory	Krupenie Expt	Ohtsuka Theory
$a\ ^1\Delta_g$	0.9302	-0.8980	0.9641	0.9817	1.274
$b\ ^1\Sigma_g^+$	2.3530	-1.6871	1.6241	1.6360	2.000
$c\ ^1\Sigma_u^-$	3.1912	-3.3470	4.1187	4.0986	6.266
$A'\ ^3\Delta_u$	3.7302	-3.8368	4.3287	4.3065	6.538
$A\ ^3\Sigma_u^+$	3.4752	-3.6191	4.3952	4.3888	6.538
$B\ ^3\Sigma_u^-$	8.126	-6.7756	6.3266	6.1736	8.172

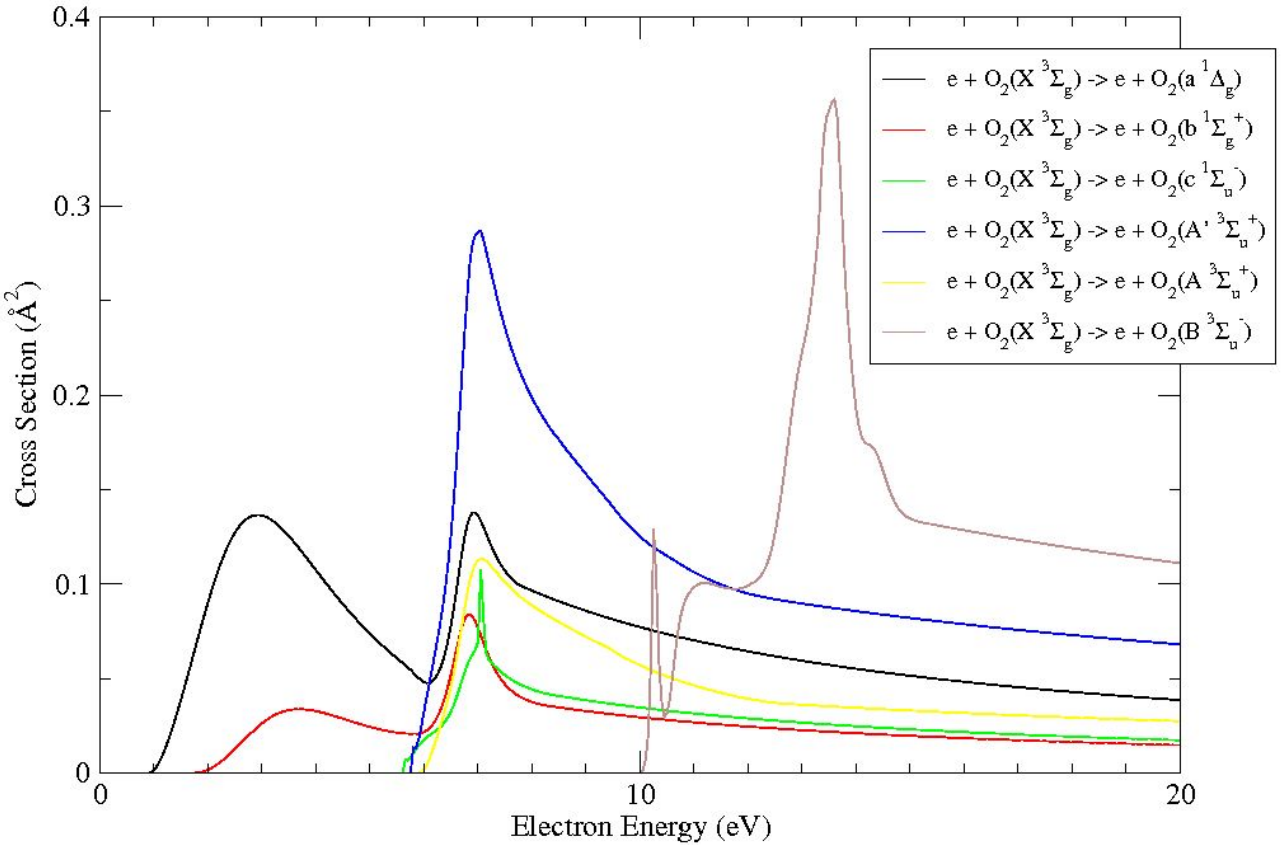
State	cc-pVTZ CAS(6,9)		aug-cc-pVTZ CAS(6,9)	
	Adiabatic	Vertical	Adiabatic	Vertical
$a\ ^1\Delta_g$	0.9302	0.9415	-0.8980	0.9170
$b\ ^1\Sigma_g^+$	2.3530	1.6897	-1.6871	1.6952
$c\ ^1\Sigma_u^-$	3.1912	5.4284	-3.3470	5.6080
$A'\ ^3\Delta_u$	3.7302	5.5944	-3.8368	5.7685
$A\ ^3\Sigma_u^+$	3.4752	5.7413	-3.6191	5.9209
$B\ ^3\Sigma_u^-$	8.126	11.2921	-6.7756	10.0487

