Electronic structure and spectroscopy of O_2 and O_2^+

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Outline

In this presentation I will show a sample of ongoing electronic structure calculations of O_2 and O_2^+

<u>O_2 molecule</u>

- Some singlets
- Triplets
- Quintets
- Septets

<u>O_2^+ cation</u>

- Some doublets
- Quartets
- Sextets

<u>Comments of the computation of O_2^{**} superexcited states</u>

Type: SCF MRSD(TQ)–CI

Package: *MRD–CI* [a]

O basis: cc–pVQZ +
   + diffuse(three *s*, three *p*, one *d*)

Functions: O(8s7p4d2f)
   Total 16s14p8d4f

   146 atomic functions

SCF: D_{2h} symmetry

Core: $1\sigma_g^2\ 1\sigma_u^2$ 1s(O_1) and 1s(O_2)

CI: 12 active e^-

Excitations: S + D + (T, Q)

MO's $O_2(X^3\Sigma^-)$

Conf. $O_2(X)$ $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2$

Molecular states correlating to the lowest dissociation limits of O_2, along with their respective dissociation energies.[a]

| Molecular states	Number of states	Limit	D_0(eV)[a]
$^5[\Sigma^-, \Pi, \Delta]_{g,u}$	6	O(^{1}D)+O(^{5}S$^\circ$)	
$^{1,5}[\Sigma^+(2), \Delta]_g, ^3[\Sigma^+(2), \Delta]_u, ^{1,5}[\Sigma^-]_u, ^3[\Sigma^-]_g, ^{1,3,5}[\Pi]_{g,u}$	18	O(^{3}P)+O(^{3}P)	
$^{1,3,5,7}[\Sigma^+, \Pi]_{g,u}$	16	O(^{3}P)+O(^{5}S$^\circ$)	
$^1[\Sigma^+]_g$	1	O(^{1}S)+O(^{1}S)	
$^1[\Sigma^+, \Pi, \Delta]_{g,u}$	6	O(^{1}D)+O(^{1}S)	
$^3[\Sigma^-, \Pi]_{g,u}$	4	O(^{3}P)+O(^{1}S)	
$^1[\Sigma^+(3), \Delta(2), \Gamma]_g, ^1[\Sigma^-(2), \Delta]_u, ^1[\Pi(2), \Phi]_{g,u}$	15	O(^{1}D)+O(^{1}D)	
$^3[\Sigma^+, \Sigma^-(2), \Pi(3), \Delta(2), \Phi]_{g,u}$	18	O(^{3}P)+O(^{1}D)	
$^{1,5}[\Sigma^+(2), \Delta]_g, ^3[\Sigma^+(2), \Delta]_u, ^{1,5}[\Sigma^-]_u, ^3[\Sigma^-]_g, ^{1,3,5}[\Pi]_{g,u}$	20	O(^{3}P)+O(^{3}P)	5.1156

