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The adiabatic potentials of low-lying electronic states of the NaRb molecule

M Wiatr, P Jasik and J E Sienkiewicz

Department of Theoretical Physics and Quantum Information, Faculty of Applied Physics and Mathematics, Gdansk University of Technology, ul. Gabriela Narutowicza 11/12, 80-233 Gdansk, Poland

Abstract

Adiabatic potential energy curves and spectroscopic constants have been calculated for the NaRb molecule. The results of ten states of the symmetry Σ^+, six states of the symmetry Π, and two states of the symmetry Δ are obtained by the nonrelativistic quantum chemical method used with pseudopotentials describing the interaction of valence electrons with atomic cores. Analysis is based on a comparison with the results of other theoretical and experimental studies.

Keywords: adiabatic potential curves, spectroscopic parameters, NaRb dimer, quantum chemistry methods, diatomic molecules

(Some figures may appear in colour only in the online journal)

1. Introduction

In recent decades alkali dimers have been intensively investigated by theoreticians and experimentalists. The results of their research are valuable in studies of collision dynamics, laser cooling, Bose–Einstein condensation (BEC), photoassociation, and photodissociation [1–4]. The NaRb molecule is a frequently studied alkali dimer. It is a special candidate for two species of BEC [5].

In 1928, a band in the green region of the spectrum was observed by Walter and Barratt [6]. In 1936, Kusch used magnetic rotation spectroscopy to find a red band system coming from the $^1\Pi$-$^1\Sigma^+$ transitions [7]. The photodissociation of the NaRb molecule was observed in 1987 [1]. Next, this photodissociation was studied with a variety of Doppler-free laser techniques by the Kato group [8–12]. In 2000, heteronuclear hyperfine-state changing cold collisions (a magneto-optical trap containing both Na and Rb atoms) were studied by Young *et al* [13]. In 2002, Tamanis *et al* [14] presented a study of a fully mixed $2^1\Sigma^+$-$1^3\Pi$ complex of the NaRb molecule based on high-resolution sub-Doppler spectroscopy and intensity measurements. The authors also provided *ab initio* relativistic calculations of energies, transition moments, and spin–orbit interactions, as well as an inverted channel-coupling approach deperturbation analysis. Two years later, the $1^1\Sigma^+$ state of NaRb was studied by Fourier transform spectroscopy [15], providing the data required for modeling cold collisions at 1 mK and below. Next, Jastrzebski *et al* [16] presented the first detailed experimental study of the $3^1\Sigma^+$ state of the NaRb molecule. They used two different high-resolution spectroscopic methods: the Fourier transform spectroscopy of laser-induced fluorescence and the V-type optical-optical double resonance polarization labeling spectroscopy. The three low-lying states of the NaRb molecule were studied experimentally by Docenko *et al* [17, 18] using the Fourier transform spectroscopy of laser-induced fluorescence. Thanks to observation of rovibrational levels with the technique of polarization labeling spectroscopy, the long-range potential of the $1^1\Pi$ state of NaRb was investigated in 2006 [19].

The majority of theoretical investigations were conducted using the CIPSI program package of Toulouse (e.g., [20]), which is based on configuration interaction by perturbation of the multiconfiguration wave function method. Two theoretical studies of the electronic structure were performed by Korek *et al* [21, 22]. In the first paper, their calculation used an *ab initio* method based on nonempirical pseudopotentials, parametrized by *l*-dependent polarization potentials and full valence configuration interaction calculations. The potential energy was calculated for the 28 lowest molecular states. In the second paper, the spin–orbit effect was taken into account through a semiempirical spin–orbit pseudopotential added to the electrostatic Hamiltonian. Gaussian basis sets were used for both atoms. In 2001, Zaitsevskii *et al* [23] applied many-

body multipartitioning perturbation theory to calculate the potential energy of the 11 lowest electronic states. A theoretical study of the electronic structure of NaRb was completed by Dardouri *et al* [24], who used the CIPSI program package. Very recently, a comprehensive adiabatic study was performed on the NaRb molecule by Chaieb *et al* [20]. They also used CIPSI with an *ab initio* approach, which involved the effective core potential and the core polarization potential with l-dependent cutoff functions.

The aim of our work is to present the results of calculations on adiabatic potential energy curves and spectroscopic parameters for the NaRb molecule. We apply the nonrelativistic method to compare our results with nonrelativistic results given by other authors, specifically because of some existing disagreements in previous publications. In this way, we would like to check the reliability of our two effective electron computational approach for relatively heavy diatomic molecules. Reliable data on heteronuclear alkali dimers is also important for studies of ultracold molecules (e.g., to control chemical reactions and measurements of the electron dipole moment). Unlike these previous calculations, the present theoretical work was conducted with the MOLPRO suite of programs [25], while the majority of the other theoretical results were prepared with the CIPSI program package.

The theoretical and computational methods for our adiabatic potentials are described in the next two sections. In section 4, we discuss the calculated potential curves, and we compare them with available experimental data and other theoretical results. Conclusions are provided in the last section.

2. Theoretical method

This section introduces the main aspects of the theory previously described in our earlier papers [26–28]. Here, we present the theoretical method implemented in MOLPRO [25]. We consider the interaction between two different alkali atoms. The Schrödinger equation is solved using the Born–Oppenheimer approximation. Two atomic cores are represented by l-dependent pseudopotentials and only two valence electrons are treated explicitly.

An effective, nonlocal pseudopotential, $\hat{V}^{\lambda}$, can be written as

$$\hat{V}^{\lambda} = \sum_{i=1}^{2}\left[\frac{Q_{\lambda}}{r_{\lambda i}} + \sum_{lk} B_{lk}^{\lambda} \exp\left(-\beta_{lk}^{\lambda} r_{\lambda i}^{2}\right)\hat{P}_{l}^{\lambda}\right], \tag{1}$$

where the index λ may be equal to A or B, and it respectively corresponds to the sodium or rubidium atomic core. In the above equation, index i goes over two valence electrons, Q_{λ} is the net charge of the λ core, B_{lk}^{λ} and β_{lk}^{λ} are the parameters of semilocal energy-consistent pseudopotentials [29–31], and $\hat{P}_{l}^{\lambda}$ is the projection operator onto the Hilbert subspace of angular symmetry l with respect to the λ core. The effective core polarization potential, $\hat{V}_{\mathrm{pol}}^{\lambda}$, which describes the core-valence correlation, can be written as

$$\hat{V}_{\mathrm{pol}}^{\lambda} = -\frac{1}{2}\alpha_{\lambda}\vec{F}_{\lambda}^{2}, \tag{2}$$

where α_{λ} is the dipole polarizability of an atomic core (for the A core it is 0.9947 a_0^3 [29], while for the B core it is 8.67 a_0^3 [30, 31]). $\vec{F}_{\lambda}$ is the electric field acting on the λ core, which comes from another core and the valence electrons. The electric field for the A core can be represented by the following formula

$$\vec{F}_{A} = \sum_{i=1}^{2}\frac{\vec{r}_{Ai}}{r_{Ai}^{3}}\left[1 - \exp\left(-\delta_{A} r_{Ai}^{2}\right)\right] - \frac{Q_{B}\vec{R}}{R^{3}}\left[1 - \exp\left(\delta_{A} R^{2}\right)\right]. \tag{3}$$

The analogous equation can be written for the electric field, $\vec{F}_{B}$. The distance between two nuclei is denoted by R, and δ_{A} and δ_{B} are the cutoff parameters of the atomic cores (for Na $\delta_{A} = 0.62\ a_0^{-2}$ [29], for Rb $\delta_{B} = 0.23\ a_0^{-2}$ [30, 31]).

