



Cite this: *Phys. Chem. Chem. Phys.*,
2025, 27, 18734

Understanding the binding in excited states of the yttrium anion[†]

Maria Barysz 

Recent experimental studies, for example those by Rui Zhang *et al.* [*J. Chem. Phys.*, 2023, **158**, 084303], have provided a precise new value for the electron affinity of the yttrium atom and fresh insights into its excited states. However, a comprehensive theoretical understanding of its binding and electron affinity remains lacking. Inspired by these findings, we present a detailed theoretical investigation of the excited-state electronic structure of Y^- . To achieve this, we employ the multiconfiguration Dirac–Hartree–Fock (MCDHF) method, as well as the relativistic infinite-order two-component (IOTC) approach combined with multiconfiguration complete active space self-consistent field (CASSCF) and second-order multireference perturbation theory (CASPT2). Spin–orbit coupling effects are incorporated using the restricted active space state interaction (RASSI) method with atomic mean field integrals (AMFI). Our IOTC CASSCF/CASPT2 calculations yield an electron affinity (EA) of 0.298 eV in spin-free computations and 0.258 eV when spin–orbit effects are included via RASSI, representing one of the most accurate theoretical predictions to date. Notably, our results closely align with the recent experimental measurement of 0.3113 eV, reinforcing the reliability of our approach and deepening our understanding of the electronic structure and binding in Y^- . Our investigation highlights potential discrepancies between the predicted symmetries of the excited states of the yttrium anion and experimental observations. Additionally, we calculated the binding energies for transitions from Y^- to Y and identified four potential bound or quasi-bound states in the yttrium anion.

Received 11th April 2025,
Accepted 21st July 2025

DOI: 10.1039/d5cp01388g

rsc.li/pccp

This paper focuses on the electronic spectra and electron attachment mechanisms of the yttrium atomic anion. In particular, we investigate its ground and excited states, along with their electron detachment energies, which serve as a measure of the binding strength of the extra electron. By integrating experimental spectroscopic data with theoretical models, we aim to identify key electronic transitions and elucidate the electronic structure governing the stability of the anion.

Negative atomic anions play a crucial role in low-temperature plasmas, including those found in the upper atmosphere, the interstellar medium, and various technological applications.^{1,2} Under specific conditions such as in the gas phase or at high temperatures, neutral atoms can form anions, which may exist in either bound or quasi-bound (metastable) excited states. Bound states in atomic anions are characterized by energy levels below the ionization threshold, making them essential for understanding anion electronic structures and behaviors. Unlike neutral atoms and positive ions, which possess a large number of bound states, atomic anions typically exhibit far fewer.

Faculty of Chemistry, Nicolaus Copernicus University in Toruń, Gagarina Street 7, 87-100 Toruń, Poland. E-mail: teomjb@umk.pl

[†] This work is dedicated to Professor Christel Marian, a distinguished figure in Theoretical Chemistry, on the occasion of her 70th birthday.

This distinction makes them particularly intriguing for research. The energy levels of bound states are fundamental in determining the absorption and emission spectra of atomic anions. These spectra can be studied experimentally to gain deeper insights into their electronic structure. Advances in understanding the properties of negative ions have largely been driven by the dynamic interplay between experimental and computational studies, underscoring the importance of both approaches in advancing the field.

Yttrium is a non-radioactive transition element, and the electron affinity (EA) and electronic structure of its anion were measured by Feigerle *et al.*³ for the first time in 1981 using the laser photoelectron spectroscopy (LPES) method. They observed two bound states (¹D and ³D) and a possible third bound state (³F). The additional electron in the Y^- anion was assigned to the p orbital, with the two observed bound states corresponding to the electronic configuration of 4d5s²5p. The binding energies of the ground state ¹D and the excited state ³D were determined to be 0.308 ± 0.012 eV and 0.165 ± 0.025 eV, respectively. However, no conclusive results were obtained for the excited states of the Y^- anion due to the complex and dense nature of the photoelectron energy spectra.

More recently, Zhang *et al.*⁴ reported an accurate electron affinity value for yttrium and investigated the electronic

structure of its negative anion using the slow-electron velocity-map imaging (SEVI) technique. The electron affinity of Y was determined to be 0.31129(22) eV.

The ground state of Y^- was identified as $4\text{d}5\text{s}^25\text{p}^1\text{D}$ which is consistent with previous findings. Additionally, several excited states of Y^- were observed such as $^3\text{D}_1$, $^3\text{D}_2$, $^3\text{D}_3$, $^3\text{F}_2$ and $^3\text{F}_3$ with their corresponding excitation energies determined to be 0.1500, 0.1689, 0.1869, 0.2166 and 0.2464 eV, respectively. Notably, the energy levels of the ^3F were measured for the first time in this study.