[a] Energies are referred with respect to O_2(X$^3\Sigma_g^-$, $v'' = 0$).
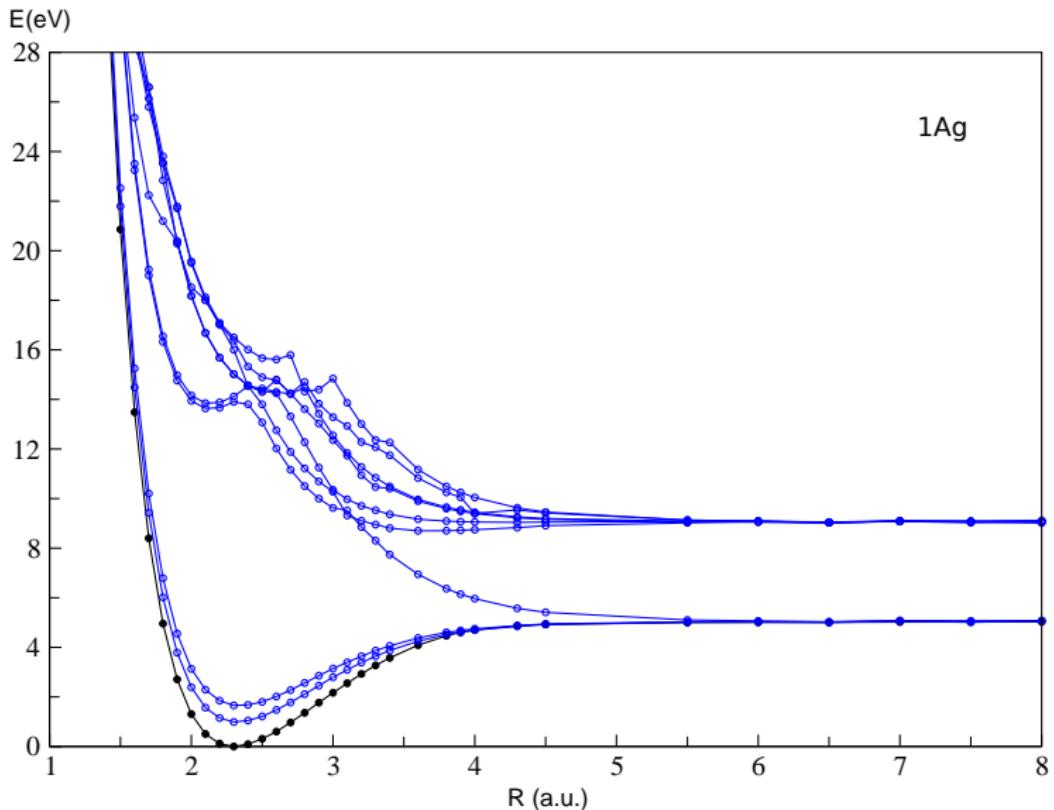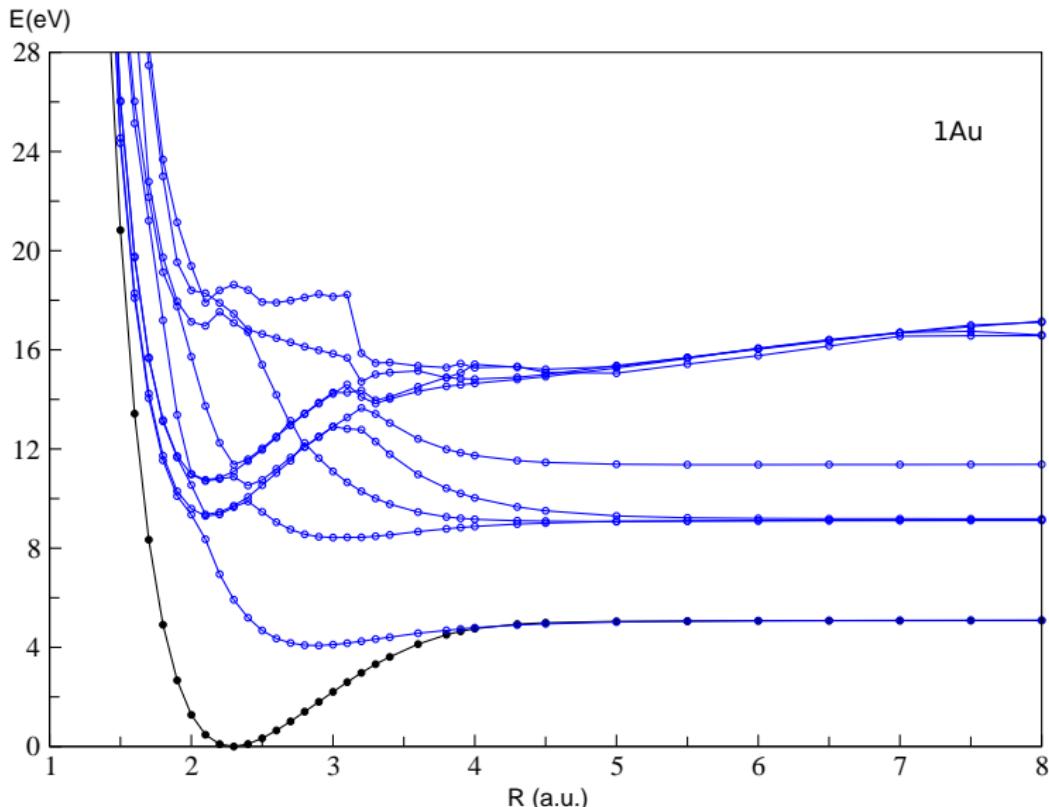