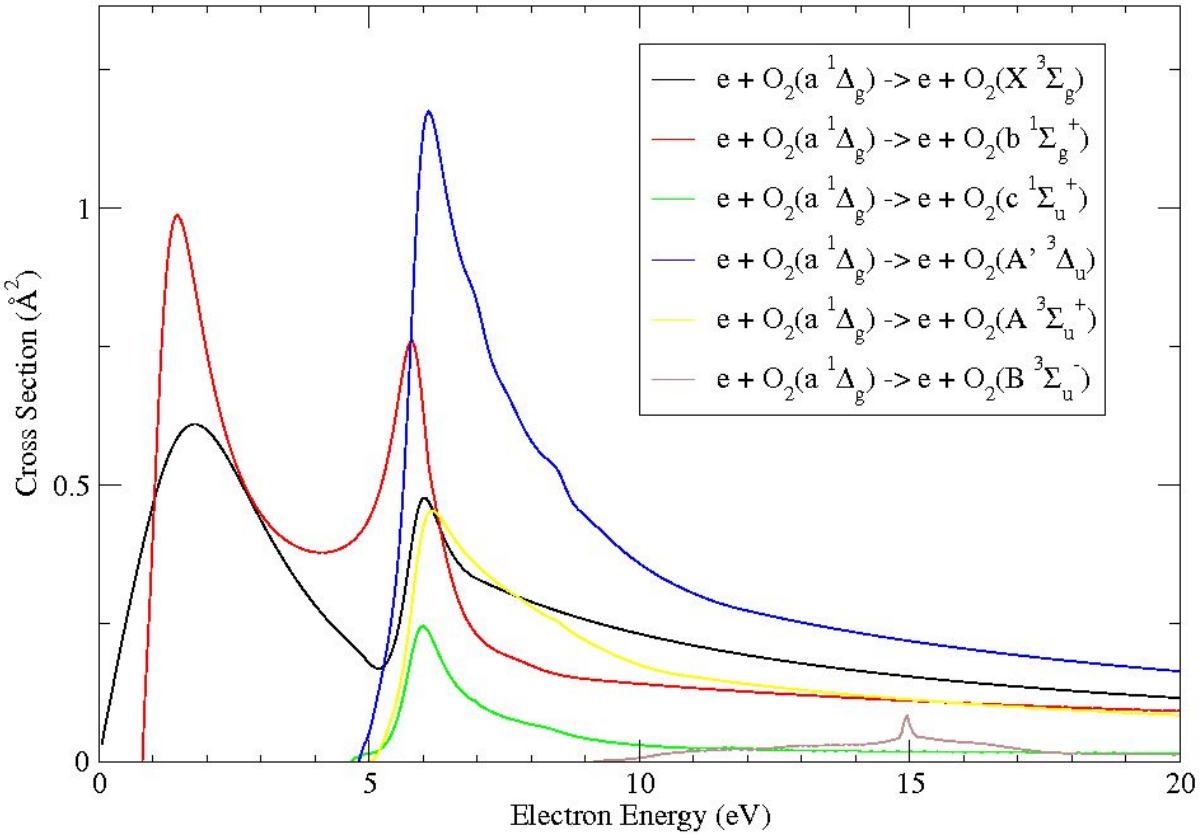


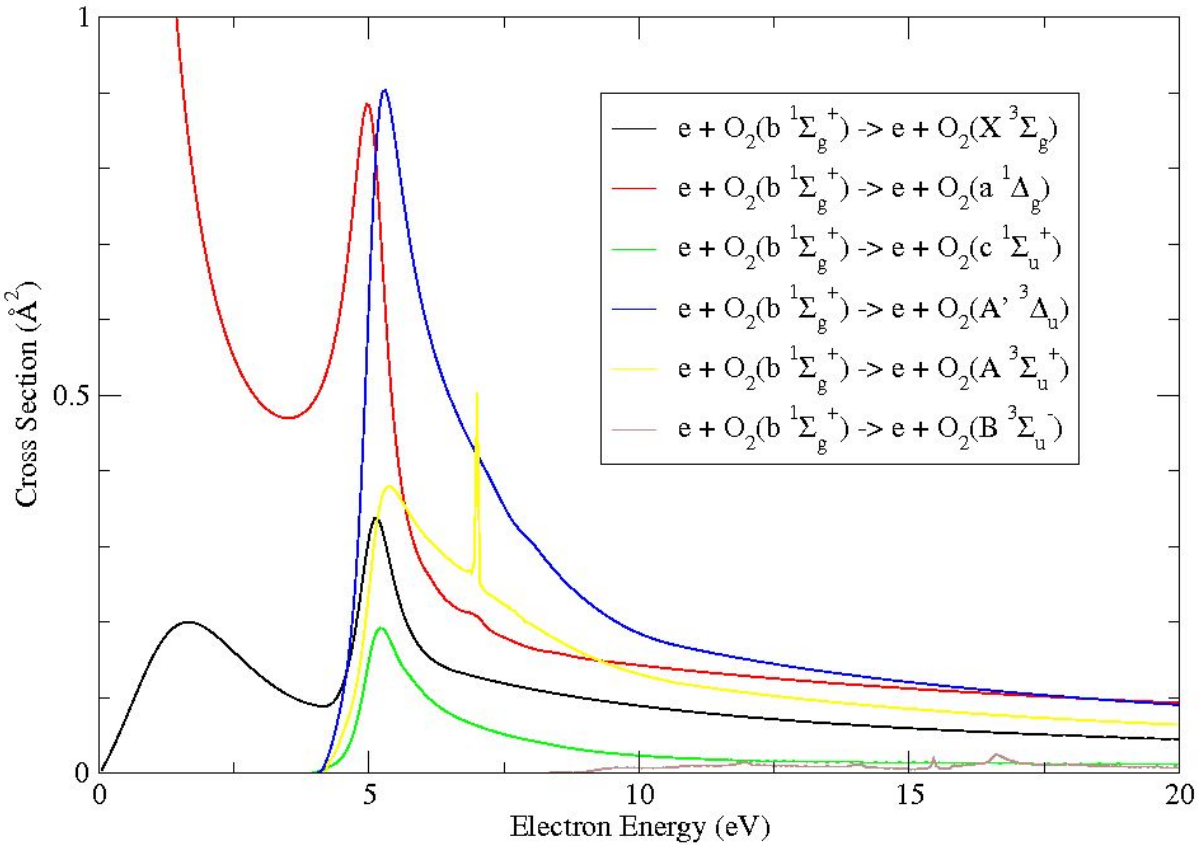
Resonant Mechanisms in the Vibrational Excitation States of Ground State O_2
Noble et. al. Physical Review Letters, 76, 19, 1996