3. Computational method

The cores of the Na and Rb atoms are represented by pseudopotentials ECP10SDF [29] and ECP36SDF [30, 31], respectively. The sodium basis for the s and p orbitals, which come with the effective core potential, ECP10SDF, is enlarged by functions for the d and f orbitals given by Prascher and assigned by CC-PVQZ [32]. In turn, the rubidium bases for the s and p orbitals, which comes with the effective core potential ECP36SDF, is enlarged by functions for the d and f orbitals, which come as a basis set with the effective core potential ECP28MDF [33]. Additionally, our basis sets are augmented by thirteen s functions for both sodium and rubidium atoms, six p functions for sodium atoms, seven p functions for rubidium, seven d functions for sodium atoms, nine d functions for rubidiumatoms, and two f functions for both sodium and rubidium atoms. All exponents of the augmented Gaussian functions are listed in table 1.

The quality of our basis sets was checked by performing configuration interaction calculations for the ground states and several excited states of the isolated sodium and rubidium atoms. We use d the multiconfigurational self-consistent field/complete active space self-consistent field (MCSCF/CASSCF) method and the multireference configuration interaction (MRCI) method to calculate the adiabatic potential energy curves of the NaRb diatomic molecule.

The calculated NaRb adiabatic potentials correlate to Na (3s)+Rb(5s), Na(3s)+Rb(5p), Na(3p)+Rb(5s), Na(3s)+Rb (4d), and Na(3s)+Rb(6 s) atomic asymptotes. The comparison of the experimental and theoretical asymptotic energies for different states is shown in table 2. Calculated atomic energies are compared with the experimental data [34, 35] and other theoretical results [20, 21, 24]. The overall agreement of our results with the experimental data is very reasonable and the ΔE differences for the Na(3s)+Rb(5p), Na(3p)+Rb(5s), Na (3s)+Rb(4d), and Na(3s)+Rb(6 s) asymptotes are equal to

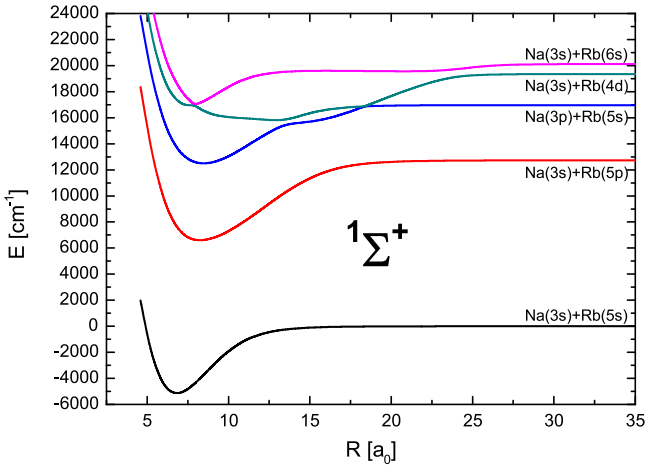

Figure 1. Adiabatic potential energy curves for the ground and four excited $^1\Sigma^+$ electronic states of the NaRb molecule correlating to the Na(3s)+Rb(5s), Na(3s)+Rb(5p), Na(3p)+Rb(5s), Na(3s)+Rb(4d), and Na(3s)+Rb(6 s) asymptotes.

2.12, 0.6, 2.26, and 3.99 cm^{-1}, respectively. Other theoretical asymptotic energies also agree very well with the experimental ones. However, we are able to notice significant discrepancies for the highest atomic asymptote considered here, Na(3s)+Rb(6 s), where the ΔE differences are equal to 31.21, 29.59, and 34.83 cm^{-1} for the results of Korek *et al* [21], Dardouri *et al* [24], and Chaieb *et al* [20], respectively. In table 2, we can also see surprising disagreement for the first asymptote calculated by Chaieb *et al*. The difference between this value and the experimental result equals 19.81 cm^{-1}, while the difference for the next two asymptotes does not exceed 1 cm^{-1}.

4. Results and disscusion

4.1. Adiabatic potential energy curves

To precisely describe the low-energy electronic structure and the related spectroscopic parameters of the NaRb molecule, we consider the adiabatic potential energy curves of five singlet and triplet states of the symmetry Σ^+, three singlets and triplets of the Π states, and one singlet and one triplet of the Δ states. All adiabatic potential energy curves presented in this paper are calculated for the internuclear distance, R, in the range from 4.6 a$_0$ to 86 a$_0$. Potentials of electronic $^1\Sigma^+$ states are presented in figure 1. The ground state and the first excited state are Morse-shaped curves, but the higher excited electronic states, 3-5$^1\Sigma^+$, reveal the exotic character. It is very well visible that the 3$^1\Sigma^+$ state and the 4$^1\Sigma^+$ state show an avoided crossing (AC) at two internuclear distances, R. The first AC occurs at around 18.5 a$_0$, and the energetic gap between these curves is less then 30 cm^{-1}. The second AC is seen at around 13.8 a$_0$, but now the energy gap is bigger and equals approximately 413 cm^{-1}. As one can see in figure 1, the 4$^1\Sigma^+$ electronic state shows very exotic behavior due to two additional ACs with the higher excited state, 5$^1\Sigma^+$. One AC appears in the long-range part of these potentials, around 24.5 a$_0$ with the 590 cm^{-1} difference at this point. Another AC occurs in the Franck–Condon region at around 7.8 a$_0$, and the energy gap is now quite small (less then 140 cm^{-1}). Due to these four ACs the highest excited $^1\Sigma^+$ state possesses a double-well potential energy curve. The first minimum, which lays at the small internuclear separation region, is well visible, sharp, and narrow, while the second one, which is seen at the long-range area, is hardly noticeable, because it is wide and shallow.

