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# Born-Oppenheimer potential energy curves of NaK from the optimised atomic basis sets

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#### ABSTRACT

The article presents adiabatic potential energy curves of the ground and excited electronic states for the diatomic NaK molecule. The calculations were made using the *ab initio* computational methods to include electron correlation. The studied molecule was calculated as the effective two-electron problem, in which only the valence electrons of the molecule are explicitly taken into account. The remaining electrons with atomic nuclei are described with appropriate, energy-consistent relativistic pseudopotentials. Additionally, a bespoke basis set, generated and optimised for both ground and excited electronic states of the NaK system was developed. The spectroscopic parameters of the calculated potential energy curves were determined and compared with the available experimental and theoretical results. The compliance of the obtained results, despite slight differences, is very satisfactory.

#### **KEYWORDS**

NaK, potential energy curves, effective core potential, basis set optimisation, diatomic molecules

## 1. Introduction

The knowledge of the structure of diatomic molecules is essential for understanding and testing physical theories of the structure of molecular systems. The simplest of all molecules – the hydrogen dimer – has been the benchmark for accuracy and understanding of molecular quantum mechanics and, more recently, quantum electrodynamics. Starting with pioneering computations by James and Coolidge [1] through seminal high-accuracy work of Kołos and Wolniewicz [2] and its subsequent improvements [3– 6] it became clear, that accurate calculation based on rigorous theoretical methods can provide guidance for experimental work and sometimes even correct it. Although ultra-accurate calculations for hydrogen molecule, taking into account higher-order nonadiabatic, relativistic and QED effects [7], is still an active field of investigation and provides excellent agreement with experiment, significant progress was also obtained for heavier diatomic systems. When looking for molecules that are most similar to diatomic hydrogen one can think in two ways. Firstly, systems with three or four electrons, such as HeH, He<sub>2</sub>, or LiH can be thought of as molecules that are most similar to hydrogen. However, as it is well known, atoms share similar traits according to their electron configuration, resulting in their position in the periodic table

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of elements. Subsequently, molecules and their properties also depend on electronic structure and therefore properties of helium dimer are very different from hydrogen molecules. Thinking along the line of electronic configuration, molecular systems that are most similar to hydrogen dimer are alkali metal dimers and hydrides. Since alkali metal atoms have, analogously to hydrogen atom, only one valence electron they share a lot of similarity. Knowledge of potential energy curves and spectroscopic parameters of such systems helps with resolving spectra, planning new experiments, and looking for ro-vibrational energy levels, through which cooling is possible. Furthermore, ultracold systems of alkali metal atoms are currently the active and important field of study in ultracold physics and chemistry [8, 9]. Accurate data is required not only for the ground state of the system but also for excited states with various values of angular momentum and spin.

The purpose of this work is to show the consistency between different theoretical approaches and to present the original method of optimisation of the atomic basis sets. This optimisation takes into account the excitation energies of the atomic states, thanks to which it gives very good asymptotic values of the potential energy curves. Obtained basis sets are relatively small sets and yet, they give accurate results. Due to their relatively small size, the calculations are less time-consuming than with larger, but not fully optimised basis sets.

Therefore, in this work, we theoretically determine the potential energy curves for ground and excited states of the NaK molecule in singlet and triplet states of  $\Sigma^+$ ,  $\Pi$ , and  $\Delta$  symmetries. The approach using large-core relativistic pseudopotentials allows to calculate the excited states that are needed to resolve molecular spectrum along the wide ranges of temperature. Particular attention was paid to the optimisation of the bespoke atomic basis sets, which in turn are used in calculations of ground and excited states. For this purpose we use high-level, accurate quantum chemistry methods. Based on the obtained results, spectroscopic parameters are also determined and then compared with the available experimental and theoretical values.