On the theoretical side, Bauschlicher *et al.*⁵ performed calculations in 1989 to determine the binding energies of three possible bound states ^1D , ^3F , and ^3D using the second-order configuration interaction (SOCl) method. The calculated binding energies were 0.398 (EA), 0.179 and 0.103 eV, respectively. However, in contrast to the experimental results, the theoretical study predicted the ^3F state as the first excited state.

The preceding discussion emphasizes the need for further theoretical exploration of the Y^- anion.

Before going into theoretical studies of the yttrium anion using particular methods, it will be crucial to first evaluate the accuracy of these methods when applied to the neutral yttrium atom. This is especially important due to the abundance of experimental data available for the neutral yttrium atom.

In the present work, we employ two methods: the multi-configuration Dirac–Hartree–Fock (MCDHF) atomic method^{6,7} and the spin-free version of the IOTC method,^{8–10} in combination with the multi-configuration complete active space self-consistent field (CASSCF) molecular method^{11–13} followed by the second-order single-state multi-reference perturbation (CASPT2) scheme.^{14,15} Within the IOTC CASSCF/CASPT2 approach, the effect of spin-orbit (SO) coupling is introduced *via* the restricted active space state interaction (RASSI) method, utilizing atomic mean field one-electron SO integrals (Schimmelpfennig *et al.* modified AMFI).^{16–18} Since the quantum states within the same energy term are not always entirely degenerate in CASPT2 RASSI calculations, an accuracy of 0.01 eV was assumed. For consistency, this accuracy was applied throughout all tables.

It is worth noting that for a considerable period, the relativistic second-order two-component Douglas–Kroll–Hess (DKH2) method^{19,20} was among the most widely used approaches for calculating atomic and molecular relativistic effects. However, in the 2000s, new exact two-component methods began to emerge.^{21–30} One of these, the infinite-order two-component (IOTC) method, was formulated by the author.^{8–10}

All calculations were carried out using the MOLCAS7.3^{31,32} and GRASP2018³³ packages of quantum chemistry programs.

1 Theoretical background and computational details of the MCDHF and IOTC methods

The four-component MCDHF calculations used in the present work were described in detail in ref. 6 and 7 so that, hereafter, only the most important features of the MCDHF approach will

be briefly reviewed. In the MCDHF method, a system of N electrons is described using the relativistic Hamiltonian

$$H = \sum_{i=1}^N h_{\text{D}}(i) + \sum_{j > i=1}^N 1/r_{ij}, \quad (1)$$

where $h_{\text{D}}(i)$ is the one-electron Dirac operator for the i th electron:

$$h_{\text{D}}(i) = \alpha p_i + \beta c^2 + (V_i - c^2)I \quad (2)$$

In eqn (2), c represents the velocity of light, α and β are the Dirac matrices, p_i is the electron momentum, V_i is the one-electron Coulomb potential ($V_i = -Z/r_i$), and I is the unit matrix. The $1/r_{ij}$ describes the two-electron Coulomb interaction.

Relativistic corrections beyond the Dirac–Coulomb approximation for a many-electron system are implemented using assumptions based on the one-electron concept. For example, in the transverse photon interaction

$$H_{\text{T}} = - \sum_{i < j}^N \left[\alpha_i \alpha_j \frac{\cos\left(\frac{\omega_{ij} r_{ij}}{c}\right)}{r_{ij}} + (\alpha_i \nabla_i)(\alpha_j \nabla_j) \frac{\cos\left(\frac{\omega_{ij} r_{ij}}{c}\right) - 1}{\omega_{ij}^2 r_{ij}^2 / c^2} \right]. \quad (3)$$

which is the leading correction to the electron–electron Coulomb interaction, the frequency ω_{ij} is assumed to be the diagonal orbital energy parameter. This frequency is multiplied by a scale factor of 10^{-6} .³⁴

The transverse photon interaction with the scaled frequencies is usually referred to as the Breit interaction. The Breit interaction together with QED corrections (self-energy and vacuum polarization) is added perturbatively after the MCDHF calculations.^{35,36}

Compared to the four-component MCDHF method, the infinite-order two-component theory IOTC leads to enormous reduction of the computational effort and simultaneously recovers most of the relativistic effects which are accounted for within the Dirac formalism. This infinite-order two-component theory has been shown to completely recover the positive part of the Dirac spectrum for one electron systems.^{8,10} The method is based on the Foldy–Wouthuysen idea and the separation of the electronic and positronic spectra of the four-component Dirac theory to the exact two-component form by the unitary transformation U of the one-electron Dirac Hamiltonian h_{D} :

$$h'' = \mathcal{U}^\dagger h_{\text{D}} \mathcal{U}, \quad (4)$$

with h_{D} defined by eqn (2) and

$$h'' = \begin{pmatrix} h_+ & 0 \\ 0 & h_- \end{pmatrix}. \quad (5)$$

The unitary transformation $U^\dagger h_{\text{D}} U$ is based on the idea of Heully *et al.* and is determined in terms of the auxiliary operator R .³⁷