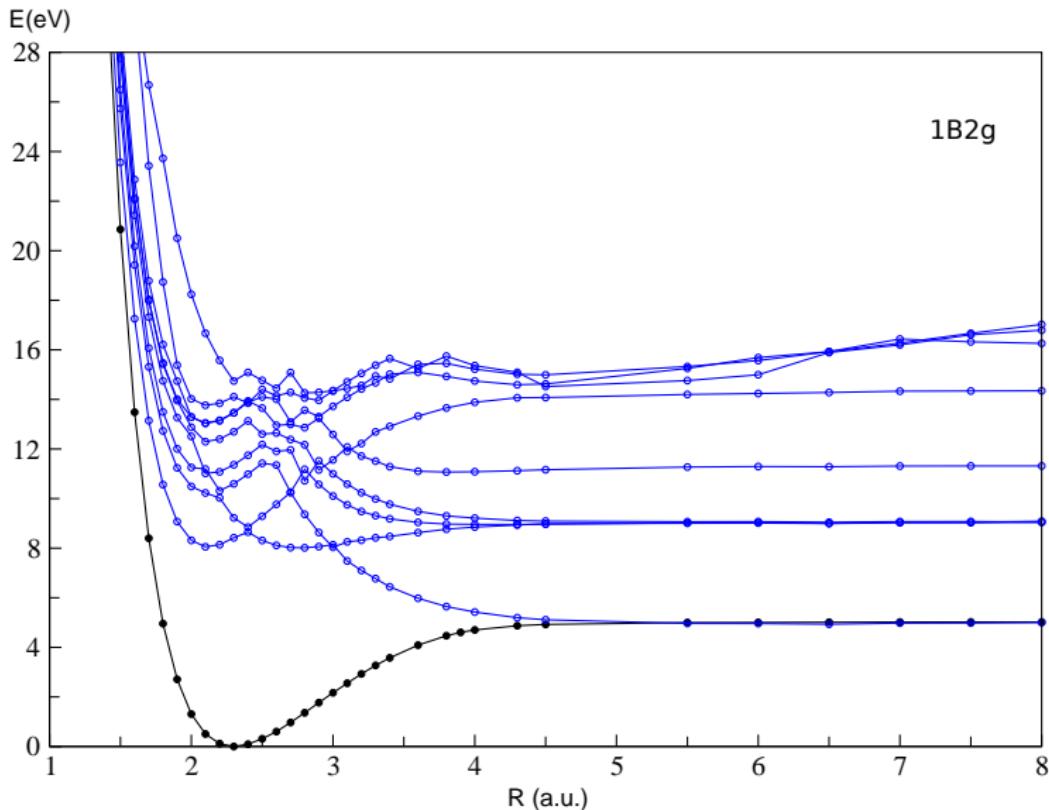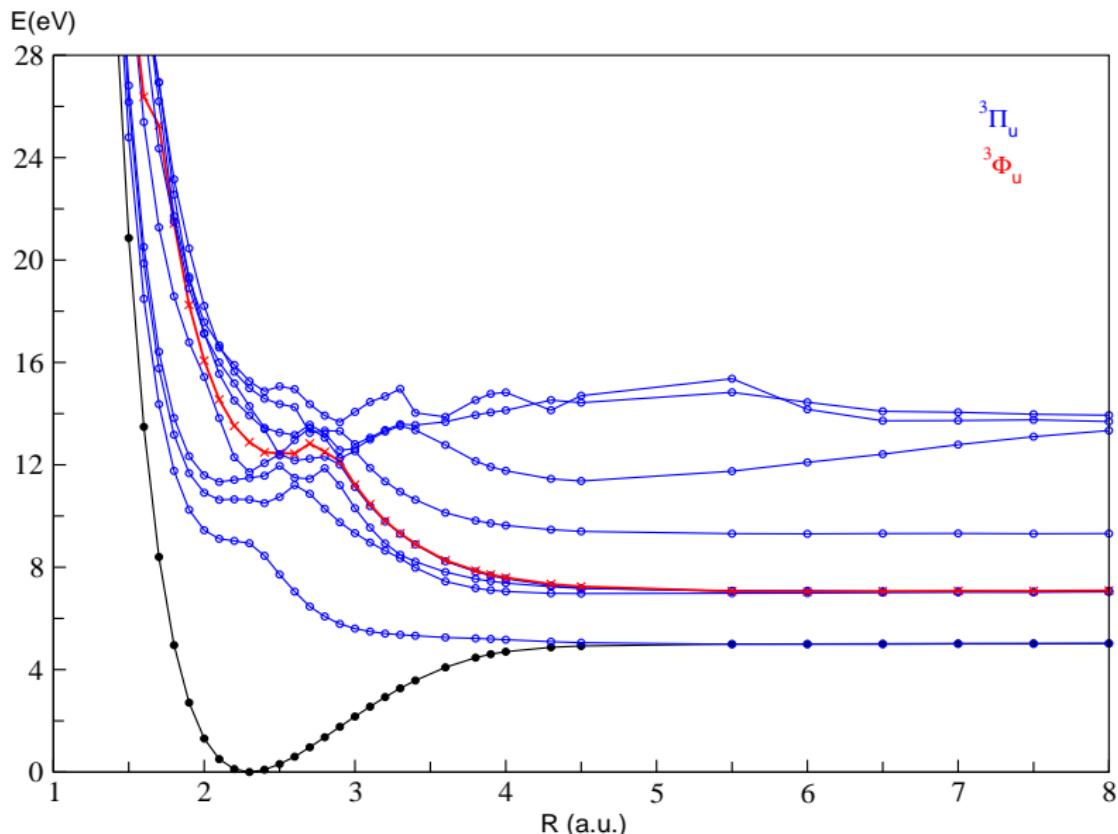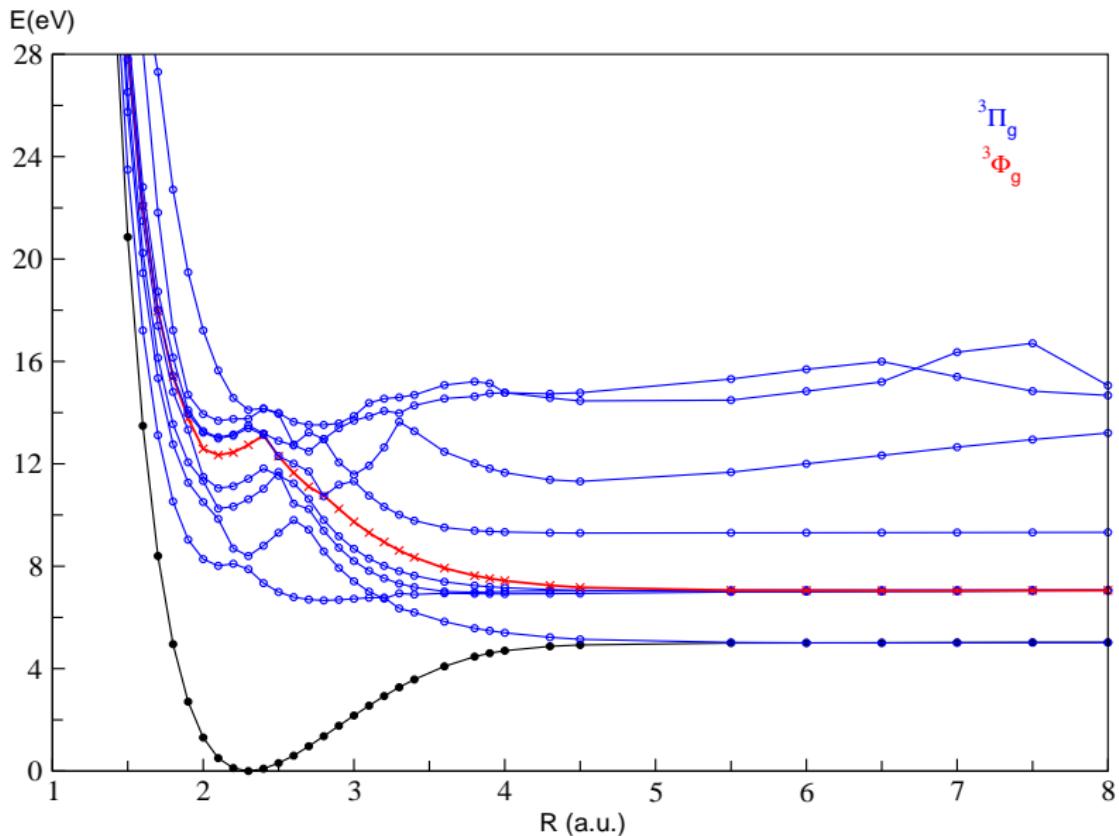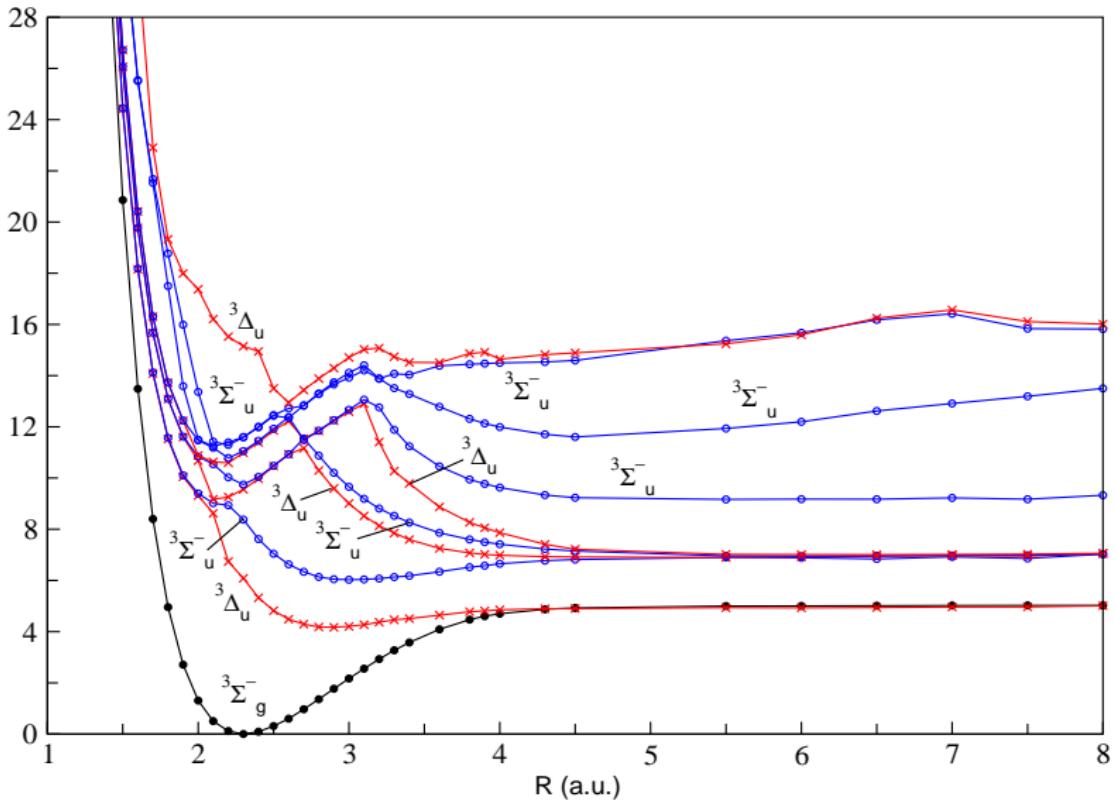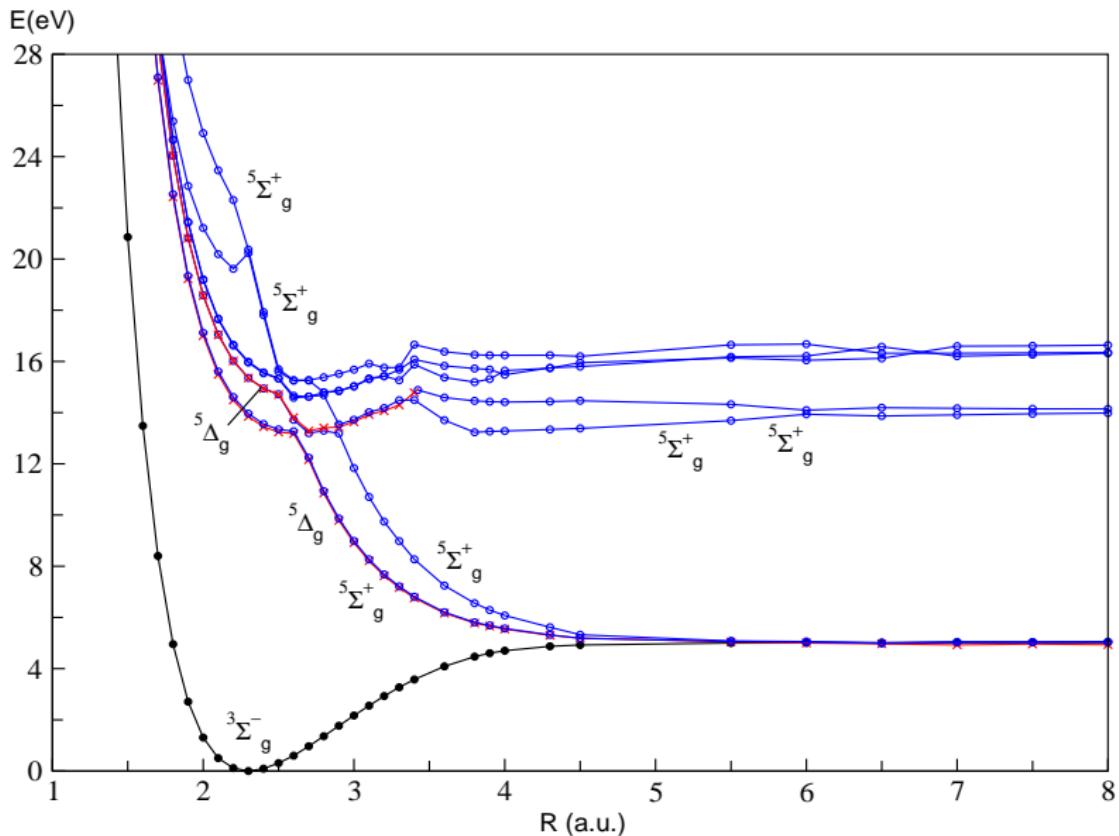