Halogen-Containing Molecules Studied with Cutting-Edge Relativistic Correlation Methods

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I. Introduction

The Problem

Quantum-chemical study of Br_2 double photoionization

Process: $Br_2 \xrightarrow{h\nu} Br_2^{2+}$, various ionization types

Double photon ionization spectra recorded (e.g. for I_2^{2+})[1] by TOF-PEPECO

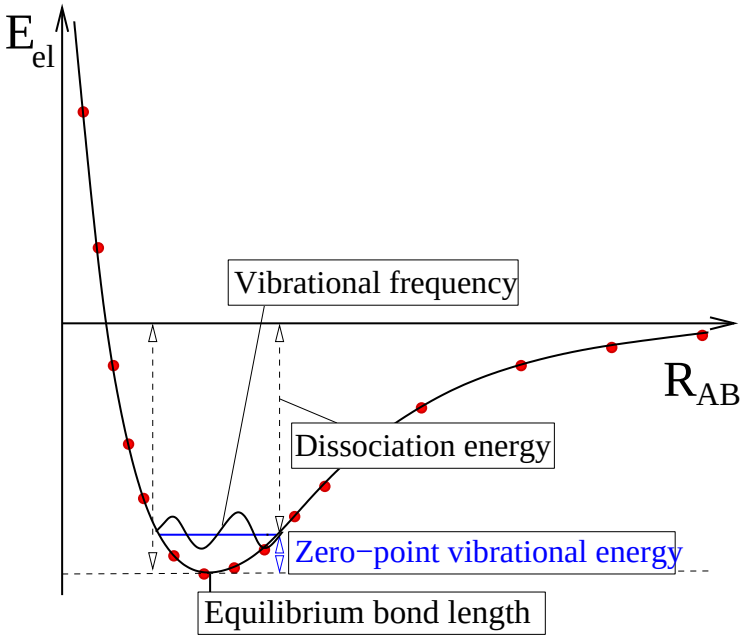
Goals:

- Assessment of accuracy:
  Calibration and benchmarks

- Simulation of photoelectron spectrum

  Single-point calculations
  PECs of Br_2^{2+} and Br_2

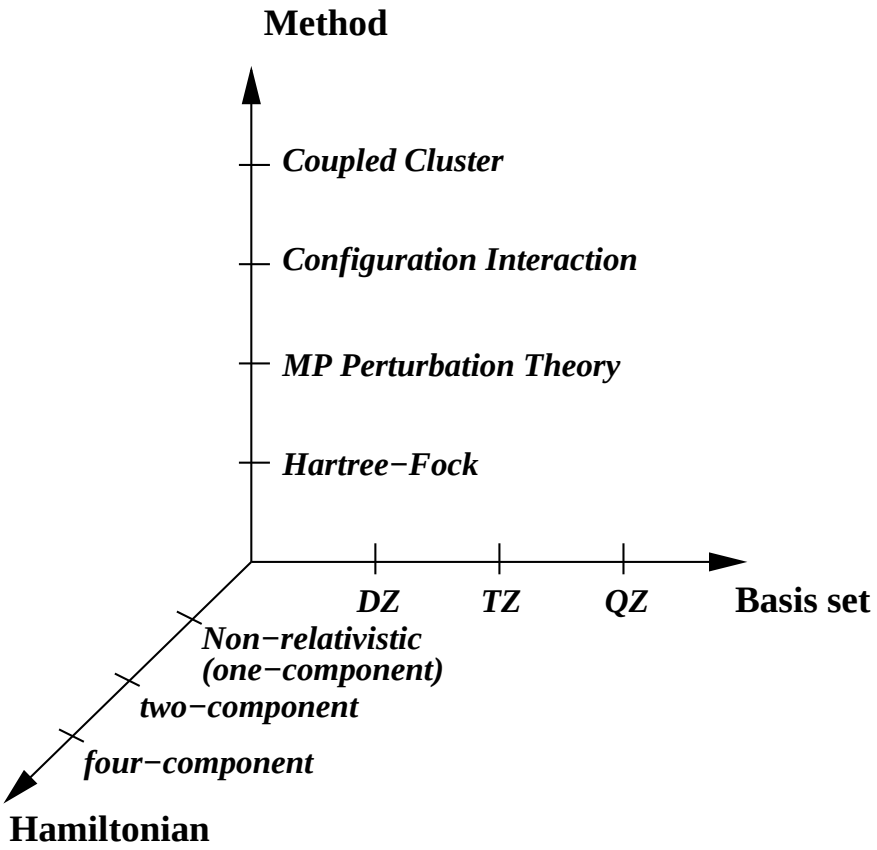
  $\longrightarrow$ R_e, ω_e, D_e, $T_{e,v}$, FCFs



[1] D. Edvardsson, A. Danielsson, L. Karlsson, J.H.D. Eland, Chem Phys **324** (2006) *674*

II. Relativistic Methodology

General Aspects



- **Electron Correlation:**
  Multi-reference approaches, Coupled Cluster and Configuration Interaction models

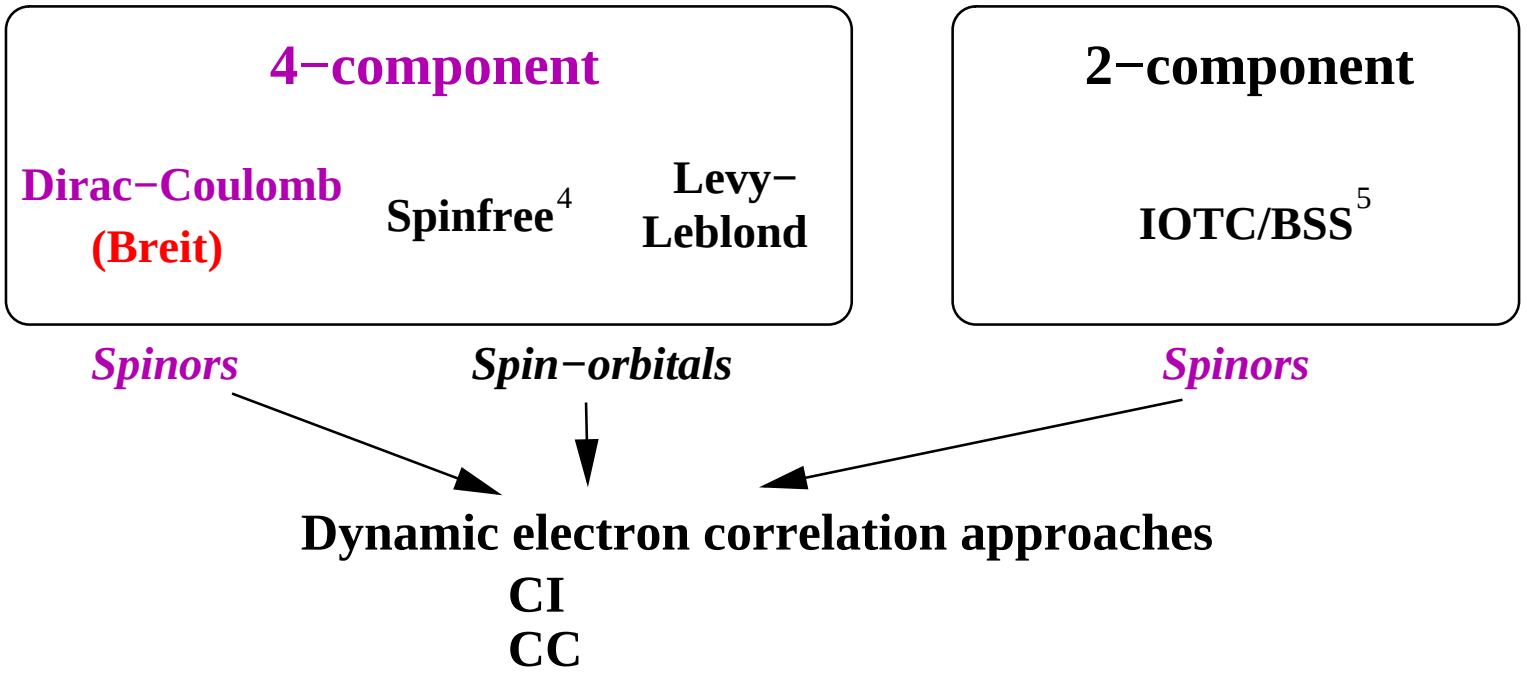
- **Basis set expansion:**
  Uncontracted one-particle basis sets