The infinite-order solution of the block-diagonalization problem is then reduced to the solution of the following operator equation:

$$R = [(h_{\text{D}})_{22}]^{-1} [-(h_{\text{D}})_{21} + R(h_{\text{D}})_{11} + R(h_{\text{D}})_{12}R]. \quad (6)$$

Once the solution R of eqn (6) is known, the exact two-component “electronic” Hamiltonian h_+ becomes:

$$h_+ = \Omega_+^\dagger (h_D)_{11} \Omega_+ + \Omega_+^\dagger R^\dagger (h_D)_{21} \Omega_+ + \Omega_+^\dagger (h_D)_{12} R \Omega_+ + \Omega_+^\dagger R^\dagger (h_D)_{22} R \Omega_+ \quad (7)$$

where the Ω operator is defined through the R operator.^{8,10} One of the possible ways to solve eqn (6) is by means of an iterative scheme. It can be made through some odd powers of α , say α^{2k-1} , $k = 2, 3, \dots$ (with α denoting the fine structure constant, $\alpha = 1/c$). Then, the unitary transformation U will be exact through the same order in α . Simultaneously, this will lead to the approximate form h_{2k} , $k = 2, 3, \dots$ of h_+ . Thus the method leads to a series of two-component relativistic Hamiltonians whose accuracy is determined by the accuracy of the iterative solution for R . In each step of the iteration, the analytical forms of the R operator (equation eqn (6)) and the Hamiltonian h_+ (eqn (7)) have to be derived.

In a very simplified way, it can be said that in such a manner, we will obtain Hamiltonians of the order n , DKH_n , $n = 1, 2, \dots$. However, the original Hamiltonians DKH_n were derived in a different way.

In the two-component infinite-order IOTC method, the analytical form of the R operator equation is formulated only once and the iterative procedure is defined inside the atomic/molecular code. The solution is exact in the given basis set. This is the main advantage of the IOTC method in comparison to the DKH_n methods.

In the IOTC CASSCF/CASPT2 RASSI methodology, all calculations are carried out using the CASSCF method followed by the CASPT2 calculation. The correct selection of the active space is crucial for the method and decides about the accuracy of the calculations. In the present research, the active space consists of the valence 4d, 5s, and 5p atomic orbitals of yttrium. In total, this gives nine active orbitals. The CASSCF wave function is formed from a complete distribution of a number of active electrons n_{el} in a set of active orbitals. For the neutral atom and negative anion of yttrium, n_{el} is equal to 3 and 4, respectively. Inactive orbitals are always doubly occupied in all configurations. The frozen orbital space is empty in CASSCF and is not modified in the calculations. Active and inactive orbitals are optimized during the CASSCF procedure.

12 doublet levels and 18 quartet levels are calculated for the yttrium atom, and 1 singlet and 6 triplet levels for the yttrium anion. State average CASSCF calculations are performed.

The CASSCF wave functions and energies need to be further improved to account for the dynamic electron correlation contribution due to subvalence shells. This is done by using the CASPT2 method. In CASPT2, the electron correlation treatment is extended to the 4s, 4p electrons of Y, which are included in the inactive space, while the remaining orbitals are frozen. The zeroth-order Hamiltonian in CASPT2 is the Dyall Hamiltonian with an IPEA shift of 0.25.

All calculations performed within the study of the yttrium neutral atom and its anion are carried out with the contracted Gaussian-type orbitals (GTO/CGTO). We employ the atomic natural orbital relativistic core correlating (ANO-RCC) large

Gaussian basis (L-ANO-RCC): Y 21s18p13d6f4g2h.10s9p8d5f4g2h.³⁸

In the MCDHF method, systematic expansions of configuration state functions with a given parity and symmetry are generated by substitutions from reference (Dirac-Fock) orbitals to a set of correlation orbitals. The set of correlation shells is systematically increased until the convergence of the energies is obtained. In the present paper, we adopted a scheme in which the correlation orbital space is optimized for single and double substitutions.

The generation of the wave function followed essentially the scheme described in ref. 34. For each state, the spectroscopic orbitals required to form a reference wave function were obtained at first. The correlation orbitals were generated in several consecutive steps, with the expansions formed by single and double substitutions from the reference space. At each step, the correlation space has been extended by one layer of correlation orbitals, with all previously generated orbitals frozen, and all new orbitals made orthogonal to others of the same symmetry.

The 4d5s5p5d6s6p correlation orbitals are used as the active space in the MCDHF calculations for both the yttrium neutral atom and its anion.