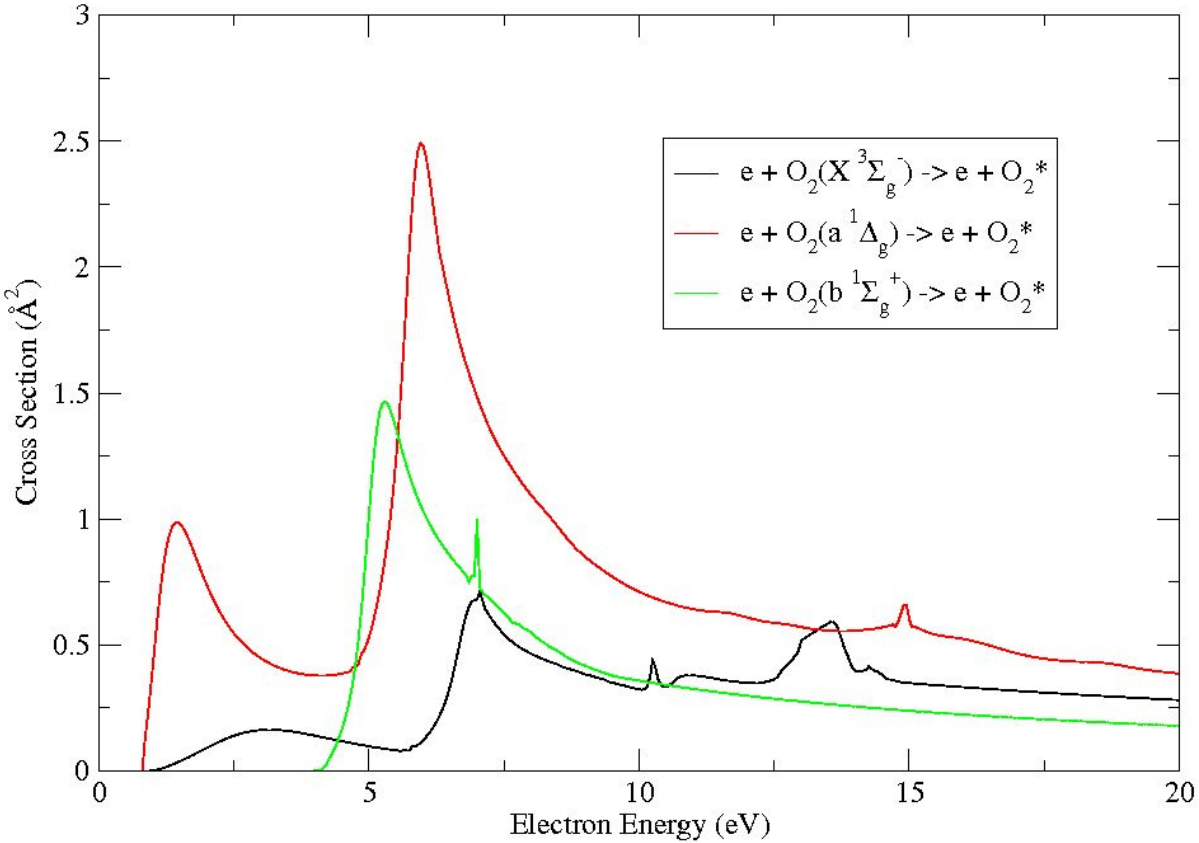

e + O2(X 3Σg-) -> e + O2(a 1Δg) This Work
e + O2(X 3Σg-) -> e + O2(a 1Δg) Shyn and Sweeney (1993)
Cross Section (Å2)
Electron Energy (eV)
0
0.05
0.1
0.15
0
5
10
15
20


0.08
0.06
0.04
0.02
0
0
Cross Section (Å^2)
Electron Energy (eV)
e + O$_2$(X $^3\Sigma_g^-$) -> e + O$_2$(b $^1\Sigma_g^+$) This Work
e + O$_2$(X $^3\Sigma_g^-$) -> e + O$_2$(b $^1\Sigma_g^+$) Shyn and Sweeney (1993)

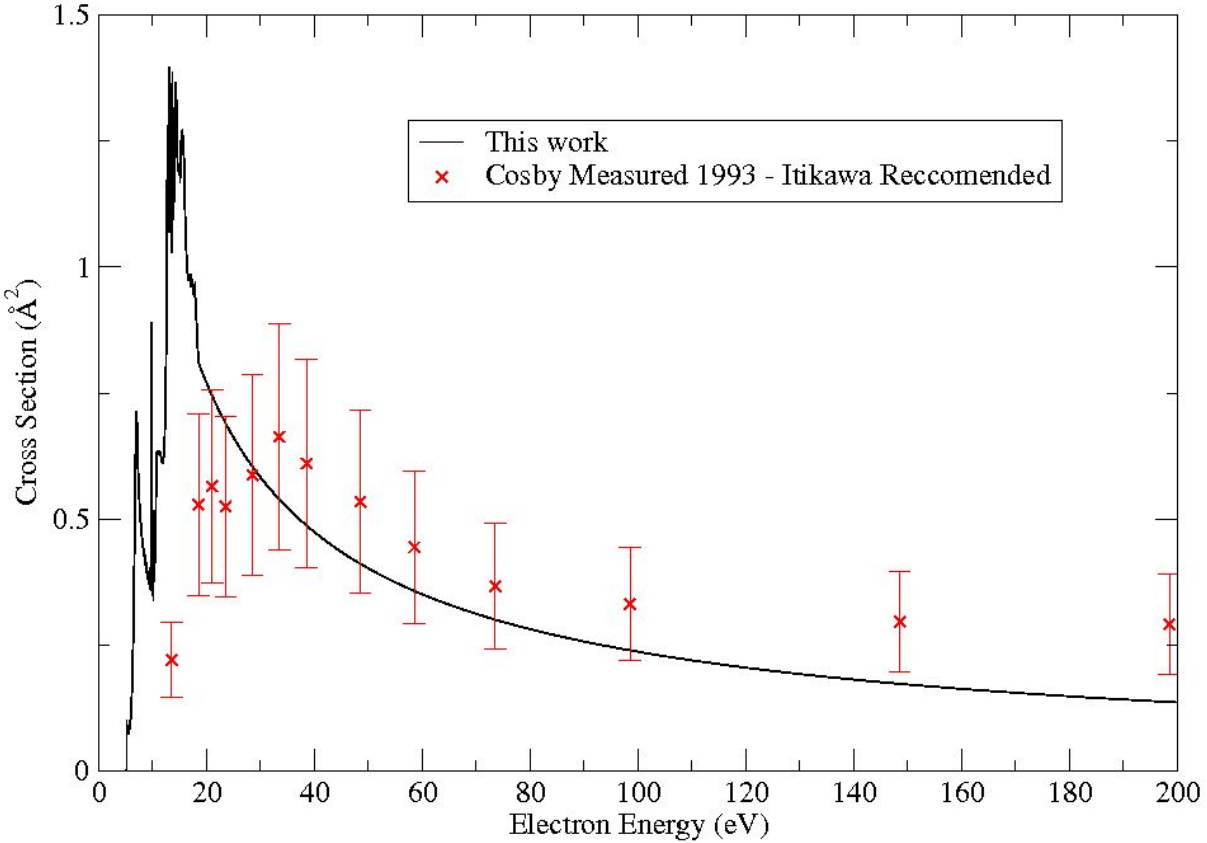

0.4
0.3
0.2
0.1
0
Cross Section (Å^2)
0
10
20
Electron Energy (eV)
e + O$_2$(X $^3\Sigma_g^-$) -> e + O$_2$(a $^1\Delta_g$)
e + O$_2$(X $^3\Sigma_g^-$) -> e + O$_2$(b $^1\Sigma_g^+$)
e + O$_2$(X $^3\Sigma_g^-$) -> e + O$_2$(c $^1\Sigma_u^-$)
e + O$_2$(X $^3\Sigma_g^-$) -> e + O$_2$(A' $^3\Sigma_u^+$)
e + O$_2$(X $^3\Sigma_g^-$) -> e + O$_2$(A $^3\Sigma_u^+$)
e + O$_2$(X $^3\Sigma_g^-$) -> e + O$_2$(B $^3\Sigma_u^-$)


e + O2(a 1Δg) -> e + O2(X 3Σg)
e + O2(a 1Δg) -> e + O2(b 1Σg+)
e + O2(a 1Δg) -> e + O2(c 1Σu+)
e + O2(a 1Δg) -> e + O2(A' 3Δu)
e + O2(a 1Δg) -> e + O2(A 3Σu+)
e + O2(a 1Δg) -> e + O2(B 3Σu-)
Cross Section (Å2)
Electron Energy (eV)
0
0.5
1
0
5
10
15
20