- **Hamiltonian:**
  4-Component Relativistic Hamiltonian

$\longrightarrow$ Various models in direct comparison

II. Relativistic Methodology

Hamiltonians



Spinors:

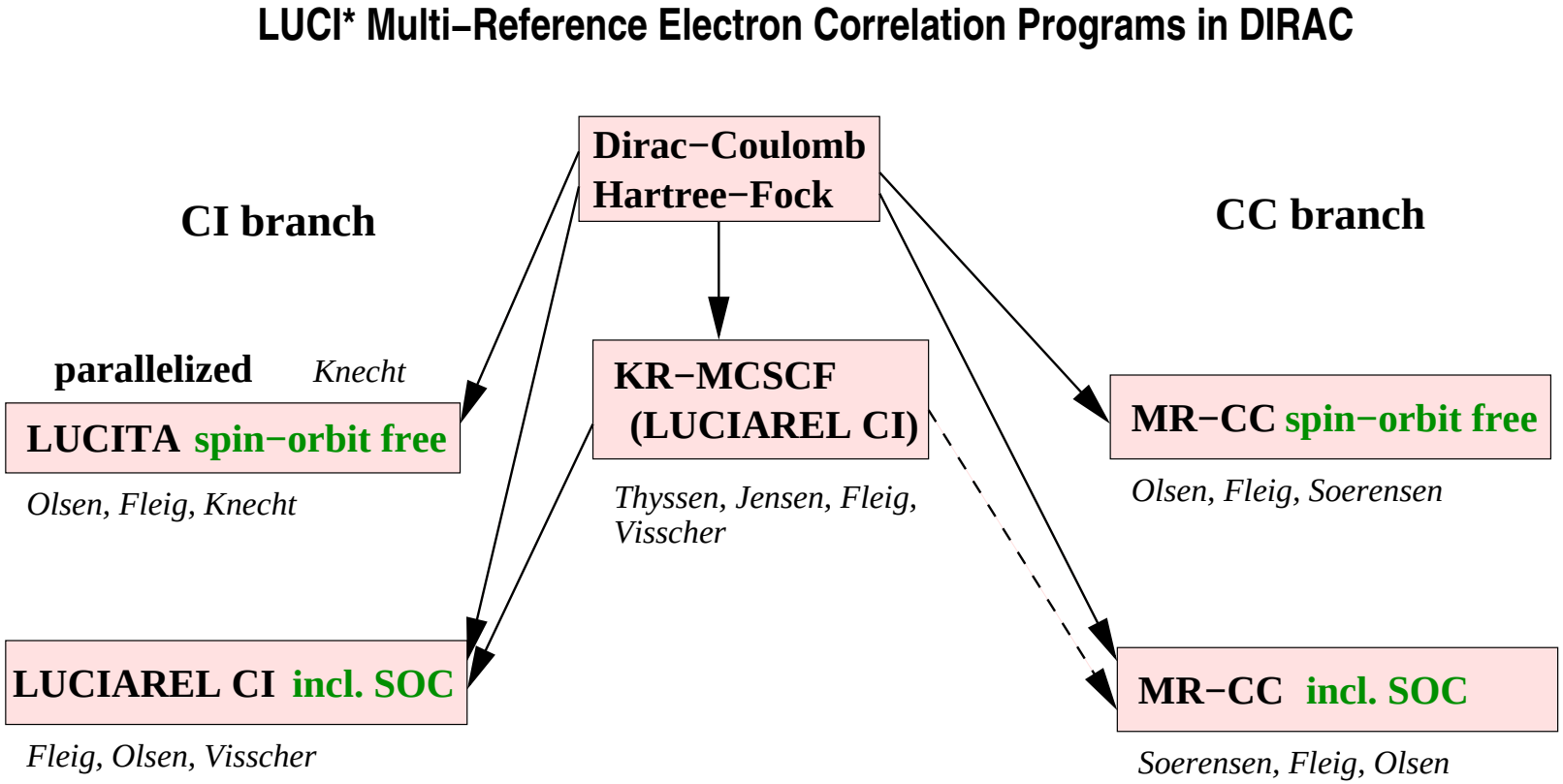
- Rigorous treatment of spin-orbit interaction
- Shorter correlation expansions[2]

[2] T. Fleig, J. Olsen, L. Visscher, J Chem Phys **119** (2003) 2963

[4] K.G. Dyall, J Chem Phys **100** (1994) 2118

[5] M. Ilias, H.J.Aa. Jensen, Implementation in DIRAC package, to be published.

II. Relativistic Methodology[5 6 7 8 9 10] : Overview



[5] T. Fleig, L. Visscher, Chem Phys **311** (2005) *113*

[6] T. Fleig, J. Olsen, L. Visscher, J Chem Phys **119** (2003) *2963*

[7] J Thyssen, H. J. Aa. Jensen, T. Fleig, J Chem Phys (2006) submitted, under revision.

[8] T. Fleig, H. J. Aa. Jensen, J. Olsen, L. Visscher, J Chem Phys **124,10** (2006) *104106*

[9] T. Fleig, L. K. Sørensen, J. Olsen, Theo Chem Acc (2007), *DOI 10.1007/s00214-007-0265-y*.

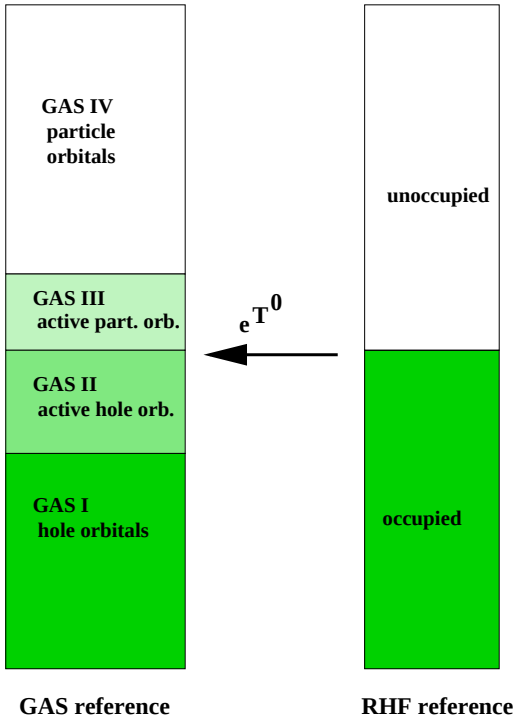
[10] L. K. Sørensen, T. Fleig, J. Olsen, Chem Phys Lett (2007), to be submitted.