The inner 4s and 4p orbital shells have no significant impact on the final calculation results, within the assumed accuracy of the calculations.

2 Results and discussion

At the beginning, it is worth noting that most theoretical methods are considered to be difficult or too tedious for calculations of the electronic excited states of atoms and ions of transition metals. This is due to the fact that there is a large number of states lying very close to each other. Considering all of them is not possible, while restricting the computational space to a smaller set causes many problems with the convergence of the calculations. This is precisely the reason why there are so few theoretical studies on these systems, and the spectra of anions of these metals are particularly difficult and complex.

The aim of this theoretical research is to investigate the anion of the yttrium atom and determine the binding energies of its excited states. The study begins with the neutral yttrium atom for which extensive experimental data are available. These data provide a basis for evaluating the quality and accuracy of the calculations. The excited states of the yttrium atom can have different parity, which necessitates performing two separate calculations in the MCDHF method. The a^2D has a 4d5s² electron configuration, a^4F , a^2F , and a^4P excited states have a 4d²5s electronic configuration and they all exhibited even parity. The excited z^2P state has a 5s²5p electronic configuration, while the excited states z^4F , z^2D , z^4D , and z^4P possess a 4d5s5p electronic configuration. All these excited states exhibit odd parity.

Table 1 presents the MCDHF excitation energies of 10 excited states, calculated relative to the ground state, $a^2D_{3/2}$.

Table 1 Atomic energy levels of the yttrium neutral atom obtained using the MCDHF method. Energy differences relative to the ground state $a^2D_{3/2}$. All data are in eV

Levels ^b	<i>J</i>	MCDHF	Exp. ^a	Electron configuration	Dominant terms
a^2D	3/2	0.00	0.00	$4d5s^2$	$0.85a^2D$
	5/2	0.06	0.07		$0.85a^2D$
a^4F	3/2	1.40	1.36	$4d^25s$	$0.99a^4F$
	5/2	1.41	1.37		$0.99a^4F$
	7/2	1.42	1.40		$0.85a^4F$
	9/2	1.45	1.43		$0.85a^4F$
a^2F	5/2	1.88	1.90	$4d^25s$	$0.85a^2F$
	7/2	1.92	1.97		$0.86a^2F$
a^4P	1/2	2.21	1.89	$4d^25s$	$0.99a^2P$
	3/2	2.22	1.90		$0.98a^2P$
	5/2	2.23	1.92		$0.94a^2P$

^a Ref. 39. ^b The level symbols “a” appearing before the symmetry symbols are in accordance with the NIST notation.³⁹

Table 2 Atomic energy levels of the yttrium neutral atom obtained using the MCDHF method. Energy differences relative to $z^2P_{1/2}$. All data are in eV

Levels ^b	<i>J</i>	MCDHF	Exp. ^a	Electron configuration	Dominant terms
z^2P	1/2	0.00	0.00	$5s^25p$	0.89^2P
	3/2	0.09	0.10		0.89^2P
z^4F	3/2	0.58	0.54	$4d5s5p$	$0.76^4F + 0.18^2D$
	5/2	0.61	0.58		$0.64^4F + 0.27^2D$
	7/2	0.67	0.64		0.95^4F
	9/2	0.73	0.70		0.96^4F
z^2D	5/2	0.67	0.68	$4d5s5p$	$0.63^2D + 0.32^4F$
	3/2	0.67	0.69		$0.69^2D + 0.20^4F$
z^4D	1/2	0.77	0.73	$4d5s5p$	0.93^4D
	3/2	0.78	0.75		0.92^4D
	5/2	0.81	0.77		0.92^4D
	7/2	0.84	0.81		0.92^4D
z^4P	1/2	1.13	1.04	$4d5s5p$	0.95^4P
	3/2	1.14	1.05		0.95^4P
	5/2	1.15	1.07		0.95^4P

^a Ref. 39. ^b The level symbols “z” appearing before the symmetry symbols are in accordance with the NIST notation.³⁹

Table 2 provides the MCDHF excitation energies of 14 excited states, referenced to the $z^2P_{1/2}$ level. The MCDHF calculations include corrections for Breit interaction, self-energy and vacuum polarization. However, the Breit and QED corrections are minimal ranging from 0.000 ± 0.003 eV across all states. Additionally, both tables include the symmetry of atomic levels, the weights of dominant configuration state functions (CSFs), and the corresponding electron configurations. To validate the results, the calculated excitation energies are compared with experimental data published by Atomic Spectra Database NIST.³⁹