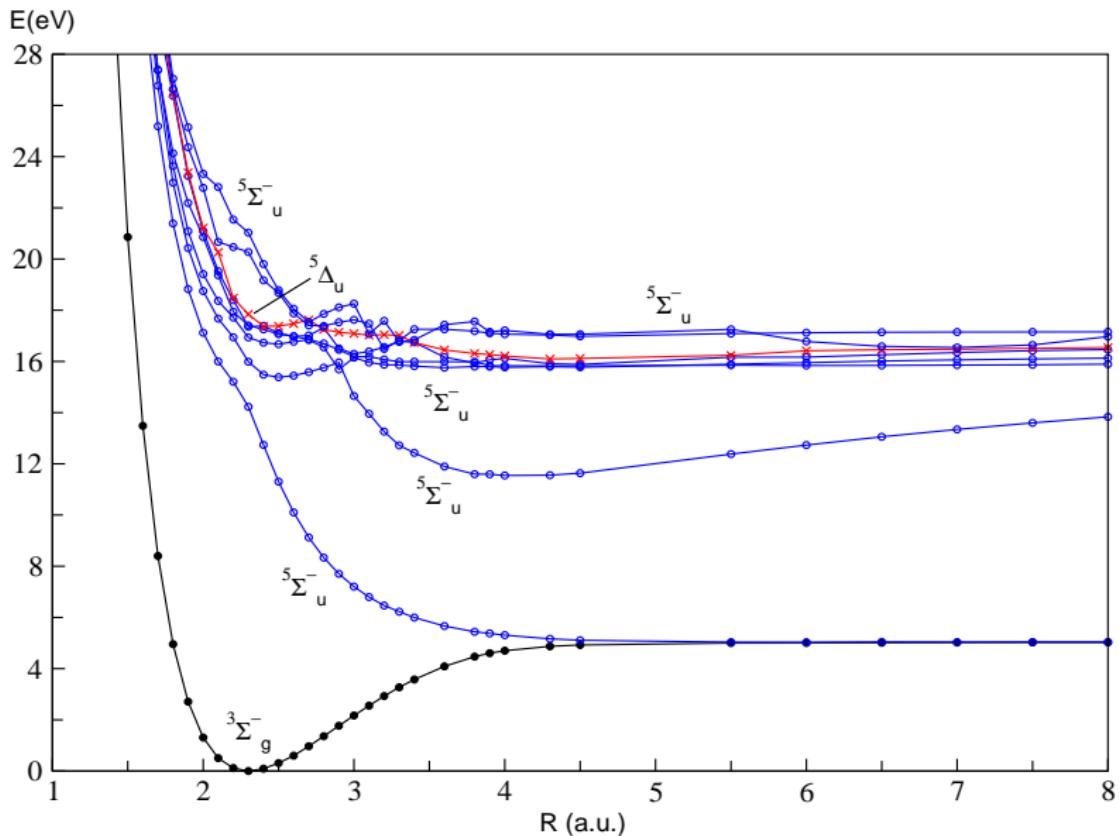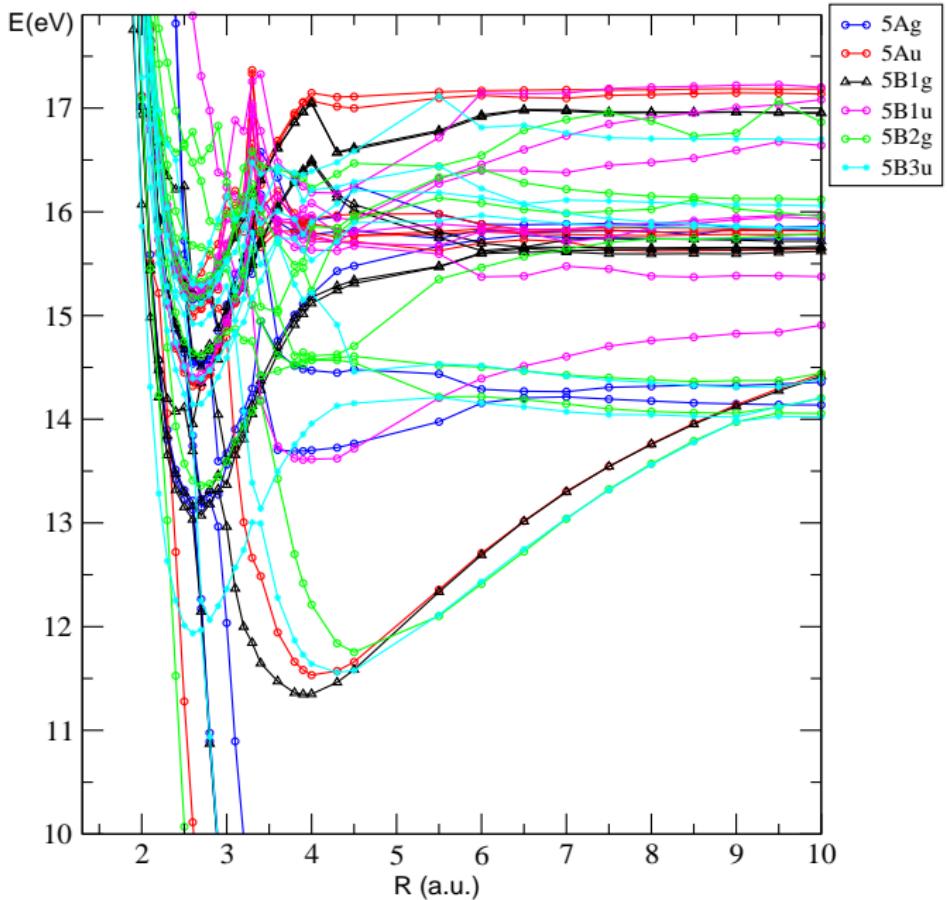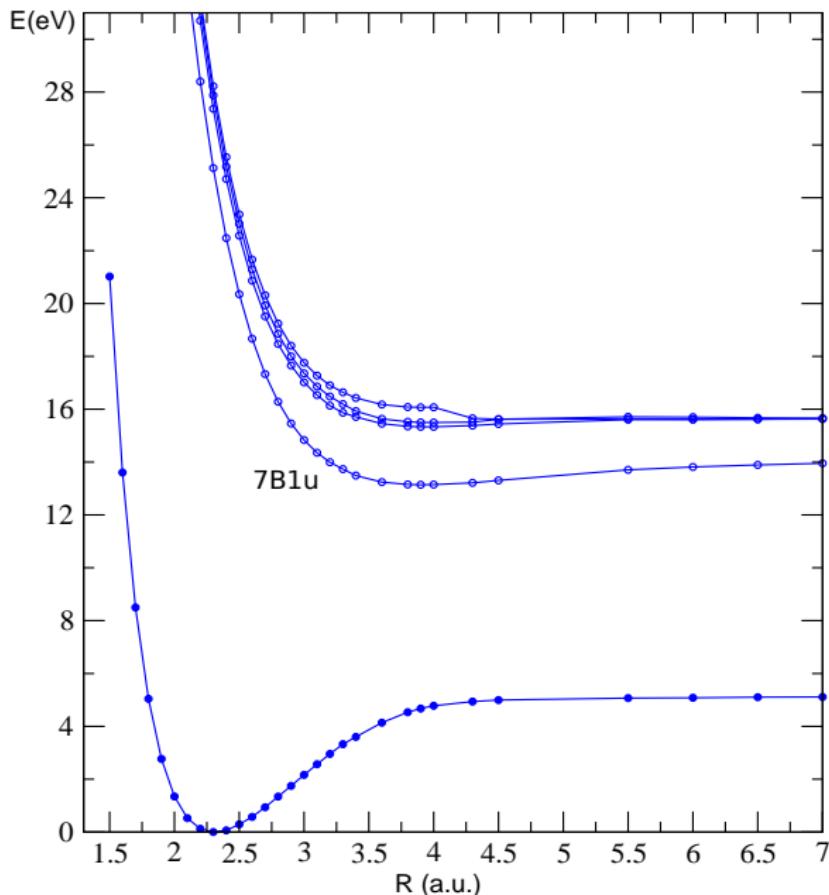
The 7B1u has a well of ~ 0.5 eV