Cross Section (Å^2)
Electron Energy (eV)
0
0.5
1
0
5
10
15
20
e + O$_2$(b $^1\Sigma_g^+$) -> e + O$_2$(X $^3\Sigma_g^-$)
e + O$_2$(b $^1\Sigma_g^+$) -> e + O$_2$(a $^1\Delta_g$)
e + O$_2$(b $^1\Sigma_g^+$) -> e + O$_2$(c $^1\Sigma_u^+$)
e + O$_2$(b $^1\Sigma_g^+$) -> e + O$_2$(A' $^3\Delta_u$)
e + O$_2$(b $^1\Sigma_g^+$) -> e + O$_2$(A $^3\Sigma_u^+$)
e + O$_2$(b $^1\Sigma_g^+$) -> e + O$_2$(B $^3\Sigma_u^-$)


Cross Section (Å^2)
Electron Energy (eV)
e + O_2($X\ ^3\Sigma_g^-$) -> e + O_2*
e + O_2($a\ ^1\Delta_g$) -> e + O_2*
e + O_2($b\ ^1\Sigma_g^+$) -> e + O_2*
0
0.5
1
1.5
2
2.5
3
0
5
10
15
20

Electron Impact Dissociation


This work
Cosby Measured 1993 - Itikawa Reccomended
Cross Section (Å^2)
Electron Energy (eV)
0
0.5
1
1.5
0
20
40
60
80
100
120
140
160
180
200

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journal homepage: www.elsevier.com/locate/saa

Accurate calculations on the 22 electronic states and 54 spin-orbit states of the O_2 molecule: Potential energy curves, spectroscopic parameters and spin-orbit coupling

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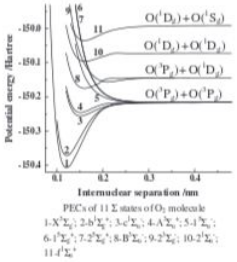
[a] College of Physics and Electronic Engineering, Henan Normal University, Xinxiang 453007, China
[b] College of Physics and Electronic Engineering, Xinyang Normal University, Xinyang 464000, China

HIGHLIGHTS

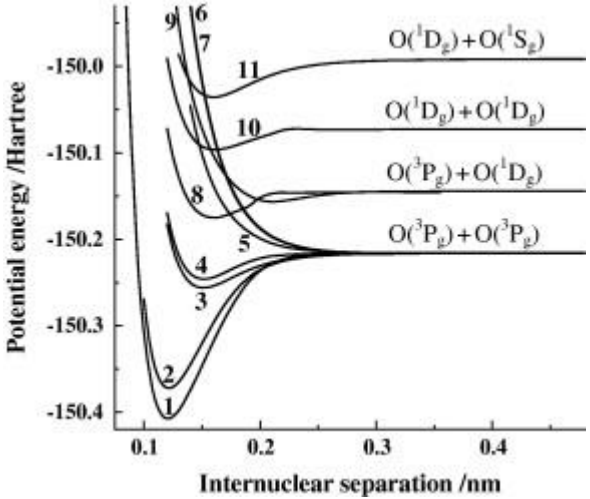
- PECs are extrapolated to the CBS limit.
- Convergence of the present calculations is found.
- Effect of SO coupling on the spectroscopic parameters is evaluated.
- Spectroscopic parameters of 16 electronic states and 35 Ω states are obtained.
- Effect of core-valence correlation and scalar relativistic corrections is included.

GRAPHICAL ABSTRACT

The PECs of 54 Ω states generated from the 22 electronic states of O_2 molecule are studied. Of the 22 states, the $X^3\Sigma_g^-$, $A'^3\Delta_u$, $A^3\Sigma_u^+$, $B^3\Sigma_u^-$, $C^3\Pi_g$, $a^1\Delta_g$, $b^1\Sigma_g^+$, $c^1\Sigma_u^-$, $d^1\Pi_g$, $f^1\Sigma_u^+$, $1^3\Pi_g$, $1^3\Pi_u$, $2^3\Sigma_g^-$, $1^5\Sigma_u^-$, $2^1\Sigma_u^-$ and $2^1\Delta_g$ are found to be bound, whereas the $1^5\Sigma_g^+$, $2^5\Sigma_g^+$, $1^1\Pi_u$, $1^5\Delta_g$, $1^5\Pi_u$ and $2^1\Pi_u$ are found to be repulsive ones. The $B^3\Sigma_u^-$ and $d^1\Pi_g$ states possess the double well. And the $1^3\Pi_u$, $C^3\Pi_g$, $A'^3\Delta_u$, $1^5\Delta_g$ and $2^5\Sigma_g^+$ states are the inverted ones. The PECs are calculated by the CASSCF method followed by the icMRCI approach. Core-valence correlation and scalar relativistic corrections are included. All the PECs are extrapolated to the CBS limit. The vibrational properties are discussed for the $1^5\Pi_g$, $1^3\Pi_u$, $d^1\Pi_g$, $1^5\Sigma_u^-$ and $B^3\Sigma_u^-$ states. The SO coupling effect is accounted for. The spectroscopic parameters are evaluated. The present spectroscopic parameters can be expected to be reliably predicted ones. The effect of SO coupling on the spectroscopic parameters are small almost for all the electronic states except for the $1^5\Sigma_u^-$, $1^5\Pi_g$ and $1^3\Pi_u$.