II. Relativistic Methodology

The Multi-Reference Coupled Cluster Approach

State-Selective (SS) GAS MRCC Method[11]

- Extended excitation manifold
  $\langle \mu_{\mathrm{MR}}| = \langle \mathrm{RHF}|\, \hat{\tau}_0^\dagger$
  $\langle \mu_{\mathrm{SSCC}}| = \langle \mu_{\mathrm{MR}}| \left\{ \hat{\tau}_{\mu_1}^\dagger, \hat{\tau}_{\mu_2}^\dagger, \ldots, \hat{\tau}_{\mu_N}^\dagger \right\}$
- Higher excitations included, e.g. in MRCCSD
  $\langle \mu_{\mathrm{SSCCSD}}| = \langle \mu_{\mathrm{MR}}| \left\{ \hat{\tau}_{\mu_1}^\dagger, \hat{\tau}_{\mu_2}^\dagger \right\}$
  contains some Q excitations
- GAS expansion (formally) replaces single-determinant reference
  $|\mathrm{SSCC}\rangle = e^{\sum_\mu t_\mu^i \hat{\tau}_\mu^i} |\mathrm{GAS}\rangle$



State-selective: memory of original reference state

[11] J. Olsen, J Chem Phys **113** (2000) 7140

III. Calibration and Benchmarks

Features of HBr

T. Fleig, L. K. Sørensen, J. Olsen, Theo. Chem. Acc. **(2007)** *DOI 10.1007/s00214-007-0265-y*

Problem:

- Influence of SO interaction on ground-state spectral constants
- Molecular dissociation with/without multi-reference Ansatz
- Effect of higher excitations (than CC doubles)

Setup

- Uncontracted cc-pVDZ/cc-pVTZ basis sets, cutoff 10 a.u.
- Dirac-Coulomb/Spinfree Hamiltonian
- Correlated orbitals: $\sigma_{sp}, 2\pi, \sigma^*_{sp}$ (6 el.), + Br $4s$ (8 el.)
- CCSD (6/8), Single Reference (SR) and Multi Reference (MR) CI/CC
- MR space: CAS 6/8 in 4 orbitals/Kramers pairs

III. Calibration and Benchmarks

Features of HBr

Method	R_e [Å]	ω_e [cm^{-1}]	D_e [eV]
DZ SOF CCSD (6)	1.4148	2705.7	4.19
DZ SOF MRCISD (6)	1.4164	2693.7	3.86
DZ SOF MRCCSD (6)	1.4162	2691.1	3.88
DZ SO CCSD (6)	1.4153	2697.8	4.05
DZ SO CCSDT (6)	1.4159	2690.8	3.74
DZ SO MRCISD (6)	1.4173	2678.7	3.72
DZ SO MRCCSD (6)	1.4173	2685.2	3.73
TZ SOF MRCISD (6)	1.4145	2675.1	4.04
TZ SOF MRCCSD (6)	1.4148	2675.1	4.05
TZ SO MRCISD (6)	1.4151	2668.4	3.90
TZ SO MRCCSD (6)	1.4154	2668.0	3.90
TZ SOF MRCISD (8)	1.4180	2641.4	3.90
TZ SOF MRCCSD (8)	1.4192	2637.1	3.90
TZ SOF CCSDT (8)	1.4178	2647.3	3.96
TZ SO MRCISD (8)	1.4187	2634.9	3.77
TZ SO MRCCSD (8)	1.4192	2635.9	
TZ SOF CCSDT (18)	1.4142	2663.9	4.01
Exp.[12]	1.4144	2649.0	3.92

Some basis set dependence

CC correlation:

Bond length: -0.004 Å

Frequency: $+17$ cm^{-1}

D_e: $+0.05$ eV

Two bromine atoms ?

III. Calibration and Benchmarks

Ground State of Br_2

		R_e [a.u.]	ω_e [cm^{-1}]
DZ SO MRCI	(CV 4s CAS)	4.447	282.7
TZ SOF MRCI	(CV 4s CAS)	4.375	308.0
TZ SO MRCI	(CV 4s CAS)	4.380	306.3
TZ SOF MRCI	(CV 3d,4s CAS)	4.359	311.4
TZ SOF MRCC	(CV 3d,4s CAS)	4.356	315.8
TZ SOF MRCC	(CC 3d,4s CAS)	4.357	312.7
ANO-RCC SOF MRCC	(CV 3d,4s CAS)	4.319	326.8
Experiment		4.311	325.3

Some important conclusions:

- DC Hamiltonian is precise
- SOC has small influence (closed shell state)
- Core correlation has moderate effect
- Basis set error surpasses all

Spectrum of the Br_2^{2+} cation; qualitatively

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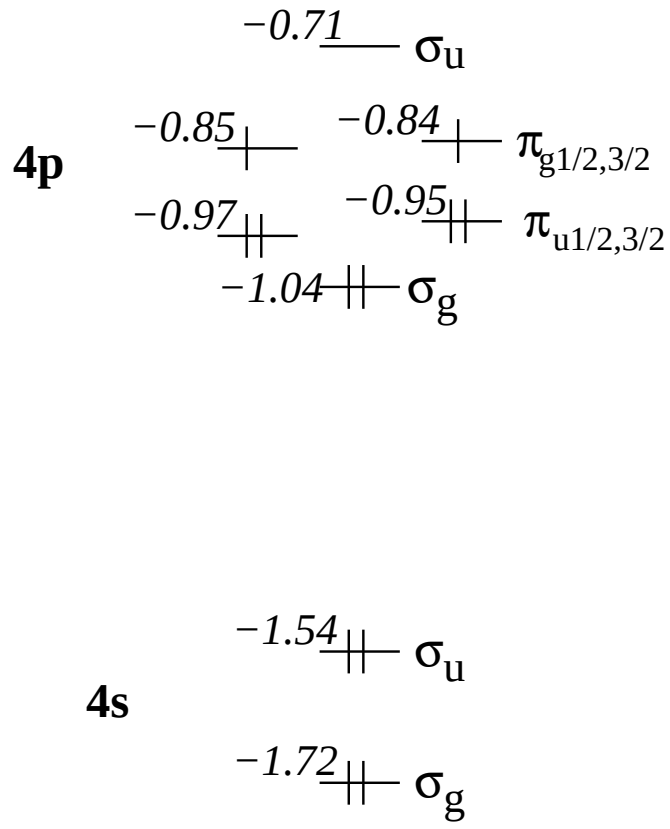
DCHF: 4p averaged

aDZ basis set



Valence excited-state manifolds:

π_g^2:
0g,2g,1g,0g

$\pi_u^1\ \pi_g^1$:
0u,0u,1u,1u,2u,2u,3u,...