In figure 2, we present the adiabatic potential energy curves of the $^3\Sigma^+$ states. The three lowest-lying potentials have regular shapes, in contrast to the two higher-lying ones, which are the typical exotic states with irregular shapes and double wells. However, the first minimum of the 5$^3\Sigma^+$ state is very shallow. The bottom of this potential well lies 43 cm^{-1} below the dissociation asymptote and only 22 cm^{-1} below the potential barrier. Again, we are able to notice an AC between the 4$^3\Sigma^+$ and 5$^3\Sigma^+$ electronic states, which is visible around 10.5 a$_0$. The energy gap between these potentials is almost equal to 300 cm^{-1}. Adiabatic potentials for the $^1\Pi$, $^3\Pi$, $^1\Delta$, and $^3\Delta$ electronic excited states of the NaRb molecule are presented in figures 3–5. Almost all of them are regular Morse-shaped potential energy curves. The only state that shows irregularity is 3$^3\Pi$. This is the double-well potential, but again the first minimum is very shallow. The depth of this well is only equal to 22 cm^{-1} from the dissociation asymptote and 26 cm^{-1} from the potential barrier. We know that the exotic shape of the 3$^3\Pi$ excited state is caused by AC with the higher $^3\Pi$ state, but this will be discussed in more detail in a separate publication.

4.2. Analysis and comparisons

All spectroscopic parameters calculated by means of the Level 8.0 program [36] are listed in tables 3 and 4. These parameters are the equilibrium bond length, R_e, the dissociation energy, D_e, the bond energy, D_0, the vertical transition energy, T_{ev}, the electronic term energy, T_e, the vibrational constant, ω_e, and the rotational constant, B_e. All constants are compared with available data derived from experimental and other theoretical results. The ground electronic state, 1$^1\Sigma^+$, is the most extensively theoretically [20–24, 37, 38] and experimentally [8, 9, 12, 15, 39, 40] investigated potential of all. Our dissociation energy, D_e, of the ground state is equal to 5141 cm^{-1}. This means that our potential well depth is 110 cm^{-1} deeper than the most recent experimental datum obtained by Docenko *et al* [15], and 179 cm^{-1} shallower than the oldest available experimental datum presented by Takahashi *et al* [8]. In two recent theoretical papers by Chaieb *et al* [20] and Dardouri *et al* [24], the authors suggest that the respective ground state dissociation energies are 187 cm^{-1} and 183 cm^{-1} smaller than the values derived from experiments by Docenko *et al*, and much smaller than the values given by Takahashi *et al*. In turn, Korek *et al* present two quite different values. In their first article [21], the potential well depth is more then 500 cm^{-1}

Table 1. The exponents of the augmented Gaussian functions of the atomic orbitals s, p, d, and f for sodium and rubidium atoms.

Na				Rb			
s	p	d	f	s	p	d	f
331.972817	124.919753	1.787376	0.398814	78.729874	5.258465	2.425571	8.194323
144.377908	19.823516	0.877639	0.050752	12.943370	1.648345	1.716379	0.061857
65.954600	3.145794	0.430939		4.937015	0.516699	1.214541	
13.103510	0.005306	0.025034		2.866915	0.004459	0.023862	
4.596767	0.002233	0.012288		2.323530	0.002001	0.009151	
1.612565	0.000940	0.006032		1.883135	0.000898	0.007758	
0.146354		0.002961		0.104504	0.000403	0.003285	
0.102758				0.068519		0.001180	
0.009202				0.007182		0.000423	
0.006548				0.003809			
0.003659				0.003386			
0.001455				0.001597			
0.000417				0.000139			

Table 2. The comparison of asymptotic energies with other theoretical and experimental results. Energies are shown in cm^{-1} units. The capital letter T refers to theoretical results and E denotes experimental data.

Asymptotes	present T	[34, 35] Sansonetti E	[20] Chaieb *et al* T	[24] Dardouri *et al* T	[21] Korek *et al* T
Na (3s)+*Rb* (5p)	12739.47	12737.35	12757.16	12737.87	12737.20
Na (3p)+*Rb* (5s)	16967.03	16967.63	16967.61	16967.61	16969.10
Na (3s)+*Rb* (4d)	19357.64	19355.38	19355.17	19355.65	19355.10
Na (3s)+*Rb* (6s)	20128.52	20132.51	20097.68	20102.92	20101.30

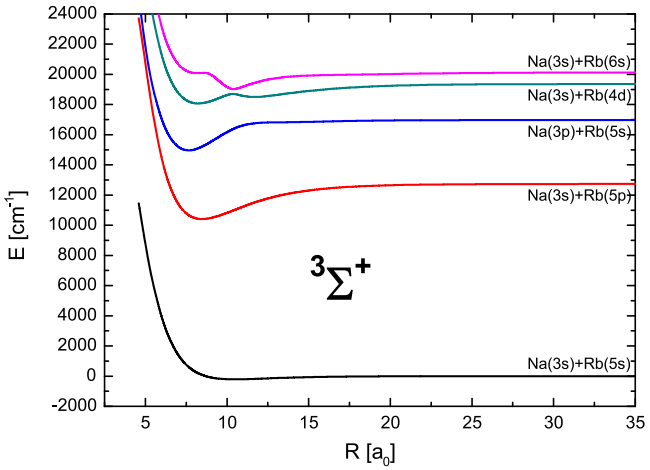

Figure 2. Adiabatic potential energy curves for the five $^3\Sigma^+$ electronic states of the NaRb molecule correlating to the Na(3s)+Rb (5s), Na(3s)+Rb(5p), Na(3p)+Rb(5s), Na(3s)+Rb(4d), and Na(3s) +Rb(6 s) asymptotes.

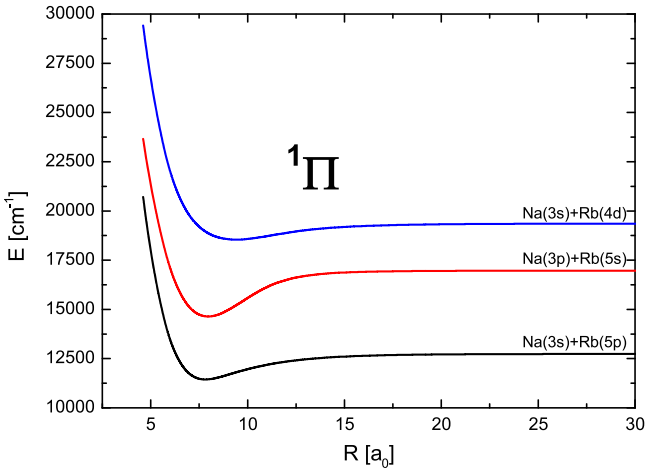

Figure 3. Adiabatic potential energy curves for the three $^1\Pi$ electronic states of the NaRb molecule correlating to the Na(3s)+Rb (5p), Na(3p)+Rb(5s), and Na(3s)+Rb(4d) asymptotes.

shallower than the experimental value [15], while in a recent publication [22], the dissociation energy is 232 cm^{-1} larger than the experimental value given by Docenko *et al* [15].