The first significant experimental work on NaK appeared in 1977, where Zmbov et al. [10] determined the dissociation energy and ground state spectroscopic parameters. A year later, the results of their experimental work were confirmed by Breford and Engelke [11]. In the same year, Janoschek and Lee [12] applied pseudopotential methods to calculate potential energy curves for several electronic states. However, the development of research on the NaK molecule took place in the 1980s, when a lot of experimental work was carried out. Spectroscopic constants for the ground [13] and several excited states were determined, these include  $2^{1}\Sigma^{+}$  [14],  $2^{3}\Sigma^{+}$  [15, 16],  $3^{1}\Sigma^{+}$ [17],  $1^{3}\Pi$  [18]. A large impact on the knowledge of the experimental electronic structure of NaK was given by Warsaw group. Using polarisation labelling spectroscopy technique Kowalczyk, Jastrzębski et al. investigated several excited electronic states of the NaK molecule [19–29]. In turn, Magnier and Millie [30] and Musiał et al. [31] provided theoretical curves of potential energy for several electronic states.

## 2. Theoretical method

The system is simplified to an effective two-electron problem in which only valence electrons are described explicitly. The remaining electrons, together with the nuclei of the respective atoms, form two atomic cores described by energy-consistent relativistic pseudopotentials developed by the Stuttgart group [34]. The details of the method with two valence electrons for the entire alkali molecule has already been described in ours earlier papers and has been proven to produce reliable results, especially for excited states [32, 33]. Such an approach could also be beneficial in larger molecules and even clusters, because the dimension of active space and the number of configurations to consider is significantly reduced.

To calculate adiabatic potential energy curves of the NaK molecule we use the multiconfigurational self-consistent field/complete active space self-consistent field (MC-SCF/CASSCF) method and the multi-reference singles and doubles configuration interaction (MRCISD) method. The initial atomic basis sets of both atoms, i.e. Na and K, were optimised separately for each symmetry of the atomic orbitals (i. e. s, p, and d) using the error function defined as  $ERR = \sqrt{\sum_i (E_i^{experiment} - E_i^{theory})^2}$ , where the sum goes over appropriate atomic energy levels. All calculations are done with the MOLPRO package [35]. The error function is minimised using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) gradient method. Specially written Python scripts support this minimisation procedure. The process itself is quite tedious but gives surprisingly good results, considering the size of the basis set.

## 3. Results and discussion

## 3.1. Optimised atomic basis sets

In the case of potassium atom, the ECP18SDF [34] pseudopotential is used on the eight-element basis set with four s and four p orbitals taken from the Stuttgart ECP database [36, 37]. This basis set has been optimised with only the ground and first excited atomic states. The initial results, using only slightly modified s orbitals, gave energy estimate of the ground state and the  $5s^2S$  atomic excitation. The initial ERR  $= 5840 \text{ cm}^{-1}$  was calculated with respect to the experimental energy difference of the ground and  $5s^2S$  excited state [38, 39]. Subsequent optimisation with the BFGS method by successively adding basis functions allowed to reduce the ERR to the value of  $0.024 \text{ cm}^{-1}$ . The exponents of the optimal at this stage basis functions of type s were 1.0826, 1.0763, 0.5992, 0.2544, 0.0483, 0.0217, 0.0041, 0.0040, and 0.0039. Attempts to expand the s-type database further lead to problems with linear dependence of the basis set. After optimisation of s-type basis functions, the basis set was supplemented with p-type functions. ERR calculated with additional experimental energy of the atomic state  $4p^2 P$  [40] during the optimisation process of p-type function drops from 30 to  $0.003 \text{ cm}^{-1}$ . This basis set was then extended by adding d-type orbitals coming with a pseudopotential ECP10MDF [41]. At this stage, ERR with additional experimental atomic energy of the state  $3d^2D$  during optimisation of the d-type function is lowered from the initial value of 1314 to  $0.003 \text{ cm}^{-1}$ . Thereafter, we make optimisation of the entire atomic basis set, including s-, p-, and d-type orbitals. The core electrons of the sodium atom are represented by the ECP10SDF pseudopotential [34] with dedicated basis set [36, 37]. The same optimisation process as for K is repeated for the sodium atom and the final atomic basis sets are shown in TAB 1.