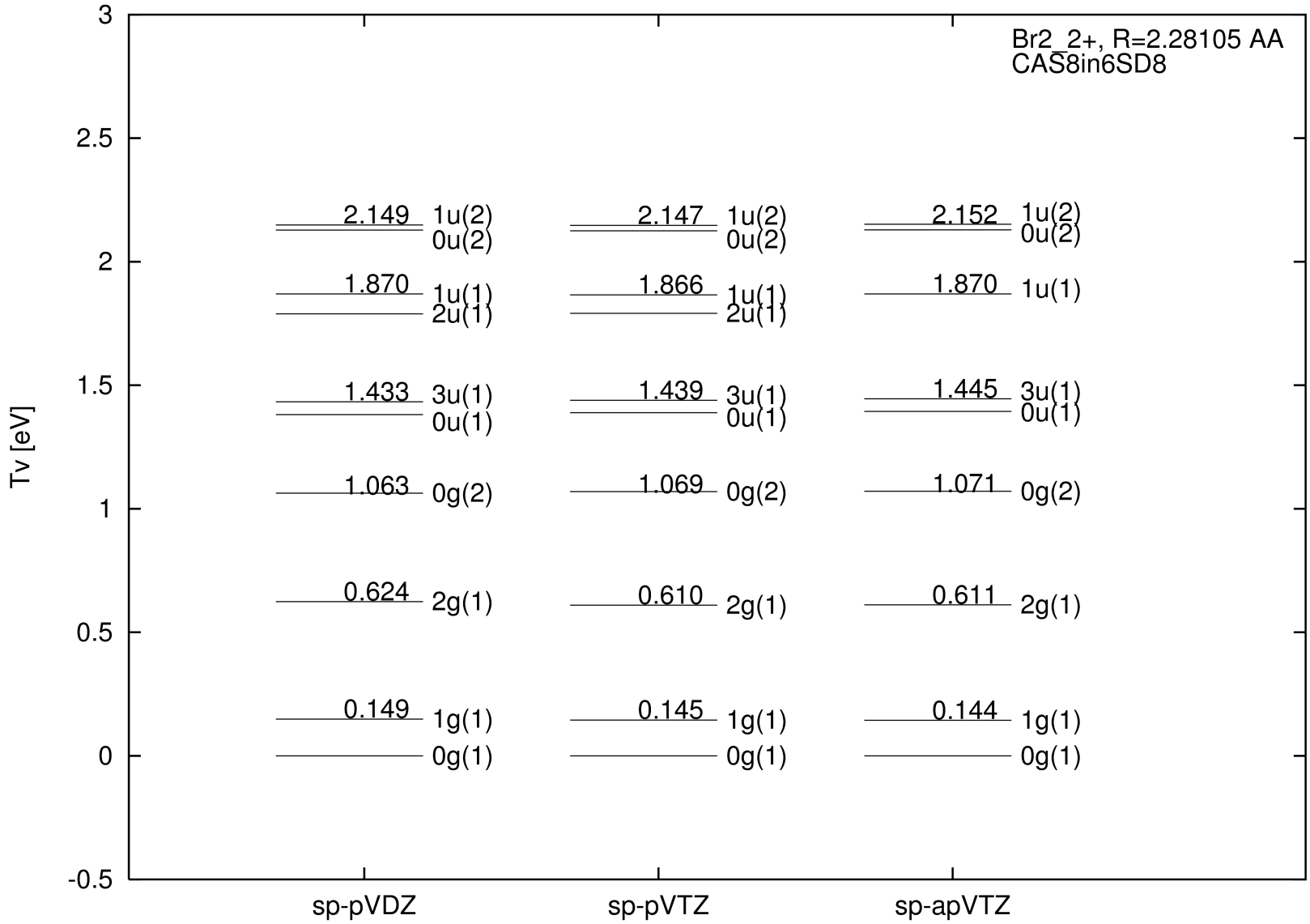
$\pi_g^1\ \sigma_u^1$:
0u,0u,...

$\pi_u^1\ \sigma_u^1$:
0g,0g,1g,1g,1g,2g,2g,3g,...

...

III. Calibration and Benchmarks

Br_2^{2+}: Basis set effects



III. Calibration and Benchmarks

Br_2^{2+}: Basis set effects, 4c spin-orbit free

MRCI, CAS8in6, SD8

	T_v [eV], 2.28105 Å	
Λ S state	aDZ	ANO-RCC
$^3\Sigma_u^+$	3.31	3.31
$^3\Pi_u$	2.70	2.87
$^3\Delta_u$	1.62	1.63
$^1\Sigma_u^+$	1.47	1.49
$^1\Sigma_g^+$	0.76	0.77
$^1\Delta_g$	0.43	0.46
$^3\Sigma_g^-$	0.00	0.00

Some important conclusions:

- Most errors < 0.03 eV
- Spin-orbit interaction:

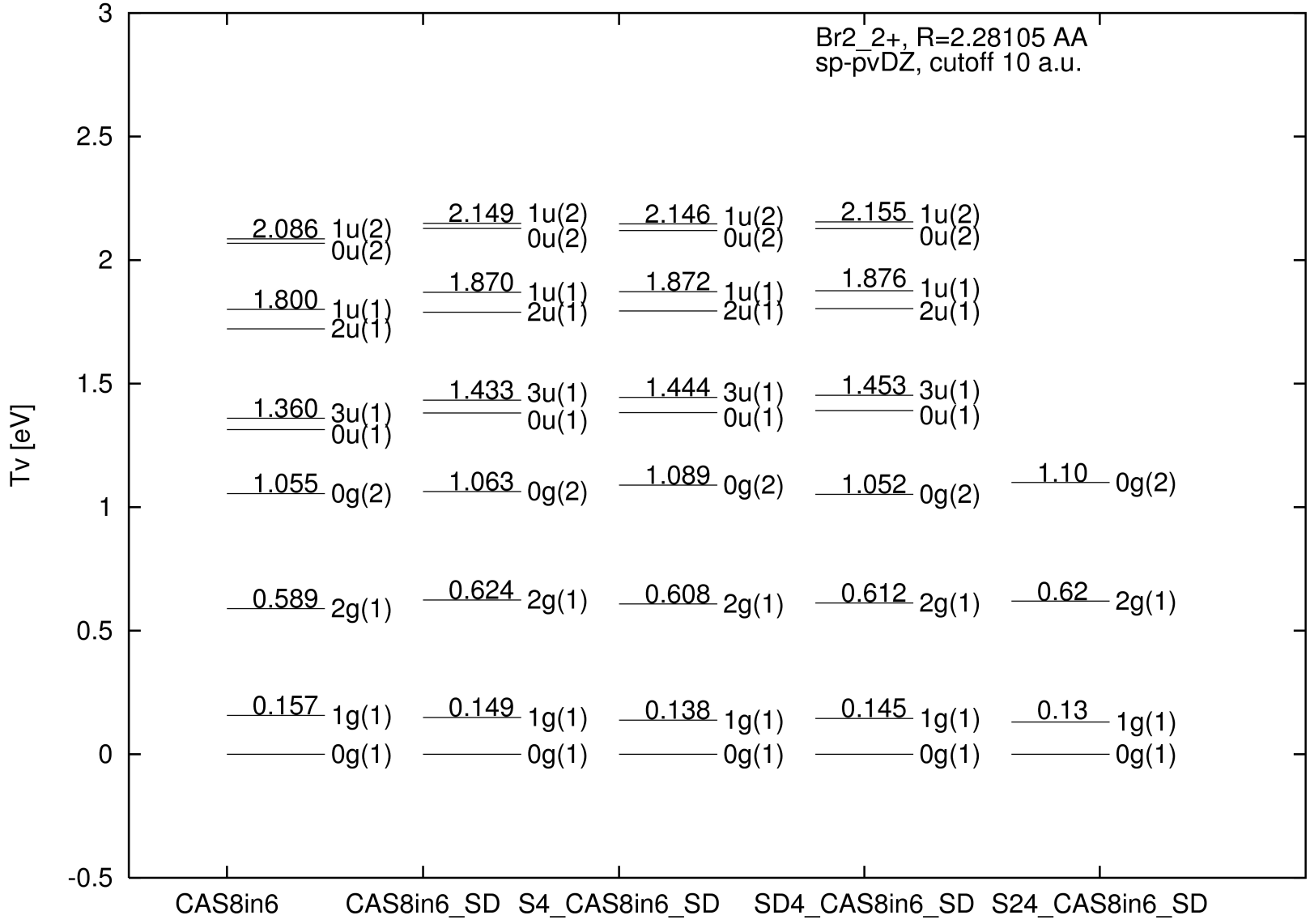
  1^{st} order:
  $^3\Delta_{3,2,1}$, $^3\Pi_{2,1,0}$: ≈ 0.5 eV