It is somewhat unexpected since the high-multiplicity states are most often unbound

Molecular states correlating to the lowest dissociation limits of O_2^+, along with their respective dissociation energies.[a]

Molecular states	Number of states	Limit	Dissociation energy, D(eV)[a]
$^2[\Sigma^+, \Pi]_{g,u}$	4	$O^+(^2P)+O(^1S)$	27.940
$^{2,4,6,8}[\Sigma^+]_{g,u}$	8	$O^+(^4S)+O(^5S)^b$	27.879
$^2[\Sigma^-, \Pi, \Delta]_{g,u}$	6	$O^+(^2D)+O(^1S)$	26.246
$^2[\Sigma^+(2), \Sigma^-, \Pi(3), \Delta(2), \Phi]_{g,u}$	18	$O^+(^2P)+O(^1D)$	25.717
$^2[\Sigma^+(2), \Sigma^-(3), \Pi(4), \Delta(3), \Phi(2), \Gamma]_{g,u}$	30	$O^+(^2D)+O(^1D)$	24.024
$^{2,4}[\Sigma^+, \Sigma^-(2), \Pi(2), \Delta]_{g,u}$	24	$O^+(^2P)+O(^3P)$	23.750
$^4[\Sigma^-]_{g,u}$	2	$O^+(^4S)+O(^1S)$	22.923
$^{2,4}[\Sigma^+(2), \Sigma^-, \Pi(3), \Delta(2), \Phi]_{g,u}$	36	$O^+(^2D)+O(^3P)$	22.057
$^4[\Sigma^-, \Pi, \Delta]_{g,u}$	6	$O^+(^4S)+O(^1D)$	20.700
$^{2,4,6}[\Sigma^+, \Pi]_{g,u}$	12	$O^+(^4S)+O(^3P)$	18.733

[a] Energies are referred with respect to $O_2(X^3\Sigma_g^-, v'' = 0)$.