The obtained asymptotic potential energy values for the NaK molecule are placed in TAB 2. The high agreement of the obtained results in comparison with the experimental data indicates that the chosen optimisation method of the atomic basis sets yields good results.

	Na			K	
s	р	d	s	р	d
1.370519	0.311924	0.887695	1.082205	0.206216	0.979704
0.939692	0.129085	0.112686	1.069245	0.047287	0.323243
0.394043	0.040638	0.031485	0.605437	0.028605	0.086434
0.083874	0.016706	0.012876	0.255401	0.012394	0.028052
0.041838	0.007092	0.006103	0.048138	0.005074	0.010874
0.021195		0.003247	0.021701		0.003537
0.006804			0.005294		0.001150
0.006103			0.004217		0.000374
0.000153			0.001999		

Table 1. The optimised Gaussian exponents of atomic orbitals s, p, and d for sodium and potassium atoms.

Table 2. Asymptotic values and  $\delta_A$ , i.e. the difference between the obtained results and the experimental data [39, 40, 42]

Na	Κ	Calculated asymptotic energies $[cm^{-1}]$	$\delta_A \ [cm^{-1}]$
$2p^{6}3s$	$3p^64p$	13023.56	-0.10
$2p^{6}3p$	$3p^{6}4s$	16967.65	0.02
$2p^63s$	$3p^65s$	21026.22	-0.33
$2p^63s$	$3p^63d$	21535.28	-0.32

## 3.2. Potential energy curves and spectroscopic parameters

We calculated a total of eighteen potential energy curves: five singlet states and five triplet states of  $\Sigma^+$  symmetry, three singlet states and three triplet states with  $\Pi$ symmetry, and one singlet state and one triplet state with  $\Delta$  symmetry. The covered distance between the nuclei ranges from 3.0  $a_0$  (1.59 Å) to 66.0  $a_0$  (34.93 Å) with varying step sizes. For small internuclear distances, these steps are smaller than for large ones. This is because usually, the minima of potential energy curves exist for small distances. Tables with all calculated potential energy curves can be found in Supplementary Materials.

The obtained potential energy curves for the five  ${}^{1}\Sigma^{+}$  states are shown in FIG 1. In TAB 3 are our present spectroscopic constants for symmetry  ${}^{1}\Sigma^{+}$  and other values obtained from experimental and theoretical research. This allows for the verification of our results. From TAB 3, it can be concluded that we obtained good agreement with the experimental results, especially for the ground state as well as for the singlet  $\Sigma^+$  and  $\Pi$  excited states. Our results look very good compared to the other theoretical results. Our binding energies  $D_e$  are basically more accurate than the other theoretical values, and additionally, we can noticed that the term energy  $T_e$  for the state  $2^1\Sigma^+$ and the vibrational constant  $\omega_e$  for the state  $3^1\Sigma^+$  are better than the other theoretical results in the comparison with experimental ones. The position of  $R_e$  is shifted towards shorter distances compared to the experiment. However, the difference between these values rather does not exceed 0.1 Å. The special attention should be directed to the  $4^{1}\Sigma^{+}$  excited state. The shape of this potential is strongly irregular, so we noticed here some discrepancies of the electronic energy term  $T_e$  in the comparison with available experimental data, but also between different theoretical results. However, we reproduce almost perfectly the shape of this potential energy curve, which is visible on FIG 2a and confirmed by R-dependent error analysis (FIG 2b). The same figure also presents comparison of our  $3^{1}\Sigma^{+}$  and  $5^{1}\Sigma^{+}$  states with available curves derived

from experimental data [25, 28]. Once again the shapes of our potentials correspond well with experimental ones and vertical energy differences do not exceed 260 cm<sup>-1</sup> (FIG 2b).

The obtained potential energy curves and spectroscopic constants of three singlet states with symmetry II and one singlet state with symmetry  $\Delta$  are shown in FIG 3 and TAB 4, respectively. Our  $R_e$  position for the 1<sup>1</sup>II state fits perfectly with the experimental value. Overall, our results are closer to different theoretical results than to the most recent experimental data.