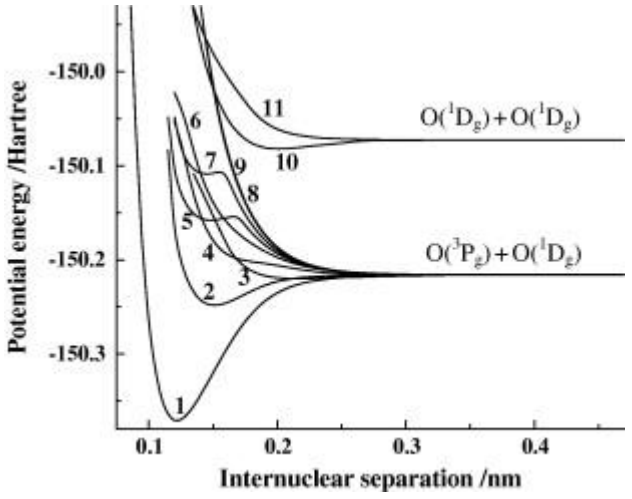


PECs of 11 Σ states of O_2 molecule
1-$X^3\Sigma_g^-$; 2-$b^1\Sigma_g^+$; 3-$c^1\Sigma_u^-$; 4-$A^3\Sigma_u^+$; 5-$1^5\Sigma_u^-$; 6-$1^1\Sigma_g^+$; 7-$2^5\Sigma_g^+$; 8-$B^3\Sigma_u^-$; 9-$2^1\Sigma_g^-$; 10-$2^1\Sigma_u^-$; 11-$1^1\Sigma_u^+$



PECs of the 11 states of O_2 molecule

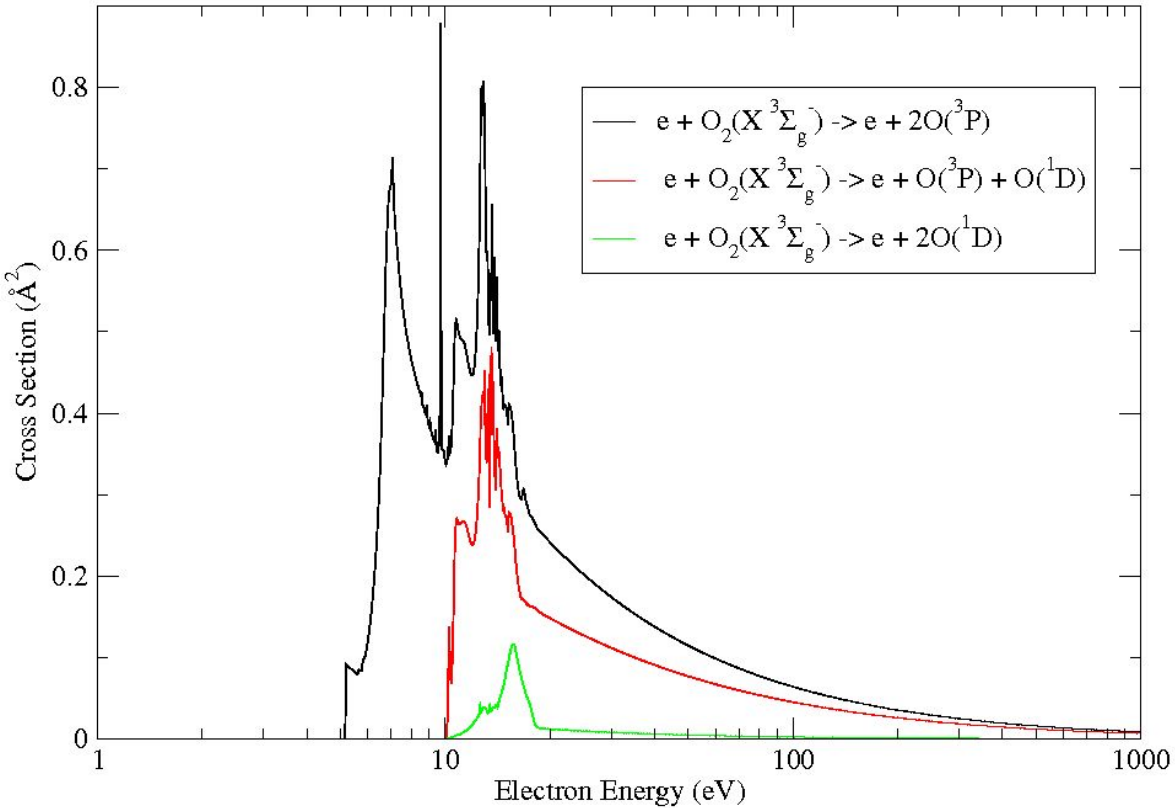
1 – X $^3\Sigma_g^-$; 2 – b $^1\Sigma_g^+$; 3 – c $^1\Sigma_u^-$; 4 – A $^3\Sigma_u^+$;
5 – 1 $^5\Sigma_u^-$; 6 – 1 $^5\Sigma_g^+$; 7 – 2 $^5\Sigma_g^+$; 8 – B $^3\Sigma_u^-$;
9 – 2 $^3\Sigma_g^-$; 10 – 2 $^1\Sigma_u^-$; 11 – f $^1\Sigma_u^+$.