When it comes to comparisons of the equilibrium bond length, R_e, we notice very good agreement with the experimental datum [15]. Our calculated result is equal to 6.83 a_0 and differs by only 0.06 a_0 from the experimental value. Almost the same agreement is obtained by Chaieb *et al* [20], Aymar *et al* [37], and Zaitsevskii *et al* [23]. Our vibrational constant, ω_e, equals 106.93 cm^{-1} and stays in the best consistent agreement with the experimental data among all theoretical results. In our case, the difference from the experimental constant [15] is equal to 0.08 cm^{-1}. In the cases of Chaieb *et al* [20], Korek *et al* [22], and Zaitsevskii *et al* [23], the differences are 0.18, 1.05, and 0.45 cm^{-1}, respectively. The experimental rotational constant, B_e, obtained by Docenko *et al* [15] equals 0.0702 cm^{-1} and agrees with both our result of 0.0713 cm^{-1} and with the recent theoretical value (0.0710 cm^{-1}) calculated by Chaieb *et al* [20].

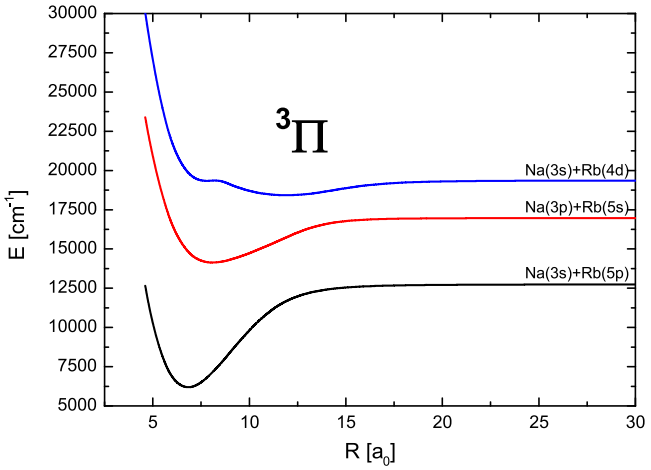

Figure 4. Adiabatic potential energy curves for the three $^3\Pi$ electronic states of the NaRb molecule correlating to the Na(3s)+Rb (5p), Na(3p)+Rb(5s), and Na(3s)+Rb(4d) asymptotes.

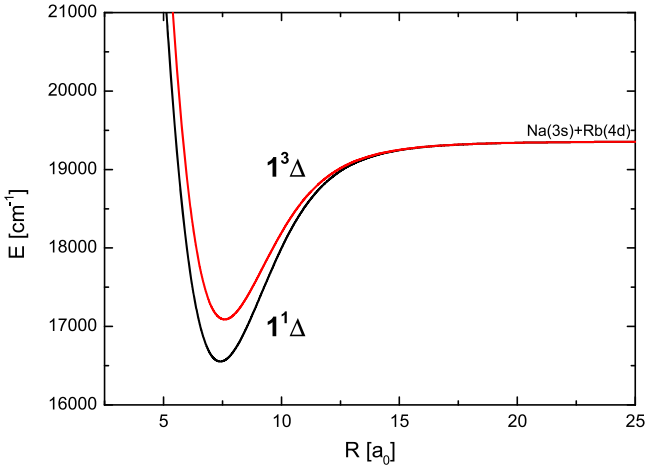

Figure 5. Adiabatic potential energy curves for the $^1\Delta$ and $^3\Delta$ electronic states of the NaRb molecule correlating to the Na(3s)+Rb (4d) asymptote.

To discuss theoretical and experimental adiabatic potential energy curves in all comparative figures, we shift all theoretical potentials by the dissociation energy, D_e = 5030.85 cm^{-1}, derived from the recent experiment by Docenko *et al* [15]. In figure 6, we present the comparison of our adiabatic potential energy curve of the electronic ground $1^1\Sigma^+$ state with other theoretical [21, 23] and experimental [9, 12, 15] results. In this figure, we can see that the shape of our curve and the potential well depth are in very good agreement with the experimental data. We can see some discrepancies for other theoretical potentials. The adiabatic potential energy curve reported by Zaitsevskii *et al* [23] is in excellent agreement with the experimental curves in the vicinity of the potential minimum, while in the long-range internuclear region we can see a big disagreement. In the case of Korek *et al*'s [21] results, the comparison with experimental curves looks quite the opposite. In the Franck–Condon region we notice significant disagreement, while for larger internuclear distances the accordance is acceptable. Summing up the discussion on the ground state, $1^1\Sigma^+$, of the NaRb molecule we can safely conclude that we obtain an excellent agreement with the experimental results within all available theoretical results.

In figure 7, we present the comparison of the excited $1^3\Sigma^+$ state correlating to the ground state asymptote, Na(3s) +Rb(5s), with experimental potential [9] and two theoretical curves [21, 23]. The shape of our adiabatic potential energy curve agrees very well with the potential derived from the experiment, especially in the larger internuclear distances, R. We can observe some discrepancies in the comparison with the other theoretical curves. Both of them lie higher in the vicinity of the potential minimum. For the potential curve calculated by Korek *et al* [21], the best agreement with our data is visible in the potential tail region, while the results of Zaitsevskii *et al* [23] agree in the repulsive part. Spectroscopic parameters for the $1^3\Sigma^+$ state are listed in table 3. Our equilibrium bond length, R_e, and dissociation energy, D_e, are equal to 10.50 a_0 and 210 cm^{-1}, respectively. The experimental values given by Wang *et al* [9] amount to 10.87 a_0 and 182 cm^{-1}, and the respective differences are equal to 0.37 a_0 and 28 cm^{-1}. The theoretical results of Chaieb *et al* [20] and Dardouri *et al* [24] provide better agreement with constants R_e and D_e derived from experiment [9]. In both cases, the discrepancies are smaller than ours. Chaieb *et al*'s results for R_e and D_e differ from the experimental values by 0.19 a_0 and 13 cm^{-1}, respectively. In the case of Dardouri *et al*'s data, these differences amount to 0.17 a_0 and 12 cm^{-1}, respectively.

For the vibrational constant, ω_e, can see the variety of presented values, from 15.30 (Korek *et al* [21]) to 48.48 cm^{-1} (Takahashi *et al* [8]). The relatively small value of this parameter indicates that the potential well is quite wide. Our value for the ω_e constant is equal to 20.22 cm^{-1} and differs from the experimental result [9] by 1.36 cm^{-1}, while this value presented in a recent theoretical paper [20] amounts to 19.30 cm^{-1}, with the analogical difference equal only to 0.44 cm^{-1}. Note that our electronic term energy, T_e, agrees very well with the experimental value [9], and the comparison displays only a 83 cm^{-1} discrepancy, while the value for other theoretical results is 200, 195, 485, 131, and 262 cm^{-1} from papers by Chaieb *et al* [20], Dardouri *et al* [24], Korek *et al* [21, 22], and Zaitsevskii *et al* [23], respectively.