In turn, the obtained potential energy curves for five triplet states with symmetry  $\Sigma^+$  are shown in FIG 4. TAB 5 contains the calculated spectroscopic constants for these states and values from other theoretical and experimental studies. We obtained a high overall agreement with experimental data. An exception should be made for the bond energy  $D_e$  for the  $2^3\Sigma^+$  state, but in this case neither of theoretical results is much better. In turn, for the  $3^3\Sigma^+$  state, we find a second minimum that has not been reported either in experimental or theoretical research.

Finally, computed energy curves of the three triplet states with symmetry  $\Pi$  and one with symmetry  $\Delta$  are shown in FIG 5. Their spectroscopic constants can be found in TAB 6. By analysing this table, it turns out that, apart from the constant  $D_e$  for the 1  ${}^{3}\Pi$  state, we achieved very good agreement with the experimental data. The determined potential energy curve for state  $3{}^{3}\Pi$  has two minima. An almost identical theoretical result was obtained by Allouche et al. [45].

## 4. Conclusions

By simplifying the NaK molecule into an efficient two-electron system and using quantum chemistry methods such as MCSCF/CASSCF and MRCI, we computed 18 potential energy curves. Only the valence electrons were explicitly included in the calculations. The remaining electrons with nuclei are referred to as pseudopotentials. The basis sets coming with atomic pseudopotentials have been extended and optimised using the gradient method from MOLPRO managed by a specially written script. We also determined selected spectroscopic constants and compared them with available experimental data and other theoretical results. The compatibility with the latest experimental data is very good. A great similarity can also be seen in the comparative chart, where the potential energy values obtained in this approach almost perfectly match the experimental results in many places. The difference between the obtained values and the experimental data is the smallest for long distances, it is the result of properly conducted optimisation of atomic basis sets. We also observed high agreement with the theoretical results obtained by Allouche et al. and Magnier et al.

To calculate the potential energy curves, we used a small but very efficient basis of Na and K. Despite small discrepancies with existing data, they give reliable results, while showing consistency between different theoretical calculations and experimental results. Newly developed basis sets can be used in systems, where Na or K atoms interact with other atoms. Moreover, in a more general sense, the proposed basis set optimisation method can be applied to other atoms.

Overall, our results can serve as a valuable comparative resource for other theoretical and experimental approaches.

## Supplementary materials

The data that support the findings of this study are available from the corresponding author upon request and also be openly available in the MOST Wiedzy portal [53].

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Figure 1. Adiabatic potential energy curves of the NaK molecule for five states with symmetry  ${}^{1}\Sigma^{+}$ 



Figure 2. (a) The comparison of the current results of the adiabatic potential energy curves with the potentials derived form experimental data [25, 27, 28] for the  $3-5^{1}\Sigma^{+}$  (the graph is scaled by the value of the bond energy for the present ground state), (b) error plot, i.e. the value of the difference between the current results and the experimental data [25, 27, 28] for given distances



Figure 3. Adiabatic energy curves of the NaK molecules for three states with symmetry  ${}^{1}\Pi$  and one state with symmetry  ${}^{1}\Delta$ 



Figure 4. Adiabatic potential energy curves of the NaK molecule for five states with symmetry  $^{3}\Sigma^{+}$ 



Figure 5. Adiabatic potential energy curves of the NaK molecule for three states with symmetry  ${}^{3}\Pi$  and one state with symmetry  ${}^{3}\Delta$ 