[b] The O fragment is excited in the 3s Rydberg state converging to $O^+(^4S)$.
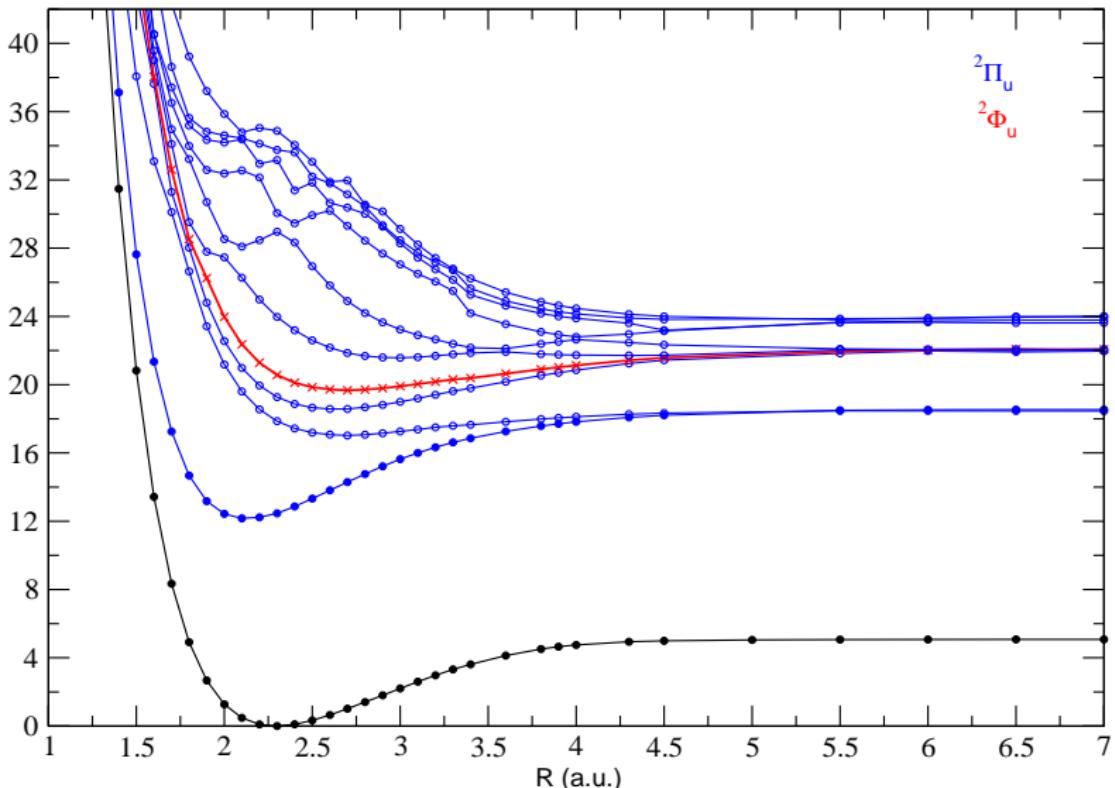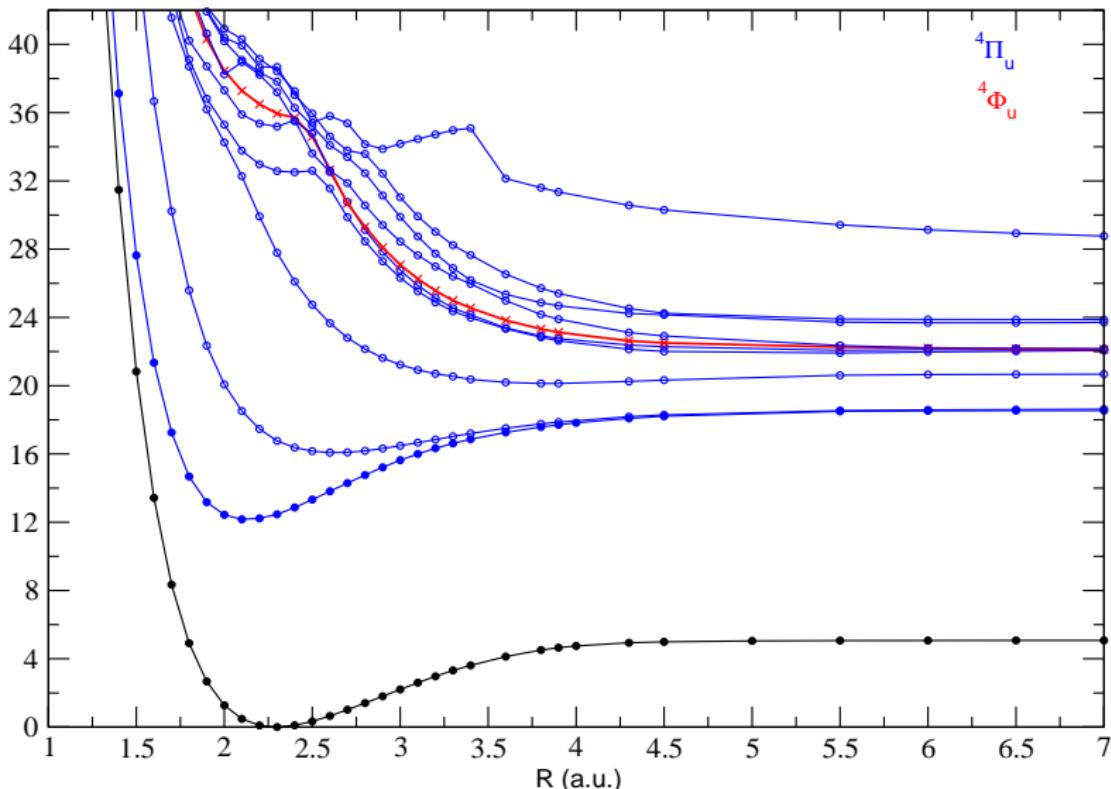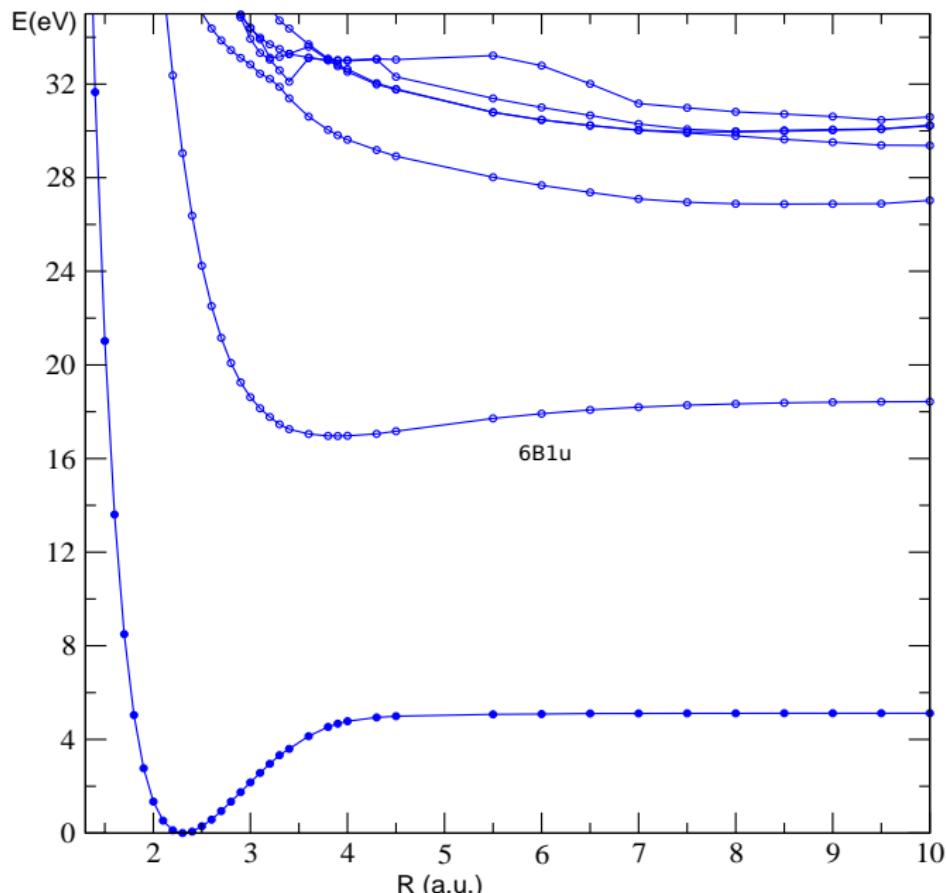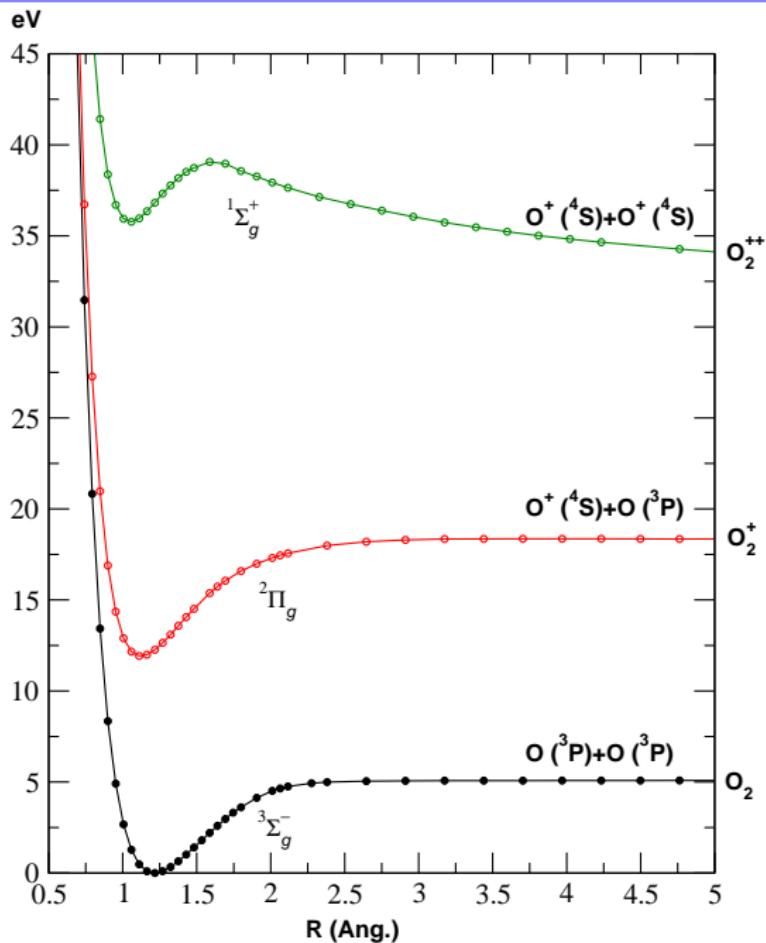
- Fairly high excitation energies (XUV, $\Delta E \gtrsim 12\,\text{eV}$)
- Numerous electronic states, mostly R-states, densely packed
- Overlap of rovibronic levels of various O_2^{**} R–states converging to different ionization limits
- Many possible perturbations/interactions
- Several relaxation processes of O_2^{**}
- Competition autoionization *vs* predissociation (and fluorescence)