As shown in Tables 1 and 2, the ground state of the yttrium atom is $a^2D_{3/2}$. The subsequent even parity levels include $a^2D_{5/2}$, a^4F_J ($J = 3/2, 5/2, 7/2$, and $9/2$); a^2F_J ($J = 5/2$ and $7/2$); and a^4P_J ($J = 1/2, 3/2$, and $5/2$). The odd parity levels include z^2P_J ($J = 1/2$ and $3/2$); z^4F_J ($J = 3/2, 5/2, 7/2$, and $9/2$); z^2D_J ($J = 3/2$ and $5/2$); z^4D_J ($J = 1/2, 3/2, 5/2$, and $7/2$); and z^4P_J ($J = 1/2, 3/2$, and $5/2$). The calculated excitation energies generally show good agreement with experimental data. However, a noticeable deviation occurs for the even-parity a^4P states, where the calculated

Table 3 Atomic energy levels of the yttrium anion obtained using the MCDHF method. All data are in eV

Levels	<i>J</i>	MCDHF	Levels	<i>J</i>	Exp. ^a	Electron configuration	Dominant terms
1D	2	0.00	1D	2	0.00	$4d5s^25p$	0.89^1D
3F	2	0.18	3D	1	0.15	$4d5s^25p$	0.90^3F
	3	0.20		2	0.17		0.89^3F
	4	0.23		3	0.18		0.90^3F
	1	0.29	3F	2	0.22	$4d5s^25p$	0.90^3D
3D	2	0.31		3	0.25		0.89^3D
	3	0.33		4	—		0.90^3D

^a Ref. 4.

excitation energies exceed the experimental value by approximately 0.3 eV. We will return to the discussion of this issue in the later part of the present work.

Table 3 presents the results of MCDHF calculations for the ground state and six excited states of the yttrium anion, together with the recent experimental data.

Negative ions with more than one bound term or level can typically attribute these to the same configuration, meaning the terms or levels share the same parity. This holds true for the yttrium anion as well. The ground state of the yttrium anion is the 1D_2 state, which is in complete agreement with the experimental findings. The configurations of the ground and excited states of the yttrium anion are $4d5s^25p$, both exhibiting odd parity. The excitation energies of the anion show strong agreement with experimental values. However, the symmetry assignments for the excited states of the anion in MCDHF calculations differ from the experimental observations. According to the MCDHF results, the first three excited levels of the yttrium anion are assigned 3F symmetry, followed by three levels with 3D symmetry. In contrast, experimental data suggest that the first three excited levels correspond to 3D terms, followed by 3F terms.

C. W. Bauschlicher,⁵ in SOCI calculations, already demonstrated the possibility of such a reversed energy ordering of these levels. Consequently, these results call for the next phase of our investigation, which will involve employing a more advanced computational approach. In the second stage of present research, we performed calculations using the IOTC CASSCF/CASPT2 RASSI method. In CASSCF, the focus is on optimizing the wavefunction within a given active space. The method involves the selection of orbitals to define the active space, and the symmetry of the system is taken into account when solving the problem. The symmetry of the wavefunction, including parity, will be consistent with the symmetry of the orbitals in the active space and we do not have to explicitly worry about parity.

Table 4 presents the excitation energies of the yttrium atom calculated relative to its ground state energy, using the IOTC CASSCF/CASPT2 RASSI method. The absence of a result indicates that convergence could not be achieved for the corresponding energy level.

Analysis of the data in Table 4 shows that the calculated excitation energies correlate well, or very well, with the experimental values. The only notable exception is the a^4P term, where the

Table 4 Atomic energy levels of the yttrium neutral atom obtained using the IOTC CASSCF/CASPT2 RASSI method. All data are in eV

Levels ^b	<i>J</i>	IOTC	Exp. ^a	Electron configuration
a ² D	3/2	0.00	0.00	4d5s ²
	5/2	0.06	0.07	
z ² P	1/2	1.34	1.31	5s ² 5p
	3/2	1.42	1.41	
a ⁴ F	3/2	1.25	1.36	4d ² 5s
	5/2	1.28	1.37	
z ⁴ F	7/2	1.32	1.40	
	9/2	1.36	1.43	
a ² F	3/2	1.84	1.85	4d5s5p
	5/2	1.88	1.89	
a ⁴ P	7/2	1.93	1.95	
	9/2	1.98	2.01	
b ² D	5/2	—	1.90	4d ² 5s
	7/2	—	1.97	
z ² D	3/2	2.36	1.89	4d ² 5s
	5/2	2.37	1.90	
z ⁴ D	5/2	2.38	1.92	
	7/2	1.95	1.90	4d ² 5s
z ² D	3/2	1.94	2.00	
	5/2	—	1.99	4d5s5p
z ⁴ D	3/2	—	2.00	
	5/2	2.02	2.04	4d5s5p
a ² G	3/2	2.02	2.06	
	5/2	2.05	2.08	
a ⁴ P	7/2	2.08	2.12	
	9/2	—	2.29	4d ² 5s
z ² P	7/2	—	2.30	
	9/2	2.36	2.35	4d5s5p
z ⁴ P	3/2	2.37	2.36	
	5/2	2.38	2.37	

^a Ref. 39. ^b The level symbols “a, b and z” appearing before the symmetry symbols are in accordance with the NIST notation.³⁹

calculated energy deviates from the experimental value by approximately 0.3 eV. However, it is worth noting that a similar discrepancy was previously obtained from MCDHF calculations, suggesting a potential inconsistency in the experimental data (see Table 1).