State	Reference	$\mathbf{R}_{e}$ [Å]	$D_e[cm^{-1}]$	$T_e[cm^{-1}]$	$\omega_e[cm^{-1}]$
$1^{1}\Sigma^{+}$	Present	3.476	5252	0	123.72
	Experiment $(2008)$ [43]	3.499	5273.62	0	-
	Experiment $(2000)$ [44]	3.499	5273.67	0	124.03
	Experiment $(1985)$ $[13]$	3.498	5275	0	124.01
	Theory $(2016)$ [31]	3.537	5034	0	119.60
	Theory $(2011)$ [45]	3.480	5186	0	123.50
	Theory $(1996)$ [30]	3.477	5187	0	123.44
	Theory $(1984)$ [46]	3.498	5170	0	123.80
	Theory $(1984)$ [47]	3.413	5491	0	127.60
	Theory $(1983)$ [48]	3.392	5000	0	132.00
$2^{1}\Sigma^{+}$	$\mathbf{Present}$	4.170	6171	12105	81.59
	Experiment $(1988)$ [14]	4.196	6220	12  137	81.25
	Theory $(2016)$ [31]	4.236	6121	11  933	78.50
	Theory $(1996)$ [30]	4.181	6121	12  089	81.00
	Theory $(1984)$ [47]	4.064	6532	$12 \ 011$	86.20
	Theory $(1983)$ [48]	4.212	5888	12  300	76.00
$3^{1}\Sigma^{+}$	Present	4.403	4359	17  861	69.12
	Experiment $(2004)$ [28]	4.438	4443	17  787	69.61
	Experiment $(1987)$ $[17]$	4.445	4455	17  787	69.66
	Theory $(2016)$ [31]	4.457	4174	17  677	67.51
	Theory $(2011)$ [45]	4.410	4322	17 818	69.00
	Theory $(1996)$ [30]	4.403	4317	17  837	68.74
	Theory $(1984)$ [47]	4.440	4104	18  368	61.70
	Theory $(1983)$ [48]	4.419	4114	$18 \ 200$	77.00
$4^{1}\Sigma^{+}$	Present	7.184	4347	21  931	33.56
	Experiment $(2003)$ $[27]$	-	-	22 583	-
	Theory $(2011)$ [45]	6.700	4352	21  862	52.40
	Theory $(1996)$ [30]	7.181	4331	21 874	33.92
	Theory $(1983)$ [48]	7.250	4309	$22 \ 245$	-
$5^{1}\Sigma^{+}$	Present	4.294	3233	<b>23554</b>	112.73
	Experiment $(2002)$ [25]	4.307	-	23 531	115.61
	Theory $(2011)$ [45]	4.290	3200	23  517	111.00
	Theory $(1996)$ [30]	4.292	3195	23  527	112.00
	Theory $(1983)$ [48]	4.329	3279	24  147	104.20

**Table 3.** Spectroscopic constants of the ground and excited  ${}^{1}\Sigma^{+}$  states

State	Reference	$R_e$ [A]	$D_e[cm^{-1}]$	$T_e[cm^{-1}]$	$\omega_e[cm^{-1}]$
$1^{1}\Pi$	Present	4.013	1209	17  067	68.82
	Experiment $(1991)$ [49]	4.013	1324	16  993	71.46
	Experiment $(1988)$ [50]	4.016	1306	16  993	71.50
	Theory $(2016)$ [31]	4.105	1169	16  885	64.80
	Theory $(2011)$ [45]	4.040	1213	$17 \ 016$	67.60
	Theory $(1996)$ [30]	4.038	1193	$17 \ 016$	67.60
	Theory $(1984)$ [47]	4.069	1079	17  365	61.30
	Theory $(1983)$ [48]	4.069	726	17  500	65.00
$2^{1}\Pi$	Present	4.133	2075	20  144	82.92
	Experiment $(2008)$ [29]	4.155	2157	20  090	82.76
	Experiment $(1986)$ $[18]$	4.191	2149	20  093	81.52
	Theory $(2016)$ [31]	4.180	2057	19  794	82.05
	Theory $(2011)$ [45]	4.130	2052	20  089	84.80
	Theory $(1996)$ [30]	4.133	2072	20  082	83.00
	Theory $(1984)$ [47]	4.011	1839	20  643	84.00
	Theory $(1983)$ [48]	4.069	1291	21  000	71.00
$3^{1}\Pi$	$\mathbf{Present}$	4.480	1127	25  661	47.28
	Experiment $(1998)$ [22]	4.449	1293	25519	48.80
	Theory $(1996)$ [30]	4.509	1155	25  568	47.20
	Theory $(1984)$ [47]	4.789	738	26 690	46.00
$1^{1}\Delta$	Present	3.794	3628	23  159	96.17
	Theory $(2011)$ [45]	3.800	3751	22  969	97.00
	Theory $(1996)$ [30]	3.794	3761	$22 \ 961$	96.60
	Theory $(1984)$ [47]	3.725	4076	$23 \ 352$	103.60