$\Rightarrow$ O_2^{**} states difficult to compute ab–initio

No calculations of M** available !

QDT describes well high–n M** R-states, but not those with low–n n=3,4,5
which mix strongly with valence states.

- Region 865–790 Å fit for the study of O_2^{**} states
- At lower energies ($E \leq 14.33$ eV) absorption bands strongly perturbed (irregular vibrational spacings)
- At higher E's ($15.69 \leq \Delta E \leq 16.53$ eV) ($790 \, \text{Å} \geq \lambda \geq 750 \, \text{Å}$)
  severe overlap of various R–progressions
  (prevents detailed analysis/interpretation)
- Region 14.26–15.20 eV lends itself to study O_2^{**} states

$\Rightarrow$ bands display fairly regular spacings/structure, enabling assignments/interpretation of absorption spectrum and of underlying (competing) decay process, i.e., autoionization, predissociation
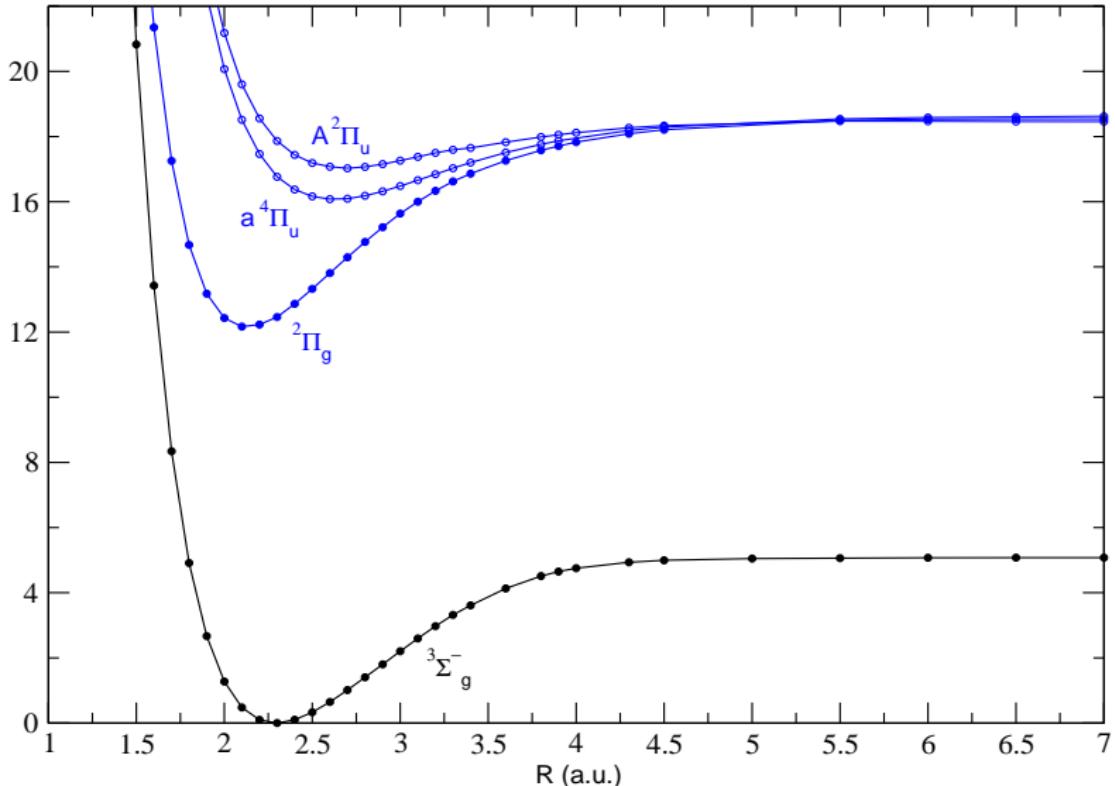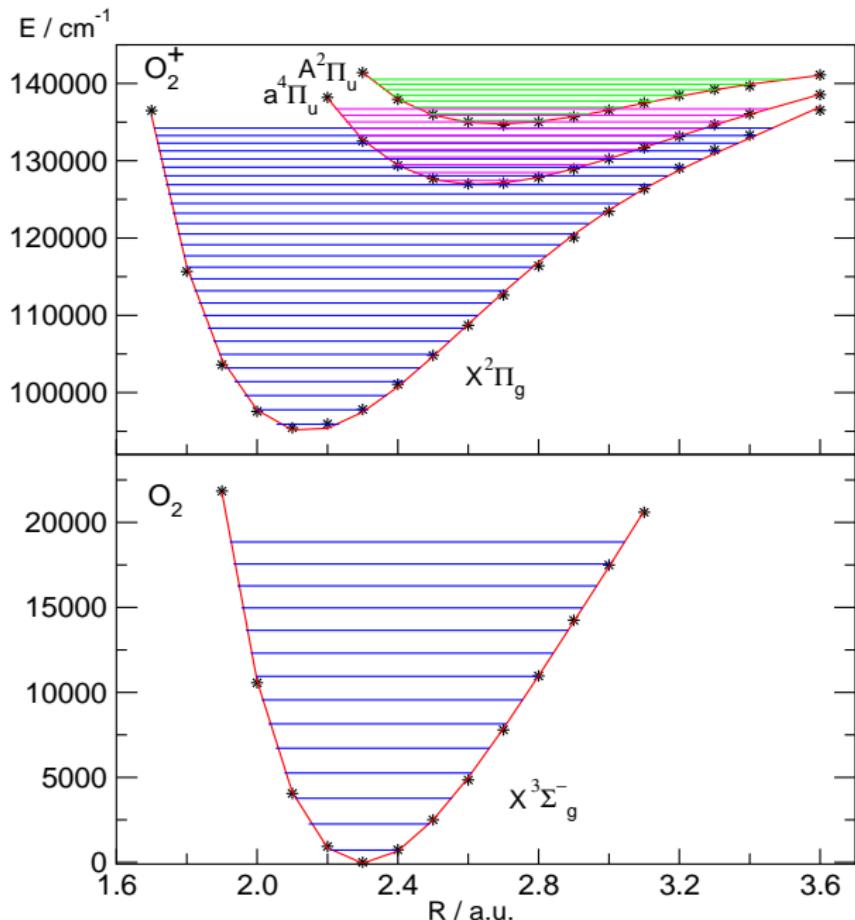
Spectroscopic constants of selected states of O_2 and O_2^{+} [a].