The study of the yttrium anion presents significant challenges, both experimentally and theoretically. In particular, determining the electron affinity (EA) and the energies of excited states is especially demanding. The most recent measurement by Rui Zhang *et al.*⁴ which reports an EA value of 0.31129(22) eV, is currently regarded as the benchmark reference. The only available theoretical EA value, 0.398 eV, comes from the calculations performed by C. W. Bauschlicher *et al.*⁵ in 1989. In the present study, theoretical calculations of electron affinity were conducted using the active space (6,3), within the IOTC CASSCF/CASPT2 approximation. These calculations yield an EA value of 0.298 eV in spin free calculations and 0.258 eV in spin-dependent RASSI calculations. Both values are in close agreement with the experimental value of 0.31129 eV, making them the most accurate theoretical estimates to date. There is still a small difference between the calculated and experimental values of the electron affinity (EA). We believe that including very diffuse functions in the ANO-RCC basis set could possibly improve our results.

Notably, the MCDHF method failed to determine the electron affinity of yttrium.

The excitation energies of the yttrium anion, presented in Table 5, show good agreement with the experimental data.

Table 5 Atomic energy levels of the yttrium anion obtained using the IOTC CASSCF/CASPT2 RASSI method. All data are in eV

Levels	<i>J</i>	IOTC	Levels	<i>J</i>	Exp. ^a	Electron configuration
¹ D	2	0.000	¹ D	2	0.000	4d5s ² 5p
³ F	2	0.10	³ D	1	0.15	4d5s ² 5p
	3	0.14		2	0.17	
	4	0.19		3	0.18	
³ D	1	0.27	³ F	2	0.22	4d5s ² 5p
	2	0.30		3	0.25	
	3	0.34		4	—	

^a Ref. 4.

However, as observed in the MCDHF results, the ordering of the ³F and ³D states is reversed compared to the experimental findings. Notably, this is not the first time theoretical calculations have suggested such a reversal. As early as 1989, W. C. Bauschlicher,⁵ using SOCI calculations, demonstrated and strongly advocated for the possibility of this energy inversion.

Additional support for our conclusions comes from the fundamental differences between the MCDHF and CASSCF/CASPT2 computational methods. Unlike CASSCF/CASPT2, the MCDHF method does not require selecting an atomic Gaussian basis set, eliminating potential errors associated with basis set selection. Such different methods yet give the same calculation results. Moreover, the energy levels of the analyzed anion states are so close that distinguishing them experimentally may be challenging.

Overall, the consistency of the results obtained from these two fundamentally different methods strengthens their reliability, suggesting that the experimental reassignment of symmetry to the ³D and ³F levels may benefit from further reconsideration.

Finally, we examined the binding energies for all transitions from the ground and excited states of the anion Y[−] to the a²D_{3/2} and a²D_{5/2} lowest levels of the neutral atom. Table 6 presents the results obtained using the MCDHF and IOTC CASSCF/CASPT2 RASSI methods. For the MCDHF transitions, the calculations were performed using the experimental electron

Table 6 Photodetachment from Y[−] to Y transitions obtained using the MCDHF and IOTC CASSCF/CASPT2 RASSI methods. All data are in eV

Transition Y [−] → Y	IOTC	MCDHF	Transition Y [−] → Y	Exp. ^a
¹ D ₂ → a ² D _{3/2}	0.26	0.31 ^a	¹ D ₂ → a ² D _{3/2}	0.31
³ F ₂ → a ² D _{3/2}	0.16	0.13	³ D ₁ → a ² D _{3/2}	0.16
³ F ₃ → a ² D _{3/2}	0.12	0.11	³ D ₂ → a ² D _{3/2}	0.14
³ F ₄ → a ² D _{3/2}	0.07	0.08	³ D ₃ → a ² D _{3/2}	0.13
³ D ₁ → a ² D _{3/2}	−0.01	0.04	³ F ₂ → a ² D _{3/2}	0.09
³ D ₂ → a ² D _{3/2}	−0.04	0.01	³ F ₃ → a ² D _{3/2}	0.06
³ D ₃ → a ² D _{3/2}	−0.08	−0.03	³ F ₄ → a ² D _{3/2}	—
¹ D ₂ → a ² D _{5/2}	0.32	0.37	¹ D ₂ → a ² D _{5/2}	0.38
³ F ₂ → a ² D _{5/2}	0.22	0.19	³ D ₁ → a ² D _{5/2}	0.23
³ F ₃ → a ² D _{5/2}	0.18	0.17	³ D ₂ → a ² D _{5/2}	0.21
³ F ₄ → a ² D _{5/2}	0.13	0.14	³ D ₃ → a ² D _{5/2}	0.20
³ D ₁ → a ² D _{5/2}	0.05	0.10	³ F ₂ → a ² D _{5/2}	0.16
³ D ₂ → a ² D _{5/2}	0.02	0.07	³ F ₃ → a ² D _{5/2}	0.13
³ D ₃ → a ² D _{5/2}	−0.02	0.03	³ F ₄ → a ² D _{5/2}	—