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Table 4. Spectroscopic constants of the excited  ${}^{1}\Pi$  and  ${}^{1}\Delta$  states

State	Reference	$\mathbf{R}_{e}$ [Å]	$D_e[cm^{-1}]$	$T_e[cm^{-1}]$	$\omega_e[cm^{-1}]$
$1^3\Sigma^+$	Present	5.461	194	5058	21.82
	Experiment $(2008)$ [43]	5.448	208	-	22.82
	Experiment $(1985)$ $[13]$	5.440	209	5066	22.99
	Theory (2016) [31]	5.498	253	4781	21.52
	Theory $(2011)$ [45]	5.460	209	4977	22.50
	Theory $(1996)$ [30]	5.451	197	4990	22.65
	Theory $(1984)$ [47]	5.276	291	5200	26.90
	Theory $(1983)$ [48]	5.588	161	4800	23.00
$2^{3}\Sigma^{+}$	Present	4.303	2557	15  719	73.65
	Experiment $(2000)$ [24]	4.308	2443	15  751	73.40
	Experiment $(1995)$ $[20]$	4.450	2461	15  857	63.17
	Experiment $(1990)$ [51]	4.260	2015	$16\ 283$	68.64
	Experiment $(1989)$ $[15]$	4.100	2319	15  998	73.79
	Experiment $(1988)$ [16]	-	2580	15  719	75.50
	Theory $(2016)$ [31]	4.390	2478	15  576	70.18
	Theory $(2011)$ [45]	4.310	2544	15  684	72.90
	Theory $(1996)$ [30]	4.310	2541	15  669	73.40
	Theory $(1984)$ [47]	4.240	2645	15  799	74.00
	Theory $(1983)$ [48]	4.340	2097	$16\ 100$	77.00
$3^3\Sigma^+$	Present (inner well)	3.930	800	$21 \ 420$	94.47
	Present (outer well)	8.228	<b>34</b>	22  186	9.43
	Theory $(2016)$ [31]	3.993	548	21  303	93.58
	Theory $(2011)$ [45]	3.940	774	21  385	96.40
	Theory $(1996)$ [30]	3.937	774	$21 \ 380$	94.20
	Theory $(1984)$ [47]	3.842	782	21 690	88.30
$4^3\Sigma^+$	Present	4.204	2380	23 898	74.78
	Theory $(2011)$ [45]	4.210	2358	23 854	74.40
	Theory $(1996)$ [30]	4.212	2355	23 850	74.00
	Theory $(1984)$ [47]	4.143	2282	23 649	70.90
$5^3\Sigma^+$	Present	5.190	1862	24 926	98.01
	Theory $(2011)$ [45]	5.190	1878	24 847	96.60
	Theory $(1996)$ [30]	5.191	1855	24 868	97.00
	Theory $(1984)$ [47]	5.234	2047	$25 \ 381$	73.70