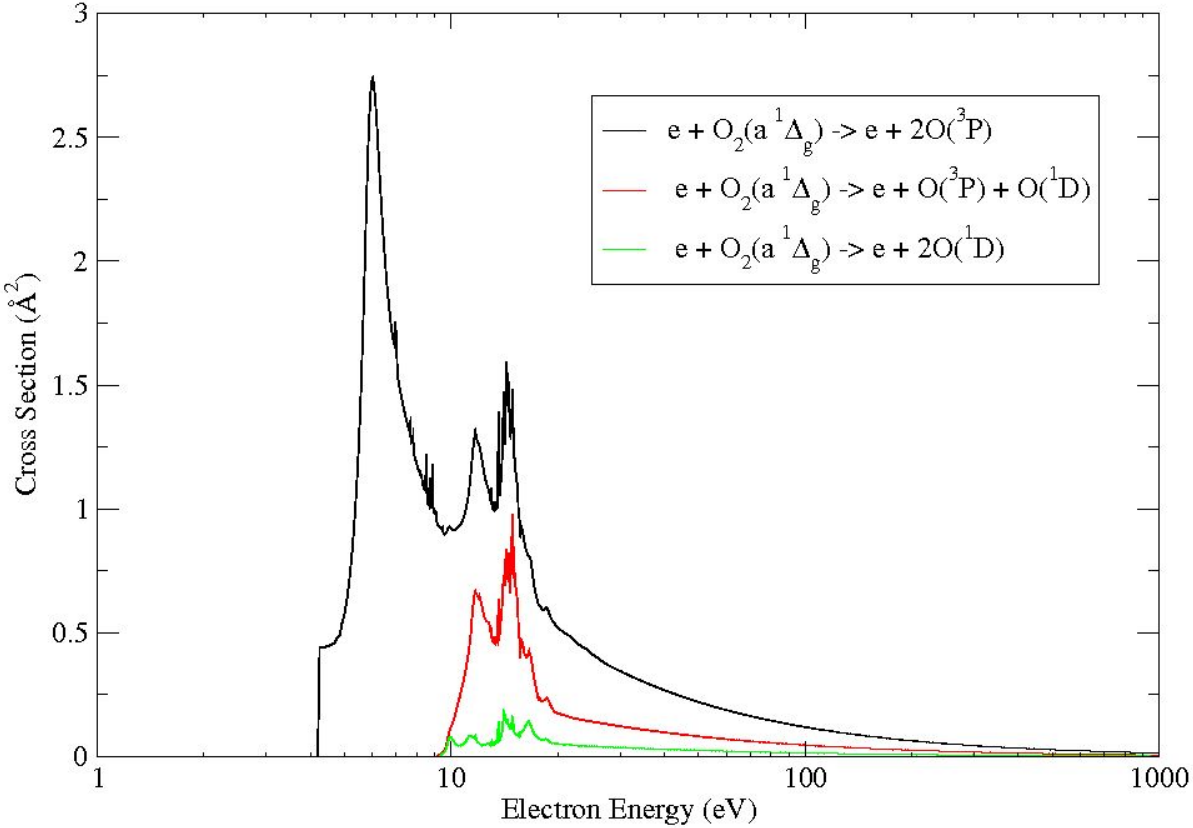


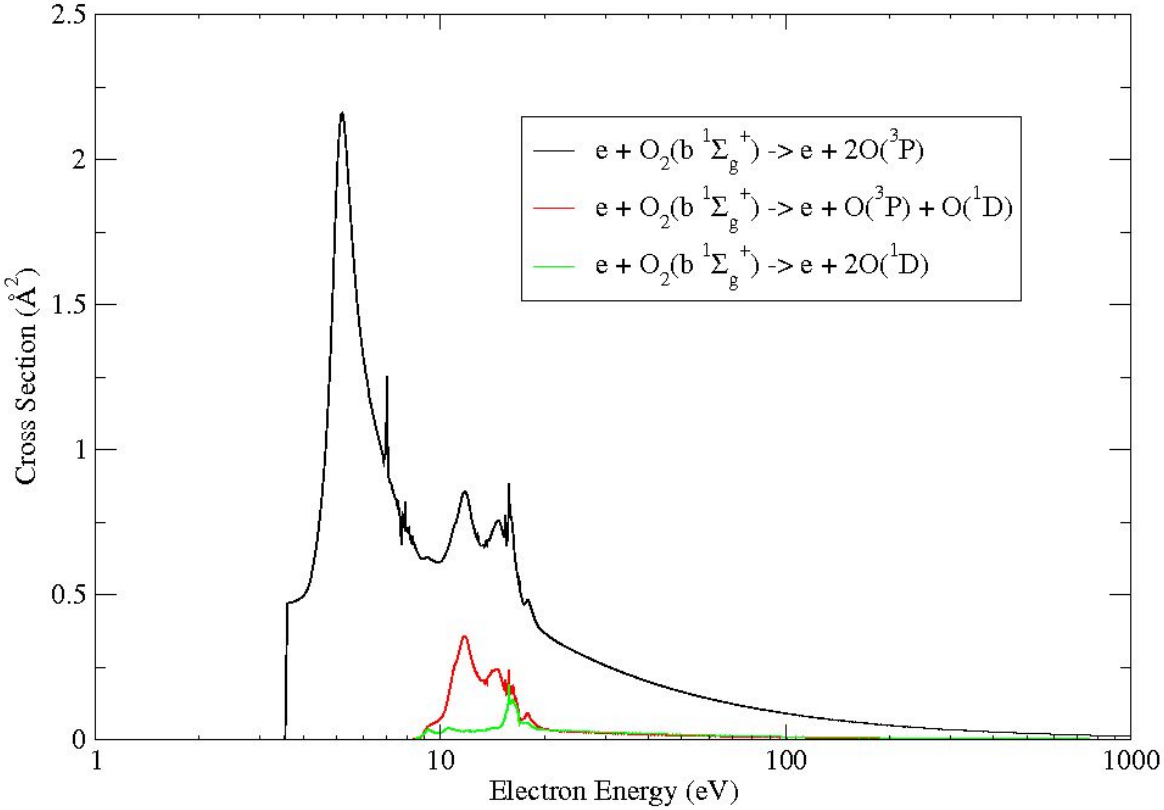
PECs of the 11 states of O_2 molecule

1 – a $^1\Delta_g$; 2 – A′ $^3\Delta_u$; 3 – 1 $^5\Pi_g$; 4 – 1 $^3\Pi_u$;
5 – C $^3\Pi_g$; 6 – 1 $^1\Pi_u$; 7 – d $^1\Pi_g$; 8 – 1 $^5\Pi_u$;
9 – 1 $^5\Delta_g$; 10 – 2 $^1\Delta_g$; 11 – 2 $^1\Pi_u$.

Dissociation Channel	Electronic States Liu *et. al.* (2014)
$O(^3P_g) + O(^3P_g)$	$B\ ^1\Sigma_g^+$, $c\ ^1\Sigma_u^-$, $d\ ^1\Pi_g$, $1\ ^1\Pi_u$, $a\ ^1\Delta_g$, $X\ ^3\Sigma_g^-$, $A\ ^3\Sigma_u^+$, $C\ ^3\Pi_g$, $1\ ^3\Pi_u$, $A'\ ^3\Delta_u$, $1\ ^5\Sigma_g^+$, $2\ ^5\Sigma_g^+$, $1\ ^5\Sigma_u^-$, $1\ ^5\Pi_g$, $1\ ^5\Pi_u$, $1\ ^5\Delta_g$
$O(^3P_g) + O(^1D_g)$	$2\ ^3\Sigma_g^-$, $B\ ^3\Sigma_u^-$
$O(^1D_g) + O(^1D_g)$	$2\ ^1\Sigma_u^-$, $2\ ^1\Pi_u$, $2\ ^1\Delta_g$
$O(^1D_g) + O(^1S_g)$	$f\ ^1\Sigma_u^+$


e + O2(X 3Σg-) -> e + 2O(3P)
e + O2(X 3Σg-) -> e + O(3P) + O(1D)
e + O2(X 3Σg-) -> e + 2O(1D)
Cross Section (Å2)
Electron Energy (eV)
0
0.2
0.4
0.6
0.8
1
10
100
1000