^a Ref. 4.

affinity of approximately 0.31 eV, as the electron affinity of the yttrium atom could not be determined using this approach. For the IOTC CASSCF/CASPT2 RASSI method, the binding energies were calculated using the corresponding spin-dependent electron affinity value of 0.26 eV.

As a result of the findings for the yttrium anion, we observe a strong correlation between the calculated energy transitions from Y^- to Y, which is achieved only when the experimental symmetry assignment of the 3D and 3F states is reversed.

The results in Table 6 indicate that in addition to the bound ground state of the anion, the calculated 3F states (experimentally assigned as 3D) may also be bound, with binding energies of 0.26 eV, 0.12 eV, and 0.07 eV for the calculated levels 3F_2 , 3F_3 , and 3F_4 , respectively. In contrast, the calculated 3D states (experimentally assigned as 3F) are predicted to be either very weakly bound or unbound. These findings are in agreement with earlier theoretical results of Bauschlicher.⁵

Conclusions

We present a comprehensive and precise theoretical description of the energy levels of the neutral yttrium atom, and its negative anion.

The electron affinity for the a^2D state, calculated using the spin-free IOTC CASSCF/CASPT2 method, is 0.298 eV for the $a^2D_{3/2}$ level, and the spin-dependent IOTC CASSCF/CASPT2 RASSI method yields 0.258 eV. These represent the most accurate theoretical electron affinity values.

The calculated excitation energies of the excited states of the neutral yttrium atom, obtained using the MCDHF method and the IOTC CASSCF/CASPT2 RASSI method, show very good agreement with the corresponding experimental values. The only exception is the excitation energy of the a^4P level, which is significantly higher than the experimental value in both methods. This may suggest that the experimental measurement for this level should be repeated.

The calculated excitation energies for the levels of the yttrium anion agree well with the experimental values. However, the MCDHF and IOTC CASSCF/CASPT2 RASSI calculations suggest a reversal of the symmetries of these states compared to the experimental results. According to theoretical predictions, the lowest excited state is 3F , followed by the 3D state. In contrast, the experiment assigns the opposite symmetries to these states.

The theoretical results suggest that most probably, the experimental assignment of symmetry to the 3D and 3F levels should be reconsidered once again.

The calculated binding energies of transitions from the Y^- to Y suggest the existence of three quasi-bound (metastable) states in the anion: 3F_2 , 3F_3 , and 3F_4 .

Finally, our study highlights the effectiveness of our relativistic two-component IOTC method.

Author contributions

I am the sole author of the presented results.

Conflicts of interest

There are no conflicts to declare.

Data availability

The author confirms that the data supporting this work have been included in the article. These data are also available from the author upon request.