**Table 5.** Spectroscopic constants of the excited  ${}^{3}\Sigma^{+}$  states

$1^{3}\Pi$ Present 3.481 6722 11 553 120.49   Experiment (1986) [18] 3.502 6698 11 562 120.37   Theory (2016) [31] 3.555 6528 11 526 117.36   Theory (2011) [45] 3.480 6663 11 503 125.70   Theory (1996) [30] 3.461 6702 11 508 121.71   Theory (1983) [48] 3.450 6291 11 900 129.00   2 <sup>3</sup> Π Present 4.225 1980 20 241 67.27   Experiment (1994) [52] 4.223 2012 20 248 67.38   Experiment (1994) [52] 4.225 2001 20 248 67.38   Theory (2016) [31] 4.333 1769 20 082 62.30   Theory (2016) [31] 4.333 1769 20 082 62.30   Theory (1996) [30] 4.233 1964 20 190 67.09   Theory (1996) [30] 4.233 1964 20 508 69.30   Theory (1984) [47] 5.165 25 167	State	Reference	$R_e$ [Å]	$D_e[cm^{-1}]$	$T_e[cm^{-1}]$	$\omega_e[cm^{-1}]$
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$1^3\Pi$	Present	3.481	6722	11  553	120.49
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		Experiment $(1986)$ $[18]$	3.502	6698	11  562	120.37
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		Theory $(2016)$ [31]	3.555	6528	11  526	117.36
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		Theory $(2011)$ [45]	3.480	6663	11  503	125.70
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		Theory $(1996)$ [30]	3.461	6702	11  508	121.71
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		Theory $(1984)$ [47]	3.440	6910	11  534	122.20
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$		Theory $(1983)$ [48]	3.450	6291	$11 \ 900$	129.00
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$2^3\Pi$	Present	4.225	1980	20 241	67.27
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		Experiment $(1994)$ [52]	4.223	2012	$20\ 248$	67.38
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		Experiment $(1989)$ $[15]$	4.225	2001	$20\ 248$	67.38
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		Theory $(2016)$ [31]	4.333	1769	20  082	62.30
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		Theory $(2011)$ [45]	4.230	1968	20  192	66.40
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		Theory $(1996)$ [30]	4.233	1964	20  190	67.09
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$		Theory $(1984)$ [47]	4.149	1964	20508	69.30
$3^3 \Pi$ Inner well <b>Present3.903157425 21395.06</b> Theory (2011) [45]3.910155525 16798.10Theory (1996) [30]3.911155825 165101.00Outer well </td <td></td> <td>Theory <math>(1983)</math> [48]</td> <td>4.461</td> <td>1049</td> <td><math>21 \ 200</math></td> <td>69.00</td>		Theory $(1983)$ [48]	4.461	1049	$21 \ 200$	69.00
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$3^3\Pi$	Inner well				
$\begin{array}{c c c c c c c c c c c c c c c c c c c $		$\mathbf{Present}$	3.903	1574	$25 \ 213$	95.06
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$		Theory $(2011)$ [45]	3.910	1555	25  167	98.10
$\begin{tabular}{ c c c c c c } \hline Outer well \\ \hline $Present$ & 5.589 & 2052 & 24 735 & 42.45 \\ \hline $Theory (1984) [47]$ & 5.556 & 2329 & 25 099 & 51.70 \\ \hline $1^3\Delta$ & $Present$ & $3.889$ & $2928$ & $23 860$ & $92.73$ \\ \hline $Theory (2011) [45]$ & $3.890$ & $3068$ & $23 651$ & $93.70$ \\ \hline $Theory (1996) [30]$ & $3.889$ & $3075$ & $23 647$ & $93.60$ \\ \hline $Theory (1884) [47]$ & $3.794$ & $3132$ & $24 296$ & $97.70$ \\ \hline \end{tabular}$		Theory $(1996)$ [30]	3.911	1558	25  165	101.00
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$		Outer well				
$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$		Present	5.589	2052	24  735	<b>42.45</b>
$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$		Theory $(1984)$ [47]	5.556	2329	25  099	51.70
Theory (2011) [45] 3.890 3068 23 651 93.70   Theory (1996) [30] 3.889 3075 23 647 93.60   Theory (1884) [47] 3.794 3132 24 296 97.70	$1^{3}\Delta$	Present	3.889	2928	23 860	92.73
Theory (1996) [30] 3.889 3075 23 647 93.60   Theory (1884) [47] 3.794 3132 24 296 97.70		Theory $(2011)$ [45]	3.890	3068	23  651	93.70
Theory $(1884)$ [47] 3.794 3132 24 296 97.70		Theory $(1996)$ [30]	3.889	3075	23  647	93.60
		Theory $(1884)$ [47]	3.794	3132	24 296	97.70

**Table 6.** Spectroscopic constants of the excited  ${}^{3}\Pi$  and  ${}^{3}\Delta$  states