3
2.5
2
1.5
1
0.5
0
Cross Section (Å^2)
1
10
100
1000
Electron Energy (eV)
e + O_2($a\ ^1\Delta_g$) -> e + 2O(^{3}P)
e + O_2($a\ ^1\Delta_g$) -> e + O(^{3}P) + O(^{1}D)
e + O_2($a\ ^1\Delta_g$) -> e + 2O(^{1}D)


2.5
2
1.5
1
0.5
0
Cross Section (Å^2)
1
10
100
1000
Electron Energy (eV)
e + O$_2$(b $^1\Sigma_g^+$) -> e + 2O(^{3}P)
e + O$_2$(b $^1\Sigma_g^+$) -> e + O(^{3}P) + O(^{1}D)
e + O$_2$(b $^1\Sigma_g^+$) -> e + 2O(^{1}D)

Electron Impact Ionisation

$e^- + AB \rightarrow AB^+ + 2e^-$

$$\sigma_{BEB} = \frac{S}{t+u+1}\left(\frac{1}{2}\left(1-\frac{1}{t^2}\right)ln(t)+1-\frac{1}{t}-\frac{ln(t)}{t+1}\right)$$

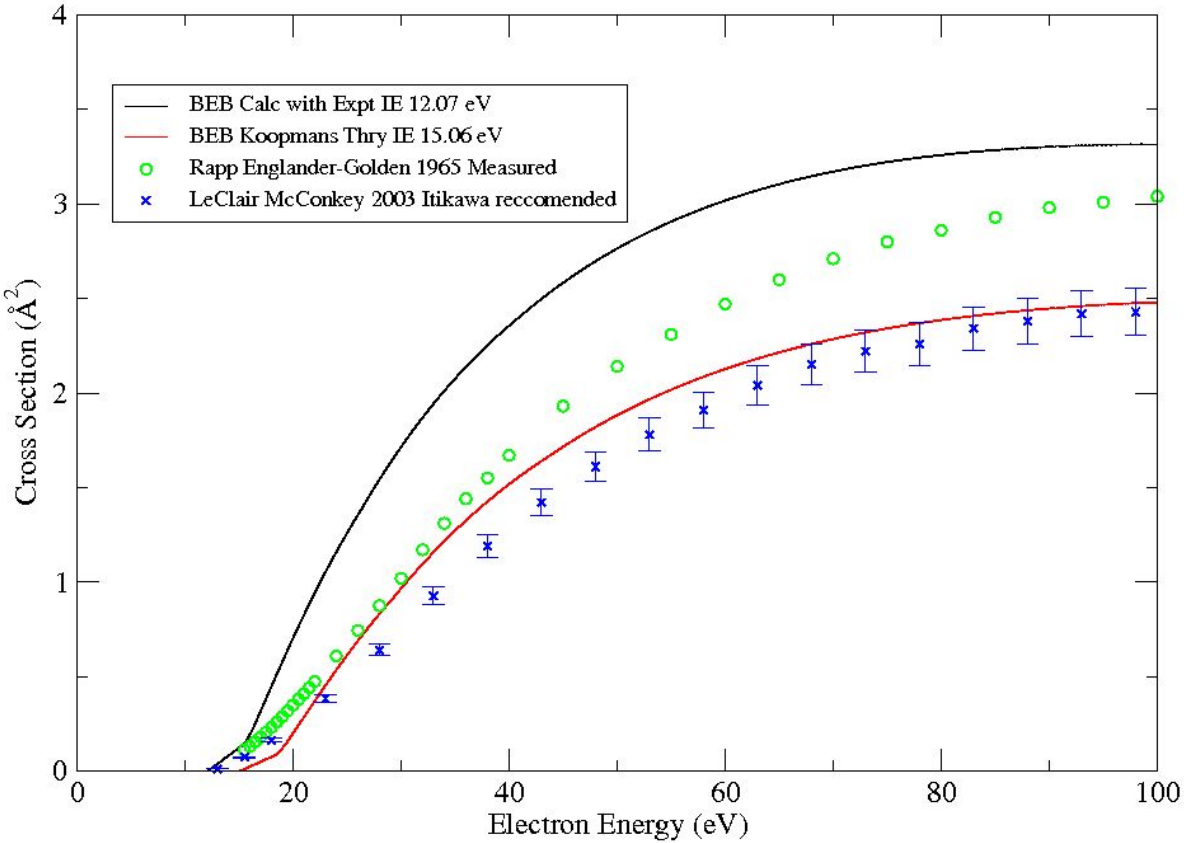
$$S = 4\pi a_0^2 N\left(\frac{R}{B}\right)^2 \qquad u = \frac{U}{B}$$

$$t = \frac{T}{B}$$

T is the kinetic energy
B is the binding energy of the electrons in a subshell
U is the average kinetic energy
N is the number of bound electrons
with the constants the
R = Rydberg constant
a_o = Bohr radius