  2^{nd} order:
  $^1\Delta_2$, $^3\Sigma_{1,0}$: ≈ 0.2 eV

- A smaller basis set suffices for (vertical) excitation energies

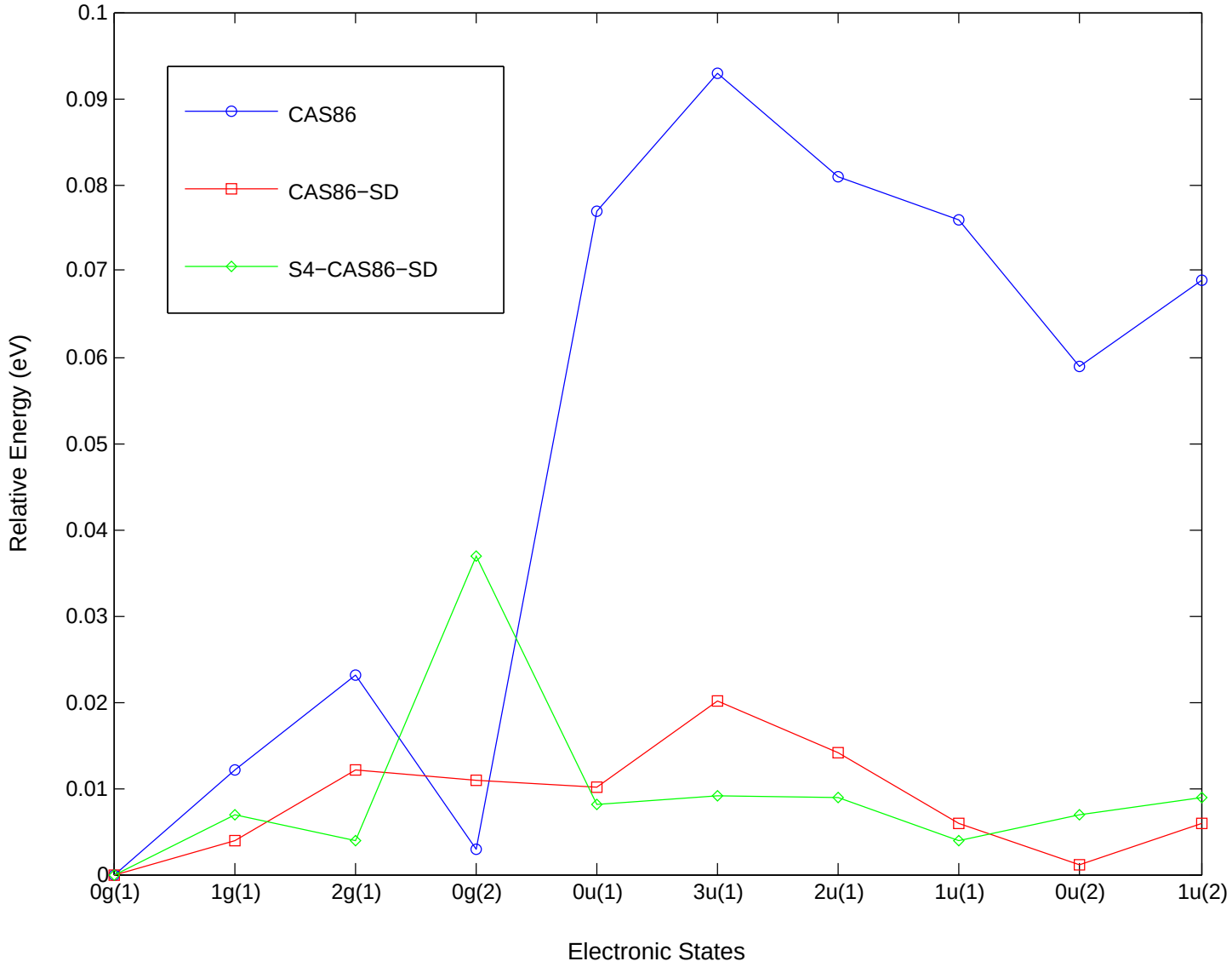
III. Calibration and Benchmarks

Br_2^{2+}: Correlation effects



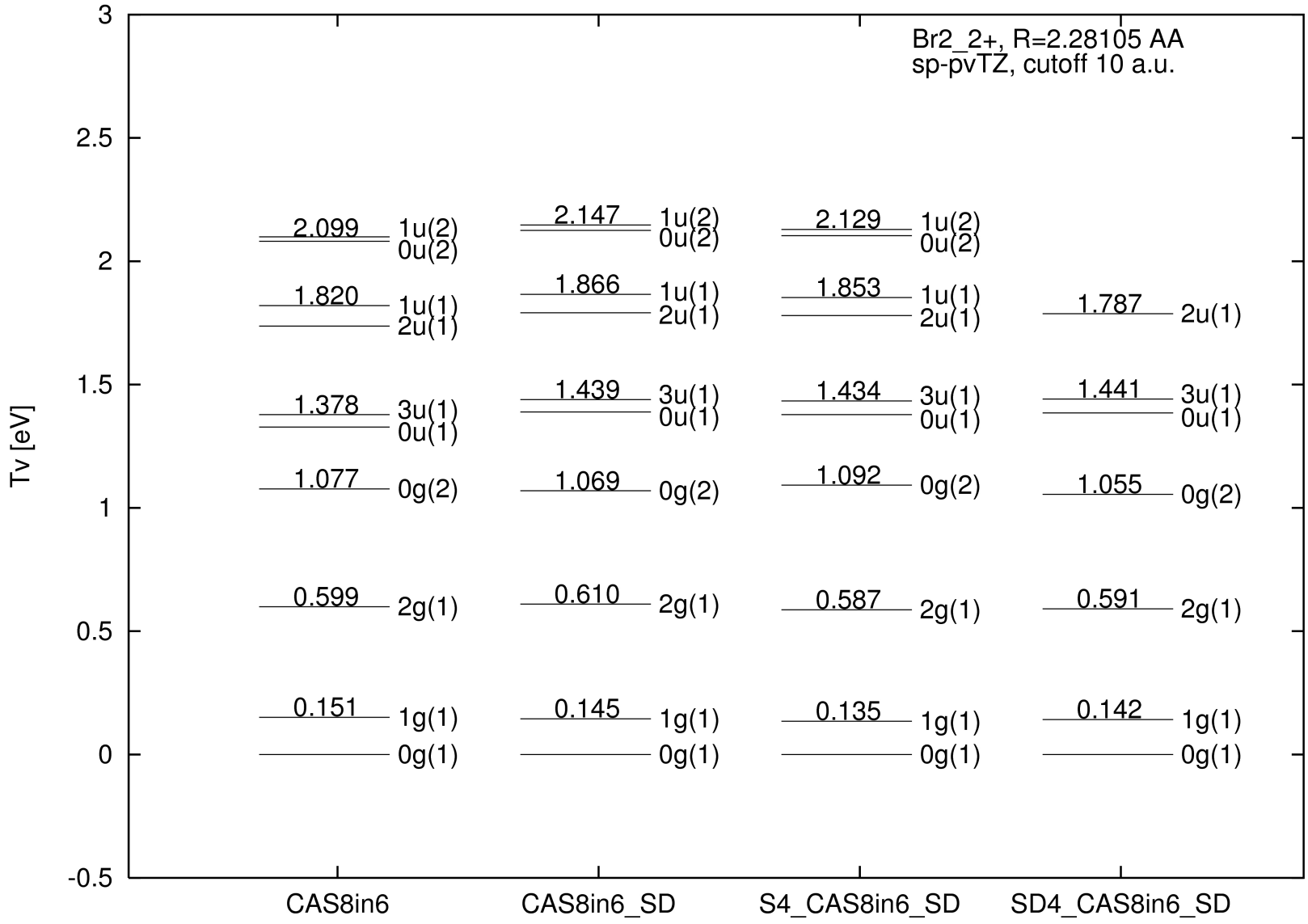
III. Calibration and Benchmarks

Br_2^{2+}: Differential correlation errors



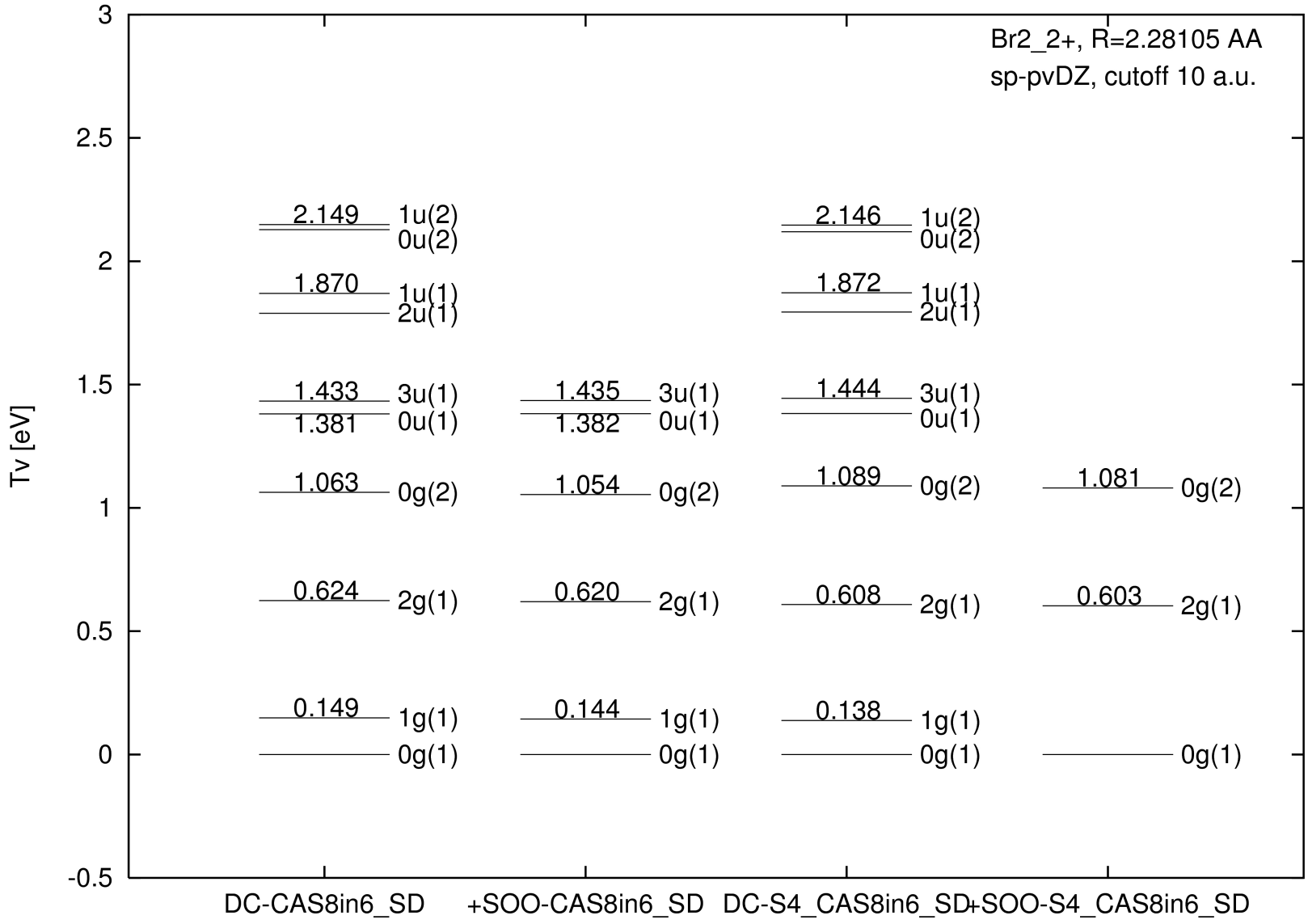
III. Calibration and Benchmarks

Br_2^{2+}: Correlation effects, aTZ basis



III. Calibration and Benchmarks

Br_2^{2+}: 2-Electron SOO terms



IV. Results

Br_2^{2+}: Vertical spectrum, CAS 8in6 SD

T_v [eV]	Omega/Symm.	Configuration(s)	Ionization type