State	AIE eV	VIE eV	r_e Å	ω_e cm^{-1}	B_e cm^{-1}	D_e eV
$A^2\Pi_u$	4.99		1.4090 (1.419)	898 (913)	(1.046)	1.76 (1.45)
$a^4\Pi_u$	4.09		1.3814 (1.389)	1036 (1060)	(1.092)	2.69 (2.54)
$X^2\Pi_g$	0.00		1.1164 (1.132)	1905 (1895)	(1.645)	6.78 (6.36)
$X^3\Sigma_g^{-}$	0.00		1.2075 (1.216)	1580.2 (1564)	(1.424)	5.21 (5.09)

[a] Theoretical values in parenthesis.
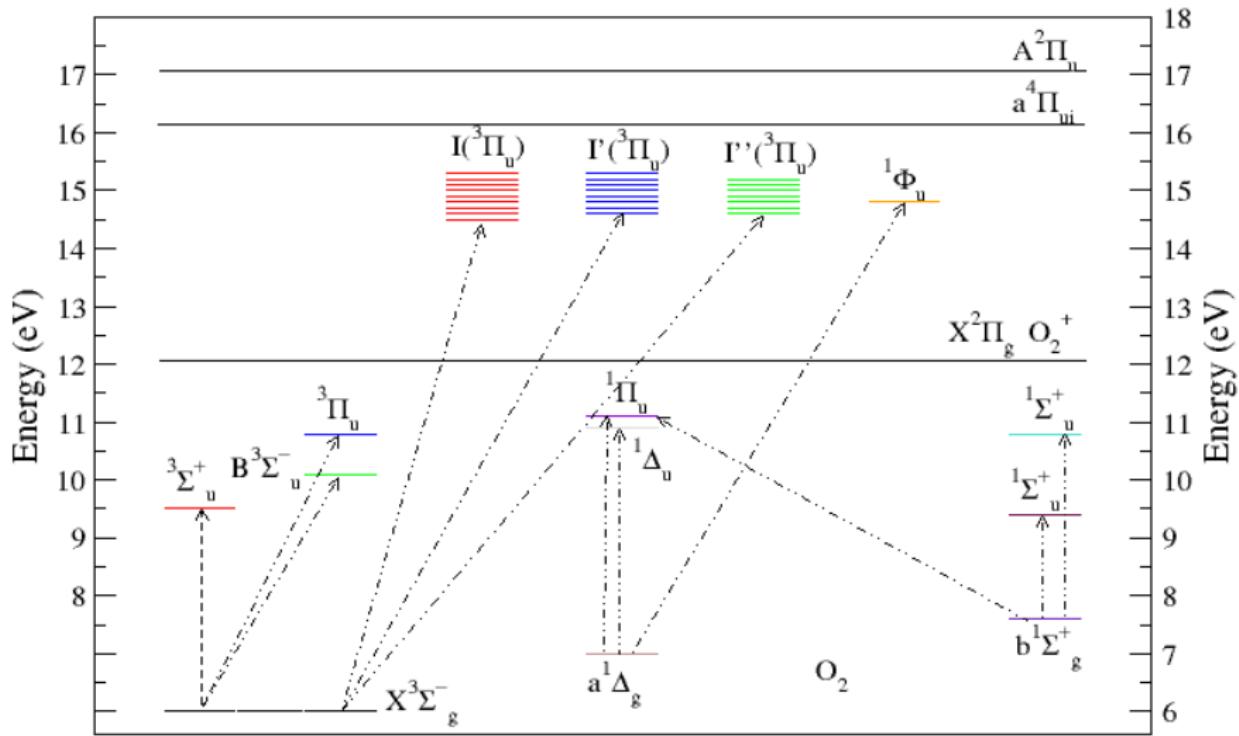
Spectroscopic constants of the I, I′ and I″
$^3\Pi_u$ states of $^{16}O_2$.

State	T_e eV	ω_e cm^{-1}	$\omega_e x_e$ cm^{-1}	B_e cm^{-1}
$A^2\Pi_u$	17.10?	913		1.046
$a^4\Pi_u$	16.137	1035.69	10.39	
$I''^3\Pi_u$	14.646	1035	10.8	
$I'^3\Pi_u$	14.609	1046.2	11.0	
$I^3\Pi_u$	14.439	1049	11.5	
$J^3\Pi_u$				
$H^3\Pi_u$				
....				
$X^2\Pi_g$	12.074	1895		1.645
....				
$X^3\Sigma_g^-$	0.000	1564		1.424

Authors	Year	I	I′	I″	Argument
Katayama & Tanaka[1]	1981	$4s\sigma_g$	$4d\sigma_g$	$3d\delta_g$	1
Wu[2]	1987	$3d\sigma_g$	$4s\sigma_g$	$3d\delta_g$	2
Čubrič et al.[3]	1993	$4s\sigma_g$	$3d\delta_g$	$3d\sigma_g$	3
Demekhin et al.[4]	2010	$4s\sigma_g$	$3d\delta_g$	$3d\sigma_g$	4

[1]QDs O_2 united–atom orbitals; [2]QD analysis; [3]Autoionization dynamics of SO levels of I–states; [4]Computed single–electron energies of Rydberg electrons.

$\Rightarrow$ Disagreement on the nature of the Rydberg orbital in the I–states.

Has this question been settled ?

- A comprehensive ab–initio study of many electronic states of O_2, O_2^+ and O_2^{++} is currently underway
- PECs of about 150 electronic states of O_2, 100 of O_2^+, and 20 of O_2^{++}
- Valence, Rydberg, ion–pair, cationic states
- Spectroscopic constants ($T_e, T_v, \omega_e, \omega_e x_e, B_e, D_e, D_0, \mu$–functions, IP's, EA, etc.)
- The calculation revealed a rich electronic structure most notably for the high–spin states
- We plan to make an update of the spectroscopic data of O_2 and O_2^+ with our computed PECs as framework
- We did not compute the O_2^{**} R–states (e.g., H, J, I, I', I'') in the first attempt. We'll try again !

  $\Rightarrow$ A lot of work ahead ...

Acknowledgements

THANK YOU FOR YOUR ATTENTION . . .