References

- 1 T. Andersen, *Phys. Rep.*, 2004, **394**, 157–313.
- 2 W. C. Lineberger, *Annu. Rev. Phys. Chem.*, 2013, **64**, 21–36.
- 3 C. S. Feigerle, Z. Herman and W. C. Lineberger, *J. Electron Spectrosc. Relat. Phenom.*, 1981, **23**, 441.
- 4 R. Zhang, Y. Lu, R. Tang and C. Ning, *J. Chem. Phys.*, 2023, **158**, 084303.
- 5 C. W. Bauschlicher and P. R. Taylor, *Chem. Phys. Lett.*, 1989, **158**, 245–249.
- 6 F. C. Fischer, M. Gofefroid, P. Jönsson and G. Gaigalas, *J. Phys. B: At., Mol. Opt. Phys.*, 2016, **49**, 182004.
- 7 I. Grant, *Relativistic Quantum Theory of Atoms and Molecules: Theory and Computations*, Springer, New York, 2006.
- 8 M. Barysz and A. J. Sadlej, *J. Chem. Phys.*, 2002, **116**, 2696–2704.
- 9 M. Barysz, Ł. Mentel and J. Leszczyński, *J. Chem. Phys.*, 2002, **116**, 2696–2704.
- 10 M. Barysz, *Two-component relativistic theories*, Springer, New York, 2010, pp. 165–190.
- 11 P. Siegbahn, A. Heiberg, B. Roos and B. Levy, *Phys. Scr.*, 1980, **21**, 323–327.
- 12 B. O. Roos, P. R. Taylor and P. E. M. Sigmund, *Chem. Phys.*, 1980, **48**, 157–173.
- 13 B. O. Roos, P. R. Taylor and P. E. M. Sigmund, *Int. J. Quantum Chem., Symp.*, 1980, **14**, 175–183.
- 14 K. Andersson, P.-A. Malmqvist, B. O. Roos, A. J. Sadlej and K. Woliński, *J. Chem. Phys.*, 1990, **94**, 5483–5488.
- 15 K. Andersson, P.-A. Malmqvist and B. O. Roos, *J. Chem. Phys.*, 1992, **96**, 1218–1226.
- 16 B. A. Hess, C. M. Marian, U. Wahlgren and O. Gropen, *Chem. Phys. Lett.*, 1996, **251**, 365–371.
- 17 B. Schimmelpfennig, L. Maron, U. Wahlgren, C. Teichtel, H. Fagerli and O. Gropen, *Chem. Phys. Lett.*, 1998, **286**, 267–271.
- 18 P.-A. Malmqvist, B. O. Roos and B. Schimmelpfennig, *Chem. Phys. Lett.*, 1998, **286**, 267–271.
- 19 B. A. Hess, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1985, **32**, 756–763.
- 20 B. A. Hess, *Phys. Rev. A: At., Mol., Opt. Phys.*, 1986, **33**, 3742–3748.
- 21 B. A. Hess, *J. Chem. Phys.*, 2002, **117**, 9215–9226.
- 22 M. Reiher and A. Wolf, *J. Chem. Phys.*, 2004, **121**, 2037–2047.
- 23 M. Reiher and A. Wolf, *J. Chem. Phys.*, 2004, **121**, 10945–10956.
- 24 M. Iliaš and T. Saue, *J. Chem. Phys.*, 2007, **126**, 064102.
- 25 W. J. Liu and D. Peng, *J. Chem. Phys.*, 2006, **125**, 044102.

26 D. Peng, W. J. Liu, Y. Xiao and L. Cheng, *J. Chem. Phys.*, 2007, **127**, 104106.

27 R. Klooster, R. Broer and M. Filatov, *Chem. Phys.*, 2012, **395**, 122–127.

28 T. Nakajima and K. Hirao, *Chem. Rev.*, 2012, **112**, 385–402.

29 W. J. Liu, *Phys. Rep.*, 2014, **537**, 59–89.

30 W. Liu, *Handbook of Relativistic Molecular Quantum Chemistry*, Springer, Berlin, 2017.

31 Molcas7.3 a program written by: F. Aquilante, L. de Vico, N. Ferr, G. Ghiago, P. Malmqvist, B. O. Roos, U. Ryde, V. Veryazov, P.-O. Widmark, M. Cossi, B. Shimmepfennig, P. Neogrady and L. Seijo, *Comput. Mater. Sci.*, 2003, **28**, 222.

32 *The IOTC method was implemented in the version of the Molcas 7.3 system of programs by Slovakia Group of Quantum Chemistry (Comenius University, Bratislava, Slovakia 2010). The corresponding patches for Molcas 7.3 release can be obtained directly from M. Barysz (e-mail: teomjb@chem.umk.pl) or Vladimir Kellö (e-mail: kelloe@fns.uniba.sk).*

33 C. Froese Fischer, G. Gaigalas, P. Jönsson and J. Bieroń, *Comput. Phys. Commun.*, 2019, **237**, 184–187.

34 C. Froese Fischer, G. Gaigalas, P. Jönsson and J. Bieroń, *Comput. Phys. Commun.*, 2019, **237**, 184–187.

35 M. Barysz and Ł. Syrocki, *Mol. Phys.*, 2014, **112**, 583–591.

36 M. Barysz, *Practical Aspects of Computational Chemistry*, Springer, New York, 2016, pp. 1–25.

37 J.-L. Heully, I. Lindgren, E. Lindroth, S. Lundqvist and A.-M. Mårtensson-Pendrill, *J. Phys. B: At., Mol. Opt. Phys.*, 1986, **19**, 2799–2815.

38 B. O. Roos, R. Lindh, P.-A. Malmqvist, V. Veryazov and P.-O. Widmark, *J. Phys. Chem. A*, 2005, **109**, 6575–6579.

39 A. Kramida, Y. Ralchenko and J. Reader, *NIST Atomic Spectra Database*, 2020, <https://physics.nist.gov/asd>.