2.994	2u	$0.87\pi^1_{g3/2}\sigma^1_u - 0.26\pi^1_{u1/2}\pi^1_{u3/2}\pi^1_{g1/2}\sigma^1_u$	
2.781	1u	$-0.71\pi^1_{g1/2}\sigma^1_u + 0.46\pi^1_{g3/2}\sigma^1_u$	
2.658	0u	$(0.62 + 0.62)\pi^1_{g1/2}\sigma^1_u$	
2.657	0u	$(-0.62 + 0.62)\pi^1_{g1/2}\sigma^1_u$	
2.133	1u	$(0.90 - 0.32)\pi^1_{u1/2}\pi^1_{g1/2}$	B
2.112	0u	$(0.66 + 0.66)\pi^1_{u1/2}\pi^1_{g1/2}$	B
1.854	1u	$0.65\pi^1_{u3/2}\pi^1_{g1/2} + 0.66\pi^1_{u1/2}\pi^1_{g3/2}$	B
1.774	2u	$0.68\pi^1_{u1/2}\pi^1_{g3/2} - 0.67\pi^1_{u3/2}\pi^1_{g1/2}$	B
1.418	3u	$0.96\pi^1_{u3/2}\pi^1_{g3/2}$	B
1.365	0u	$(0.67 + 0.67)\pi^1_{u3/2}\pi^1_{g3/2}$	B
1.059	0g	$0.81\pi^2_{g3/2} + 0.33\pi^2_{g1/2}$	A
0.622	2g	$0.89\pi^1_{g1/2}\pi^1_{g3/2} - 0.32\pi^1_{u1/2}\pi^1_{u3/2}\pi^2_{g1/2}\pi^2_{g3/2}$	A