Docenko *et al* [18] experimentally studied the two excited electronic states, $2^1\Sigma^+$ and $1^3\Pi$, correlating to the first excited atomic asymptote, Na(3s)+Rb(5p). The spectroscopic parameters calculated theoretically and derived from the experiment are presented for these states in table 3. In the case of the equilibrium bond length, R_e, we notice overall agreement of the theoretical values with the experimental data for both states, where differences do not exceed 0.13 a_0. For the dissociation energy, D_e, and the electronic term energy, T_e, the discrepancies are larger. In the case of the $2^1\Sigma^+$ state, the dissociation energy given by Docenko *et al* [18] is equal to 6080 cm^{-1}. In our calculations this value is larger by 64 cm^{-1}. The dissociation energies provided by Chaieb *et al* [20] and Dardouri *et al* [24] are smaller in comparison with Docenko *et al* [18] by 38 and 55 cm^{-1}, respectively. We notice a very

Table 3. Spectroscopic parameters R_e (a_0), D_e, T_{ev}, T_e, ω_e, B_e, and D_0 (cm^{-1}) for the ground and excited states of the NaRb molecule. The capital letter T refers to theoretical results and E denotes experimental data.

States	Asymptote	R_e	D_e	T_{ev}	T_e	ω_e	B_e	D_0	References
$1^1\Sigma^+$	Na(3s)+Rb(5s)	6.83	5141			106.93	0.0713	5087	present T
		6.89	5031			106.85	0.0702	4977	[15] Docenko *et al* (2004) E
		6.89				106.84	0.0701		[39] Docenko *et al* (2002) E
			5031						[40] Zemke *et al* (2001) E
		6.89				106.86	0.0702		[12] Kasahara *et al* (1996) E
		6.89	5030			106.86	0.0702		[9] Wang *et al* (1991) E
		6.72	5320			106.97	0.0736	5263	[8] Takahashi *et al* (1981) E
		6.84	4844			106.67	0.0710	4792	[20] Chaieb *et al* (2014) T
		6.80	4848						[24] Dardouri *et al* (2012) T
		6.78	5263			107.90	0.0723		[22] Korek *et al* (2009) T
		6.84							[37] Aymar *et al* (2005) T
		6.84				107.30			[23] Zaitsevskii *et al*(2001) T
		7.01	4490			103.90	0.0676		[21] Korek *et al* (2000) T
		6.86	4920			106.00			[38] Igel-Mann *et al* (1986) T
$1^3\Sigma^+$		10.50	210	6815	4931	20.22	0.0298	200	present T
			183						[40] Zemke *et al* (2001) E
		10.87	182		4848	18.86	0.0282		[9] Wang *et al* (1991) E
			568			48.48		544	[8] Takahashi *et al* (1981) E
		10.68	195	6621	4648	19.30	0.0291	186	[20] Chaieb *et al* (2014) T
		10.70	194		4653				[24] Dardouri *et al* (2012) T
		10.22	284		4979	22.40	0.0318		[22] Korek *et al* (2009) T
		10.32			5110	21.70			[23] Zaitsevskii *et al*(2001) T
		11.22			4363	15.30	0.0264		[21] Korek *et al* (2000) T
$2^1\Sigma^+$	Na(3s)+*Rb*(5p)	8.25	6144	12724	11736	67.54	0.0488	6110	present T
		8.32	6080		11689				[18] Docenko *et al* (2007) E
		8.29	6042	12499	11559	66.79	0.0483	6008	[20] Chaieb *et al* (2014) T
		8.27	6025		11454				[24] Dardouri *et al* (2012) T
		8.20	6578		11765				[22] Korek *et al* (2009) T
		8.45			11396	66.40	0.0466		[21] Korek *et al* (2000) T
$2^3\Sigma^+$		8.47	2330	16850	15550	61.78	0.0462	2299	present T
		8.55	2172	16811	15429	60.43	0.0454	2142	[20] Chaieb *et al* (2014) T
		8.67	2155		15324				[24] Dardouri *et al* (2012) T
		8.67			15202	58.60	0.0443		[21] Korek *et al* (2000) T
$1^1\Pi$		7.81	1297	16966	16583	61.91	0.0542	1267	present T
		7.91	1319			60.38	0.0528		[19] Pashov *et al* (2006) E
		7.89	1319		16528	61.17	0.0534		[9] Wang *et al* (1991) E
		7.73					0.0557	1492	[8] Takahashi *et al* (1981) E
		7.96	1112	16987	16489	54.58	0.0524	1084	[20] Chaieb *et al* (2014) T
		7.77	1445		16634	62.40	0.0551		[22] Korek *et al* (2009) T
		7.71			16420	58.80			[23] Zaitsevskii *et al*(2001) T
		8.37			16321	51.60	0.0495		[21] Korek *et al* (2000) T
$1^3\Pi$		6.82	6559	11267	11321	104.43	0.0715	6507	present T
		6.87	6378		11361				[18] Docenko *et al* (2007) E
		6.84	6307	11294	11294	102.88	0.0710	6256	[20] Chaieb *et al* (2014) T
		7.00			11303	103.50	0.0679		[21] Korek *et al* (2000) T
$3^1\Sigma^+$	Na(3p)+Rb(5s)	8.46	4467	18786	17641	63.49	0.0464	4436	present T
		8.52	4419		17568	63.60	0.0458	4387	[16] Jastrzebski *et al* (2005) E
		8.51	4256	18634	17554	65.10	0.0459	4225	[20] Chaieb *et al* (2014) T
		8.40	4255		17460				[24] Dardouri *et al* (2012) T
		8.34	4525		17705	64.90	0.0477		[22] Korek *et al* (2009) T
		8.61			17315	63.80	0.0449		[21] Korek *et al* (2000) T

Table 3. (Continued.)

States	Asymptote	R_e	D_e	T_{ev}	T_e	ω_e	B_e	D_0	References
$3^3\Sigma^+$		7.65	2010	20455	20097	79.37	0.0567	1971	present T
		7.67	1842	20372	19968	80.45	0.0565	1803	[20] Chaieb *et al* (2014) T
		7.79	1848		19967				[24] Dardouri *et al* (2012) T
		7.85			19837	76.80	0.0540		[21] Korek *et al* (2000) T
$2^1\Pi$		7.95	2336	20401	19772	73.39	0.0525	2299	present T
		7.99	2311		19693	73.10	0.0521	2275	[17] Docenko *et al* (2005) E
		7.97			19692	73.26	0.0524		[23] Zaitsevskii *et al*(2001) E
		7.82				73.50	0.0544	2541	[8] Takahashi *et al* (1981) E
		7.99	2104	20391	19706	74.52	0.0520	2068	[20] Chaieb *et al* (2014) T
		7.77	2381		19849	74.60	0.0538		[22] Korek *et al* (2009) T
		7.86			19475	70.30			[23] Zaitsevskii *et al* (2001) T
		8.14			19529	71.90	0.0503		[21] Korek *et al* (2000) T
$2^3\Pi$		8.08	2834	19909	19273	61.89	0.0507	2803	present T
		8.13	2705	19796	19104	58.58	0.0503	2675	[20] Chaieb *et al* (2014) T
		8.33			18946	58.50	0.0479		[21] Korek *et al* (2000) T

Table 4. Spectroscopic parameters R_e (a_0), D_e, T_{ev}, T_e, ω_e, B_e and D_0 (cm^{-1}) for excited states of the NaRb molecule where no experimental data is currently available.