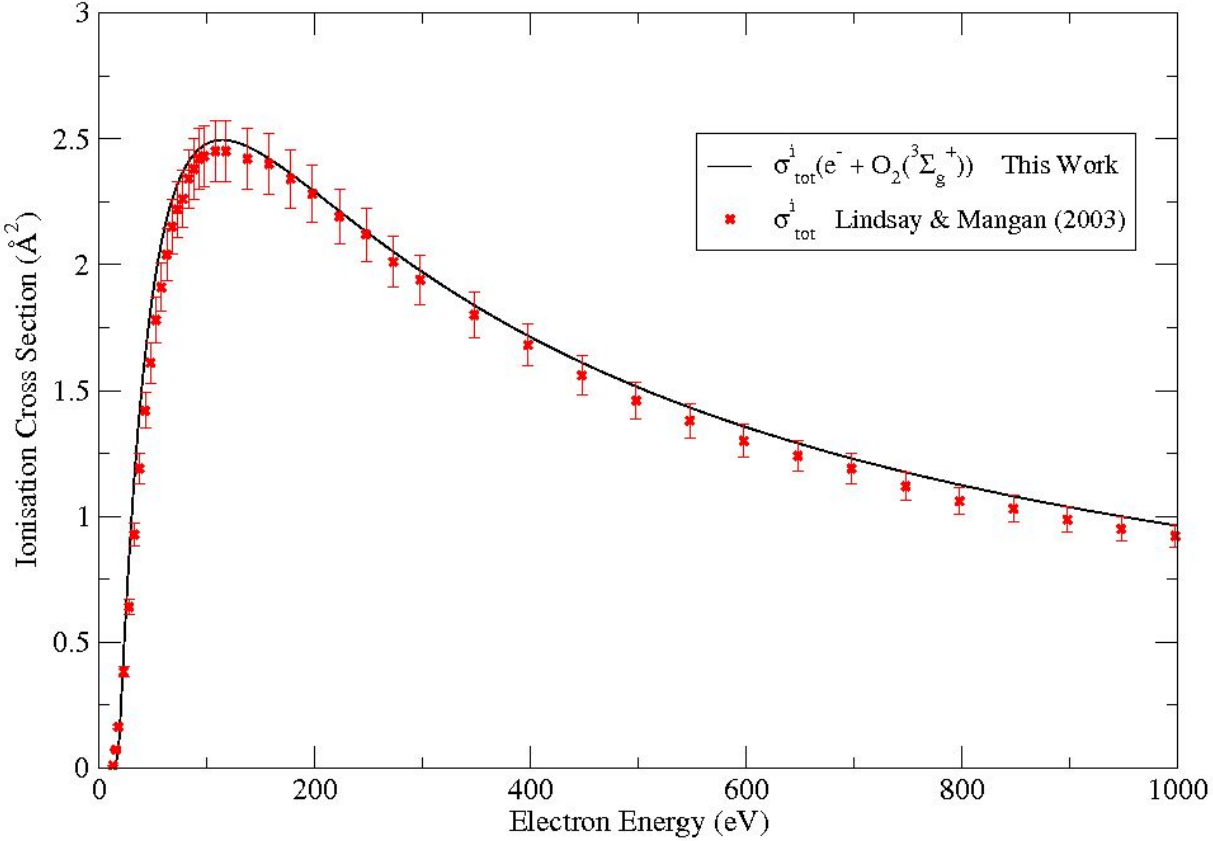
The BEB method has been shown to give reliable total ionisation cross sections for a large range of molecules.

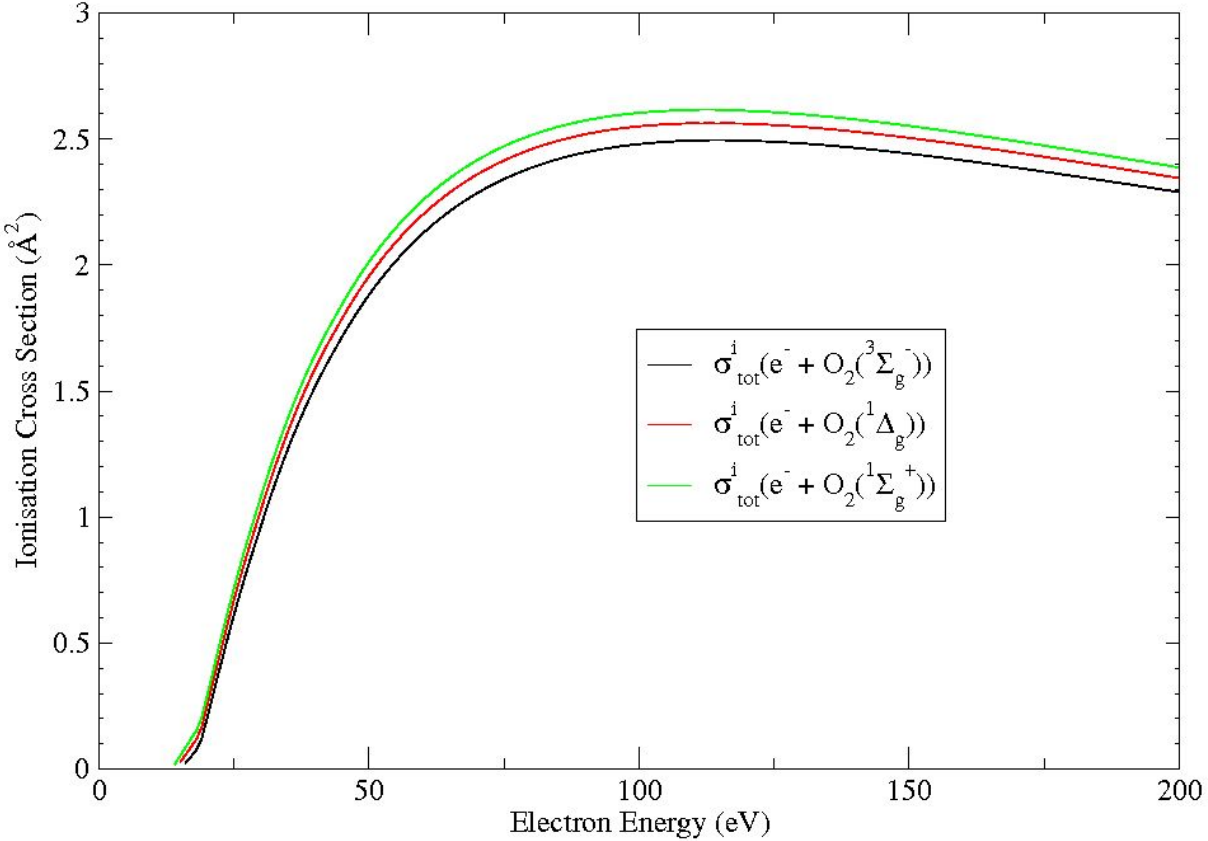
Kim, Y and Rudd, M, *Binary Encounter Dipole model for electron impact ionization*, Physical Review 50(5) (1994) 3954-3967; Mott N F, 1930 Proc. R. Soc. London Ser. A 126 259; Bethe H, 1930 Ann. Phys. (Leipzig) 5 325



Koopman *ab initio* ionisation energy, defined as the highest occupied molecular orbital binding energy, from this calculation was **15.06 eV**

The experimental ionisation energy taken from the NIST cccdbd for the ground state of O_2 is **12.07 eV**


Ionisation Cross Section (Å^2)
Electron Energy (eV)
0
0.5
1
1.5
2
2.5
3
0
200
400
600
800
1000
$\sigma^i_{tot}(e^- + O_2(^3\Sigma_g^+))$ This Work
σ^i_{tot} Lindsay & Mangan (2003)


Ionisation Cross Section (Å^2)
Electron Energy (eV)
0
0.5
1
1.5
2
2.5
3
0
50
100
150
200
$\sigma^i_{tot}(e^- + O_2(^3\Sigma_g^-))$
$\sigma^i_{tot}(e^- + O_2(^1\Delta_g))$
$\sigma^i_{tot}(e^- + O_2(^1\Sigma_g^+))$

Thank You Very Much For Your Time!

ANY QUESTIONS ?