0.149	1g	$(0.87 + 0.31)\pi^1_{g1/2}\pi^1_{g3/2}$	A
0.000	0g	$0.84\pi^2_{g1/2} - 0.37\pi^2_{g3/2} - 0.23\pi^2_{u1/2}\pi^2_{g1/2}\pi^2_{g3/2}$	A

IV. Results

Br_2^{2+}: Double Ionization Types

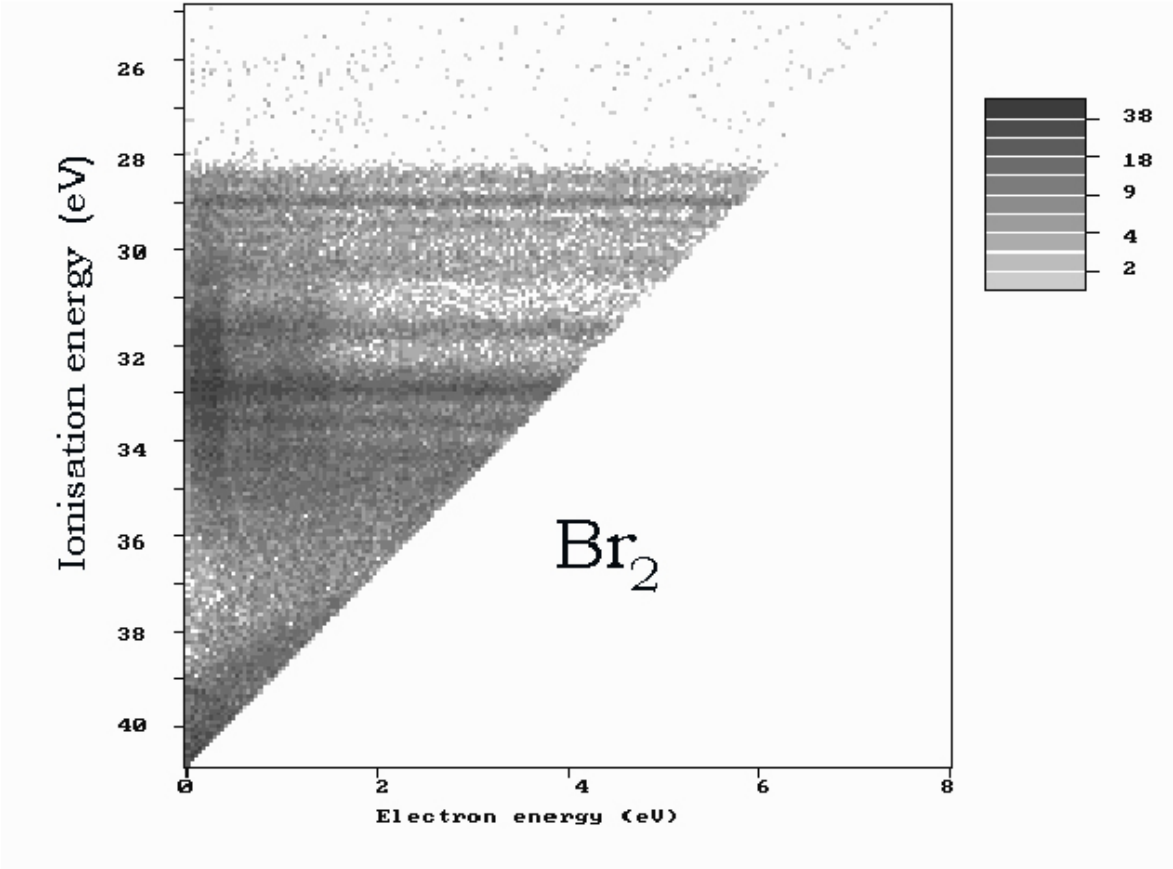
Neutral ground-state configuration: $\sigma_g^2\pi_u^4\pi_g^4$

Removed electrons	Cation configuration	Type
$-\sigma_g^1 - \pi_u^1$	$\sigma_g^1\pi_u^3\pi_g^4$	E
$-\pi_u^2$	$\sigma_g^2\pi_u^2\pi_g^4$	D
$-\sigma_g^1 - \pi_g^1$	$\sigma_g^1\pi_u^4\pi_g^3$	C
$-\pi_g^1 - \pi_u^1$	$\sigma_g^2\pi_u^3\pi_g^3$	B
$-\pi_g^2$	$\sigma_g^2\pi_u^4\pi_g^2$	A

- No further excitation; can be observed experimentally
- Types B,C,D,E yield only excited states of dication