States	Asymptote	R_e	D_e	T_{ev}	T_e	ω_e	B_e	D_0	References
$4^1\Sigma^+$	Na(3s)+Rb(4d)	12.93	3541	22447	20958	35.74	0.0202	3523	present
		12.91	3511	22365	20688	26.08	0.0199	3493	[20] Chaieb *et al* (2014)
		9.68	3247		20967				[24] Dardouri *et al* (2012)
$4^3\Sigma^+$		8.22	1286	24135	23212	65.37	0.0491	1253	present
		8.27	1193	23992	23006	64.02	0.0486	1161	[20] Chaieb *et al* (2014)
		8.12	2098		22116				[24] Dardouri *et al* (2012)
second minimum		11.68	855		23644	40.09	0.0243	835	present
		11.70	777						[20] Chaieb *et al* (2014)
$3^1\Pi$		9.38	814	25113	23685	37.41	0.0376	795	present
		9.62	647	25208	23551	36.65	0.0359	630	[20] Chaieb *et al* (2014)
		9.76			23284	35.90	0.0349		[21] Korek *et al* (2000)
$3^3\Pi$		11.95	935	24947	23564	30.11	0.0233	920	present
		12.00	907	24924	23292	33.17	0.0231	891	[20] Chaieb *et al* (2014)
$1^1\Delta$		7.40	2812	21827	21687	80.63	0.0605	2771	present
		7.48	2605	21775	21594	80.15	0.0594	2566	[20] Chaieb *et al* (2014)
		7.36			21782	80.30	0.0613		[22] Korek *et al* (2009)
		7.66			21575	76.60	0.0568		[21] Korek *et al* (2000)
$1^3\Delta$		7.59	2274	22492	22224	76.29	0.0577	2236	present
		7.67	2084	22478	22115	76.17	0.0565	2048	[20] Chaieb *et al* (2014)
		7.86			22077	70.80	0.0539		[21] Korek *et al* (2000)
$5^1\Sigma^+$	Na(3s)+Rb(6 s)	7.97	3093	23703	22177	155.25	0.0520	3015	present
		7.89	2840	23406	22101	102.73	0.0534	2775	[20] Chaieb *et al* (2014)
		8.13	1928		23012				[24] Dardouri *et al* (2012)
second minimum		20.64	562		24707	8.61	0.0079	558	present
		20.64	534						[20] Chaieb *et al* (2014)
$5^3\Sigma^+$		10.40	1111	26025	24158	103.82	0.0306	1059	present
		10.45	1035	25933	23906	81.69	0.0304	987	[20] Chaieb *et al* (2014)
		10.53	1028						[24] Dardouri *et al* (2012)

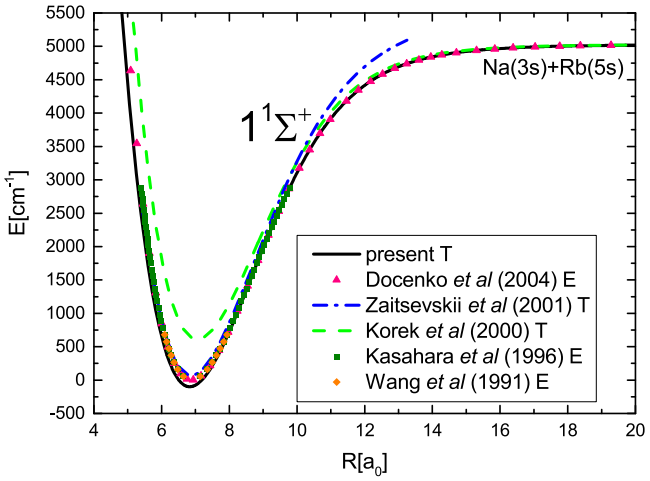

Figure 6. The comparison of the ground $1^1\Sigma^+$ state of the NaRb molecule with experimental data obtained by Docenko *et al* [15], Kasahara *et al* [12], and Wang *et al* [9], as well as with other theoretical results presented by Zaitsevskii *et al* [23] and Korek *et al* [21]. The capital letter T refers to theoretical results and E denotes experimental data.

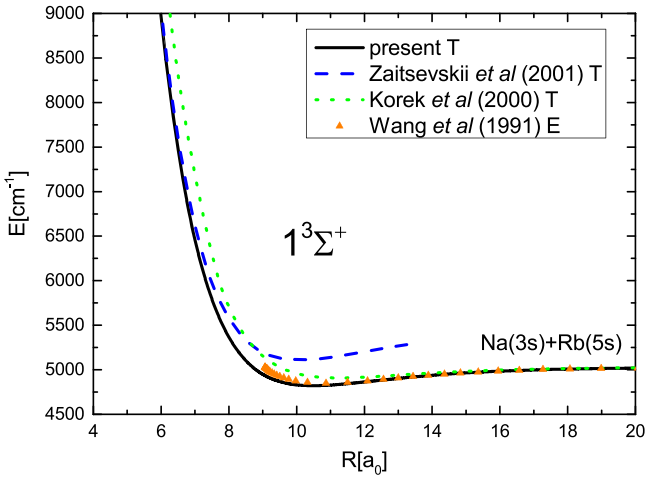

Figure 7. The comparison of the excited $1^3\Sigma^+$ state of the NaRb molecule with experimental data obtained by Wang *et al* [9], and with other theoretical results presented by Zaitsevskii *et al* [23] and Korek *et al* [21]. The capital letter T refers to theoretical results and E denotes experimental data.

big discrepancy in the case of Korek *et al*'s [22] result, where D_e is larger by 498 cm^{-1}. When it comes to T_e, we obtain the best agreement with the recent experimental datum given by Docenko *et al* [18], and the discrepancy equals only 47 cm^{-1}. In the case of the other theoretical results, all differences are larger and equal 76, 130, 235, and 293 cm^{-1} for Korek *et al* [22], Chaieb *et al* [20], Dardouri *et al* [24], and Korek *et al* [21], respectively. In turn, for the $1^3\Pi$ electronic state, we can observe some disagreements in the comparisons of the spectroscopic parameters. Our dissociation energy (6559 cm^{-1}) is larger by 181 cm^{-1} than the result derived from experiments by Docenko *et al* (6378 cm^{-1}) [18], while in the case of Chaieb *et al* (6307 cm^{-1}) [20] this energy is smaller by only 71 cm^{-1} than the experimental result. In the comparisons