IV. Results

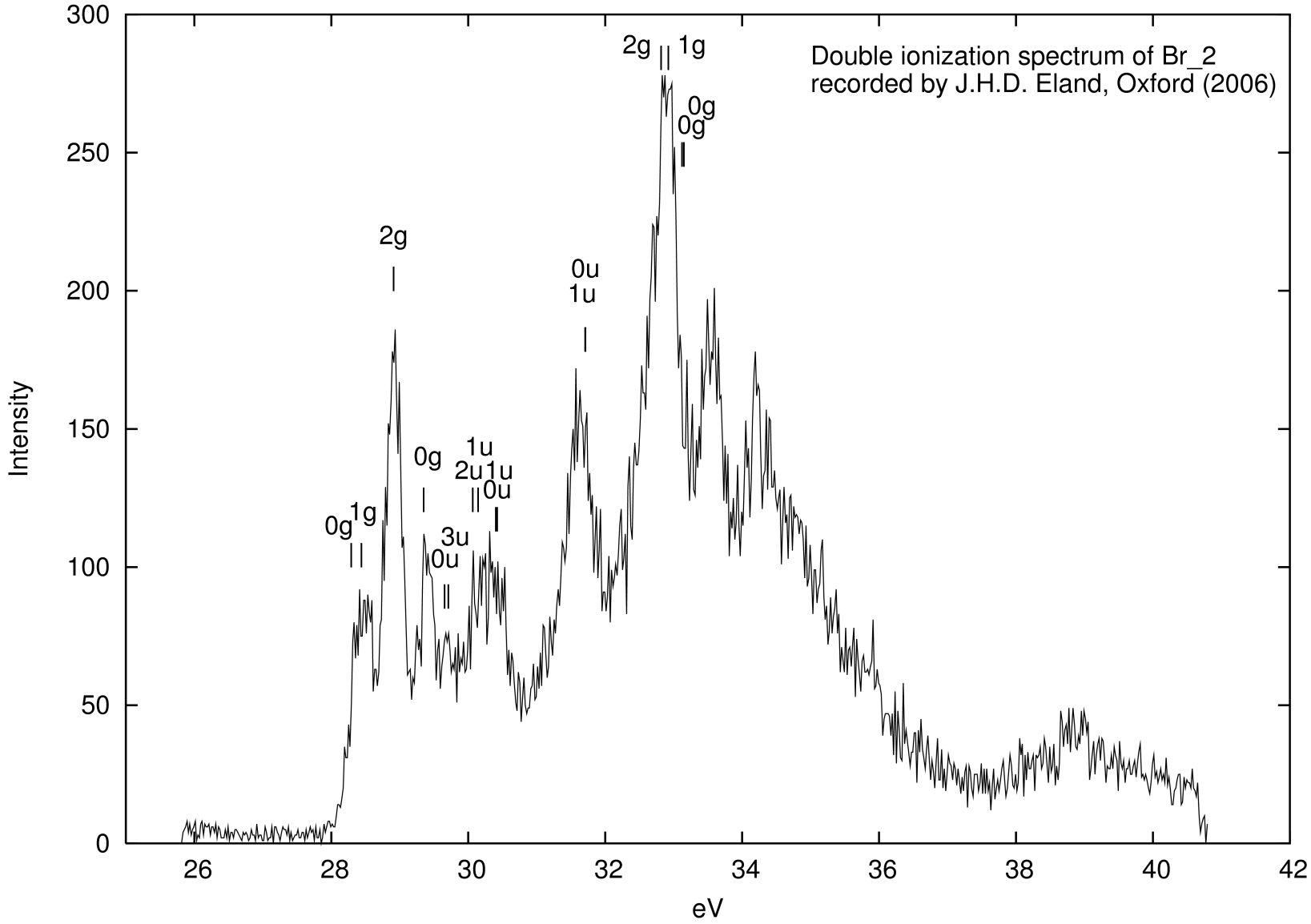
Br_2^{2+}: Experimental Photoionization of Br_2



Greyscale image of the electron pair map at 30.4 nm (40.814 eV)
John H. D. Eland, Oxford, U.K.

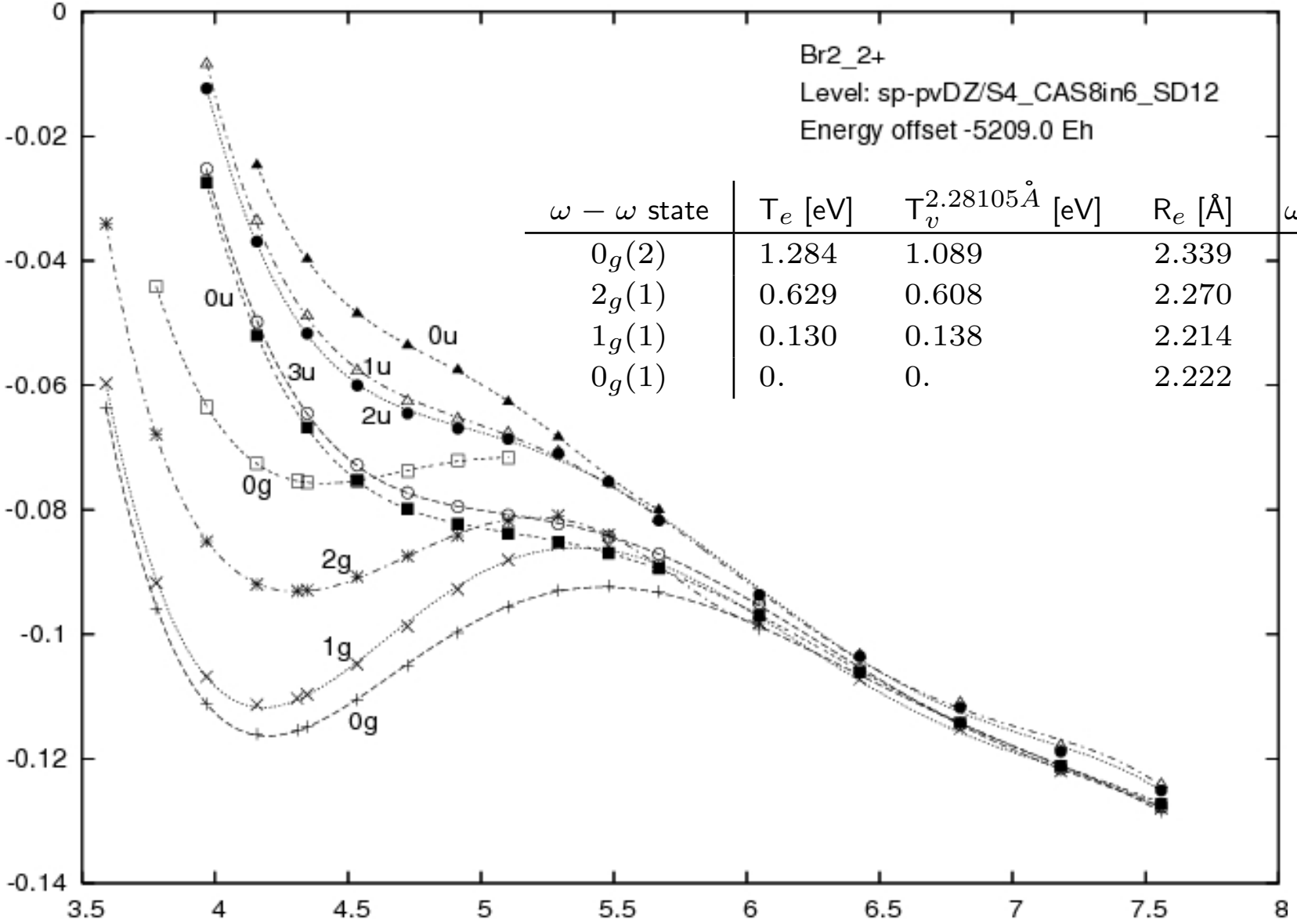
IV. Results

Br_2^{2+}: Experiment Meets Theory



IV. Results

Br_2^{2+}: Potential energy curves



$\omega - \omega$ state	T_e [eV]	$T_v^{2.28105\AA}$ [eV]	R_e [Å]	ω_e [cm^{-1}]
$0_g(2)$	1.284	1.089	2.339	215
$2_g(1)$	0.629	0.608	2.270	265
$1_g(1)$	0.130	0.138	2.214	325
$0_g(1)$	0.	0.	2.222	311

Thanks !

David Edvardsson, Oxford/Örebro

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Lasse K. Sørensen, Düsseldorf

Jeppe Olsen, Århus

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FL 356/3-1