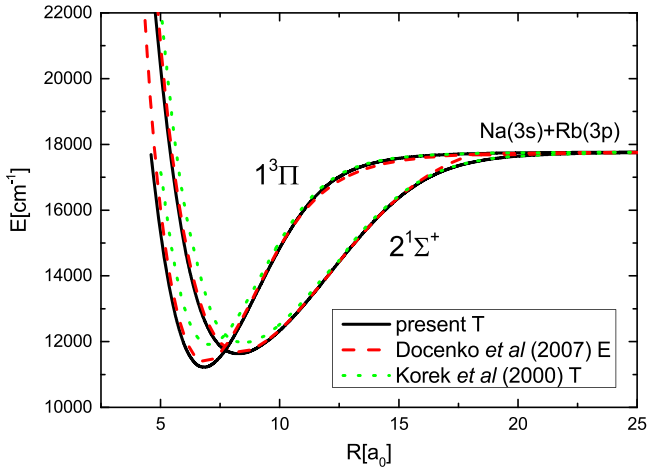

Figure 8. The comparison of the excited $2^1\Sigma^+$ and $1^3\Pi$ states of the NaRb molecule with experimental data obtained by Docenko *et al* [18], as well as with other theoretical results presented by Korek *et al* [21]. The capital letter T refers to theoretical results and E denotes experimental data.

of the electronic term energy, T_e, with the other theoretical results [20, 21], once again we can see the best agreement with the experimental datum [18]. Our difference is equal to 40 cm^{-1}, while for other results it is bigger than 55 cm^{-1}. Figure 8 presents the comparison of our adiabatic potential energy curves for the $2^1\Sigma^+$ and $1^3\Pi$ states with potentials derived from the experiments by Docenko *et al* [18], as well as with theoretical results obtained by Korek *et al* [21]. It is very well visible that the shapes of our potentials agree almost perfectly with curves determined experimentally [18], while theoretical adiabatic potentials given by Korek *et al* [21] are noticeably shallower. Only small discrepancies are seen for larger internuclear distances around 13 and 18 a$_0$ for the $1^3\Pi$ and $2^1\Sigma^+$ states, respectively. We suppose that these small differences are caused by problems with matching the experimental and analytical parts of the potential energy curves described by Docenko *et al* [18].

The next excited electronic state of the NaRb molecule, which was extensively investigated experimentally [8, 9, 19], is the $1^1\Pi$ state. In table 3 we present all available spectroscopic constants for this state. Our dissociation energy, D_e (1297 cm^{-1}), agrees very well with the value derived from two experiments [9, 19] (1319 cm^{-1}). In our case the difference equals only 22 cm^{-1}, while in the case of the recent theoretical result [20], it is much bigger and equals 207 cm^{-1}. When it comes to the electronic term energy, T_e, the comparison of our result with experimental [9] and recent theoretical [20] data is quite reasonable. The differences between our results and those of Chaieb *et al* from experimental data do not exceed 60 cm^{-1}, while for older theoretical papers [21, 23] the results are larger than 100 cm^{-1}. In turn, we obtain very good agreement in the comparison of our vibrational constant, ω_e (61.91 cm^{-1}), with experimental values. Discrepancies are equal to 1.53 cm^{-1} for Pashov *et al*'s [19] result and only 0.74 cm^{-1} for Wang *et al*'s [9] result. The disagreement between the latest theoretical results [20] and

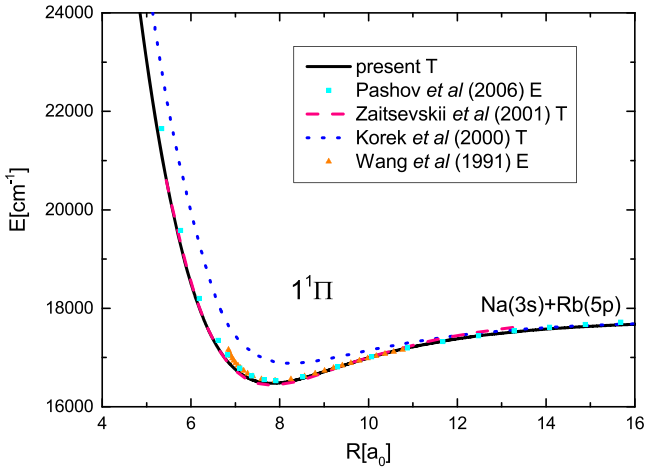

Figure 9. The comparison of the excited $1^1\Pi$ state of the NaRb molecule with experimental data obtained by Pashov *et al* [19] and Wang *et al* [9], as well as with other theoretical results presented by Zaitsevskii *et al* [23] and Korek *et al* [21]. The capital letter T refers to theoretical results and E denotes experimental data.

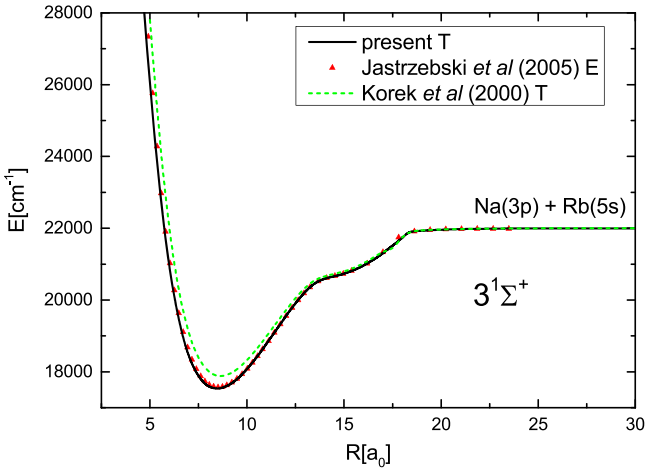

Figure 10. The comparison of the excited $3^1\Sigma^+$ state of the NaRb molecule with experimental data obtained by Jastrzebski *et al* [16] and theoretical results presented by Korek *et al* [21]. The capital letter T refers to theoretical results and E denotes experimental data.

the recent value derived from experiments [19] exceeds 5 cm^{-1}. In figure 9, we present the comparison of our adiabatic potential energy curve for the $1^1\Pi$ state, with potentials obtained in experiments by Pashov *et al* [19] and Wang *et al* [9], as well as with the other theoretical results given by Zaitsevskii *et al* [23] and Korek *et al* [21]. Once again we notice almost perfect agreement with the experimental data. The only one visible discrepancy concerns the adiabatic potential published by Korek *et al*.

Table 3 also lists spectroscopic parameters for electronic excited states, which correlate to the Na(3p)+Rb(5s) asymptote. Two of them, $3^1\Sigma^+$ and $2^1\Pi$, have both experimental and theoretical data, while only theoretical results are available for triplet states. For the $3^1\Sigma^+$ state, the present dissociation energy, D_e, is equal to 4467 cm^{-1} and it agrees almost perfectly with Jastrzebski *et al*'s [16] reported experimental value of 4419 cm^{-1}. However, the comparison of other theoretical results with the recent experiment shows larger discrepancies of 163, 164, and 106 cm^{-1} for the data of Chaieb *et al* [20], Dardouri *et al* [24], and Korek *et al* [22], respectively. In turn, for the electronic term energy, T_e, the nearest theoretical value to the experimental value was obtained by Chaieb *et al* [20], and the difference is only equal to 14 cm^{-1}, while in our case it is equal to 73 cm^{-1}. For other theoretical results [21, 22, 24], discrepancies are larger than 100 cm^{-1}. Once again, very good agreement is reached in the case of the comparison of our vibrational constant, ω_e (63.49 cm^{-1}), with the value derived from experiments, by Jastrzebski *et al* [16] (63.60 cm^{-1}), where the difference amounts to only 0.11 cm^{-1}.

Figure 10 presents the comparison of our adiabatic potential for the $3^1\Sigma^+$ state with the other theoretical curve provided by Korek *et al* [21] and the adiabatic potential energy curve obtained experimentally by Jastrzebski *et al* [16]. The shape of this potential is rather exotic, as discussed in section 4.1. Regardless of the irregular shape of the $3^1\Sigma^+$ state, we get consummate agreement with the curve derived from the experiment. It is clearly visible that the other theoretical potential is shallower in the vicinity of the curve minimum, while disagreement disappears for larger internuclear separations disagreement.

The $2^1\Pi$ state is the last excited state considered here for which experimental data are available (see table 3). For our dissociation energy, D_e, we can report close agreement with the recent experimental value of Docenko *et al* [17]. The discrepancy between these results equals only 25 cm^{-1}, while for recent theoretical data it equals 207 cm^{-1} in the case of Chaieb *et al* [20] and 70 cm^{-1} in the case of Korek *et al* [22]. Our result of R_e = 7.95 a_0 is in good agreement with both experimental results: 7.99 [17] and 7.97 a_0 [23]. However, Chaieb *et al* [20] present exactly the same value as Docenko. Our vibrational constant, ω_e = 73.39 cm^{-1}, agrees very well with all data derived from experiments and presented in table 3. The disagreements do not exceed 0.3 cm^{-1}. In the case of other theoretical results, two of them [20, 22] are greater by approximately 1.5 cm^{-1} than the recent experimental value [17], and the two other are smaller [21, 23]. Figure 11 provides the comparison of our adiabatic potential with other theoretical curves and available experimental potentials. The shape of our curve agrees almost perfectly with the result given by Docenko *et al* [17], except the high-energy repulsive part of the potential. We notice some disagreement for other theoretical data. The potential calculated by Zaitsevskii *et al* [23] lays slightly lower than ours, while the curve obtained by Korek *et al* [21] agrees with our potential only in the tail region, and for smaller internuclear distances, it is moved a little bit upward.

In table 4 we present the comparison of our spectroscopic parameters for excited electronic states correlating to the Na (3s)+Rb(4d) and Na(3s)+Rb(6 s) asymptotes only with other theoretical results [20–22, 24], because experimental data are not available for these states. The overall agreement of all listed table values is quite reasonable, but we notice some

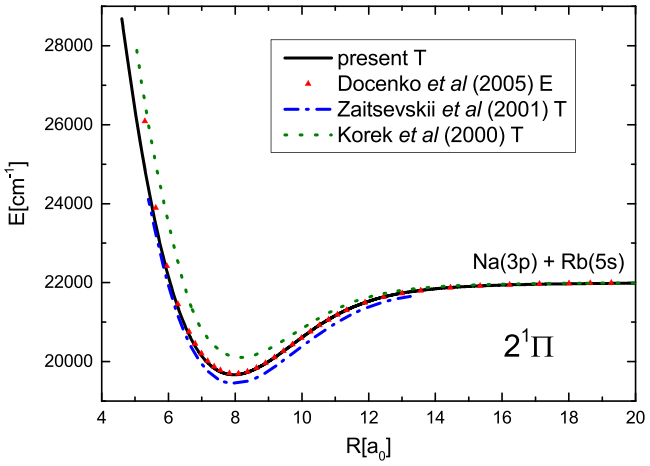

Figure 11. The comparison of the excited $2^1\Pi$ state of the NaRb molecule with experimental data obtained by Docenko *et al* [17], as well as with other theoretical results presented by Zaitsevskii *et al* [23] and Korek *et al* [21]. The capital letter T refers to theoretical results and E denotes experimental data.

significant discrepancies. For example, in the case of the comparison of our dissociation energy, D_e, with the results of Dardouri *et al* [24], differences are the most visible for $4^3\Sigma^+$ and $5^1\Sigma^+$ states and are equal to 812 and 1165 cm^{-1}, respectively. In turn, the analogical comparison with the datum provided by Chaieb *et al* [20] gives values amounting to 93 and 253 cm^{-1}, respectively. Some disagreements are also noticed for the vibrational constant, ω_e. For the $4^1\Sigma^+$, $5^1\Sigma^+$, and $5^3\Sigma^+$ excited states values calculated by Chaieb *et al* differ from our results by 9.66, 52.52, and 22.13 cm^{-1}, respectively.

Particularly, two double-well potential energy curves, $4^3\Sigma^+$ and $5^1\Sigma^+$, are noteworthy; their spectroscopic constants are listed in table 4. The equilibrium bond length, R_e, and the dissociation energy, D_e, are known for these states from the Chaieb *et al* paper [20]. For the first time, we also present other spectroscopic parameters like the bond energy, D_0, the electronic term energy, T_e, the vibrational constant, ω_e, and the rotational constant, B_e.

5. Conclusions

We have calculated the adiabatic potential energy curves for the excited states of the NaRb molecule using the CASSCF/MRCI method. The comparison with available experimental data consistently gives very good agreement. In turn, comparisons with the other theoretical results give some insight into the reliability of different theoretical calculations. Our nonrelativistic approach uses large atomic pseudopotentials and a carefully chosen extensive basis of atomic functions. In effect we perform only two-electron calculations. This method gives overall reliable results for the excited states, which are in excellent agreement with the potential curves derived from experimental data. Also, our spectroscopic constants obtained from the calculated potential curves display very reasonable overall agreement with the experimental data given by different authors. In future work, the obtained potential curves and molecular wave functions will be used to design and calculate photodissociation and photoassociation processes.

Detailed numerical data can be found at http://aqualung.mif.pg.gda.pl/results/narb.

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