


# Analytical potential energy function study for the $4^1\Pi$ electronic state of $\text{Na}^{85}\text{Rb}$ molecule

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## Abstract

In this paper, a new spectroscopic and analytical potential energy function (APEF) investigation on the  $4^1\Pi$  electronic state of the  $\text{Na}^{85}\text{Rb}$  molecule is reported. This research is conducted by using the 4-terms variation algebraic energy consistent method (VAECM(4)) with a variable parameter  $\lambda$ . The calculated full vibrational energies of 78 levels are used in a global linear reduction to molecular vibrational constants. With these new and improved vibrational constants, the potential energy curve and the vibrational force constants  $f_n$  have been calculated. Precise values for the long-range parameters and the dissociation energy have been derived. The results obtained in this study also provide valuable reference data for other areas of researches on  $\text{Na}^{85}\text{Rb}$ .

Keywords:  $\text{Na}^{85}\text{Rb}$ , vibrational energy, analytical potential energy function, variation algebraic energy consistent method

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

## 1. Introduction

In the past few decades, great progress has been made in the study of alkali metal dimers [1–4]. The investigation of the NaRb molecule is particularly interesting here and has been widely applied in other fields since the NaRb molecule and its isotopomer are rich in fine structure, from which detailed information about the internal spin–orbit interaction of this molecule can be achieved [5, 6]. On the other hand, the NaRb molecule has considerable permanent electric dipole moments that allow it to be manipulated by an external electric field [5–8]. Both experimentally and theoretically, these researches are useful in investigations of scattering length, photoassociation spectra of cold molecules, the transition spectra of electronic states, the dynamics of alkali metal atom collisions, the adiabatic potentials and Bose–Einstein condensation (BEC)

[5–11]. Furthermore, the NaRb molecule is a very promising candidate for two species Bose–Einstein condensation (TBEC) to investigate the formation of ultracold molecules [4, 9, 12]. Much research efforts have been dedicated to the electronic states of NaRb molecule in experiments and theories such as the  $1^1\Sigma^+$ ,  $2^1\Sigma^+$ ,  $3^1\Sigma^+$ ,  $14^3\Sigma^+$ ,  $1 - 9^1,3\Pi$ ,  $C(3)^1\Sigma^+$ ,  $D^1\Pi$  electronic states and so on [11, 13–16]. In [13] the spectrum of NaRb molecule was measured by the Fourier transform spectroscopy (FTS) of laser induced fluorescence (LIF) and the V-type optical–optical double resonance polarization labeling spectroscopy, and the potential energy curve (PEC) of  $C(3)^1\Sigma^+$  correlating to the dissociation limit  $\text{Na}(3p) + \text{Rb}(5s)$  was calculated by Jastrzebski *et al* utilizing the Inverted Perturbation Approach (IPA) method.

Meaningful researches have been done on the various electronic states of NaRb molecule and its isotopomers such as the  $4^1\Pi$  electronic state due to its prototypes of diatomic, heteronuclear systems and the lack of high-lying energy

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spectrum information [5]. For example, In 1999, Korek *et al* calculated potential curve, minimum-to-minimum electronic excitation energy  $T_e$ , spectrum constants  $\{\omega_e, B_e\}$ , and internuclear equilibrium distance  $R_e$  by *ab initio* method for  $4^1\Pi$  electronic state of  $^{23}\text{Na}^{85}\text{Rb}$  [15]. In 2009, an experimental investigation was formed by Bang *et al* using the polarisation labeling spectroscopy (PLS) technique, resulting in determination of the rotationless energies for the  $4^1\Pi$  state of  $\text{Na}^{85}\text{Rb}$  molecule [5]. In 2014, Chaieb *et al* applied the *ab initio* method to many electronically excited states of  $\text{NaRb}$  molecule and  $\text{Na}^-\text{Rb}^+$  ionic involving the  $4^1\Pi$  electronic state. They had computed spectroscopic constants such as  $R_e$ ,  $\omega_e$ ,  $\omega_e x_e$ ,  $B_e$ ... and built up corresponding potential energy curves [16].

Although these relevant researches enable us to characterize the electronic states of  $\text{NaRb}$  molecule and their associated spectroscopic parameters, the major focus of these investigation is still of great challenge to us due to their complex molecular structures [6, 17]. During scientific experiments, the high-lying vibration levels may not be unambiguously recorded because of their weakness and extreme overlapping for alkali dimer [18]. The wealthy high-lying energies have to be obtained using high-resolution instruments, furthermore, inadequate spectroscopic analysis experimentally is attributed, in part, to that the spectra of  $\text{Na}_2$  and  $\text{Rb}_2$  molecules often covered the spectra of heteronuclear species,  $\text{Na}^{85}\text{Rb}$  [19–21]. The  $4^1\Pi$  electronic state is one of special diatomic systems and lack of more specific spectrum information, has important research significance, where the full vibrational spectra, especially in levels very close to dissociation, are needed to construct the reliable analytical potential energy function (APEF).

Since the advent of quantum mechanics and modern spectroscopic measurements, calculation methods have been developed to directly fit the potential energy curves (PECs) or potential energy surfaces (PESs) of diatomic molecules or polyatomic molecules. For example, A double many-body expansion (DMBE) theory of molecular energy suggested by Varandas *et al* is very useful to determine the APEF of small polyatomic systems [22]. Later, to explain some issues such as the coulomb behavior of the collapsed diatomic limit at the disappearing small interatomic distance, Varandas *et al* proposed an extended Hartree–Fock-approximate correlation energy (EHFACE) model [23–25], which is expected to be a good candidate for diatomic potentials of  $\text{Cs}_2$ ,  $\text{Rb}_2$ ,  $\text{NO}$ ,  $\text{HF}$ ,  $\text{CO}$  *et al*.

Recently, Sun *et al* proposed a variational algebraic energy consistent method (VAECM) that is used to construct APEFs for diatomic molecules [17, 26–31], the results were in good agreement with the experimental data, also got more high-lying energies converging to the dissociation energy. This work is based on the VAECM(4) APEF that is a combined form of segment functions of the Morse [32] and an extended HMS (Huxley–Murrell–Sorbie) potential [33]. The calculated full vibrational energies, dissociation energy considered as converging criterion are used to generate PEC for the  $4^1\Pi$  electronic state of  $\text{Na}^{85}\text{Rb}$ , with the values from EHFACE2U potential [25], Morse potential [32], PG

(Pseudogaussian) potential [34], and Rydberg potential [35] shown for comparison. Section 2 introduces the VAECM (4) method and VAM method. The spectrum and discussion are presented in section 3. Section 4 comes to the conclusion.

## 2. Theory and method

Here is a simple characterization of variational algebraic energy consistent method (VAECM) which is improved by combining the Sun's energy consistent-method (ECM) [26] and variational algebraic method (VAM) [36]. The VAECM potential  $V_{\text{VAECM}}(R)$  is presented as [30, 31]

$$V_{\text{VAECM}}(R) = V_{\text{HMS}}(R) + \Lambda(R)[V_{\text{HMS}}(R) - V_M(R)]. \quad (1)$$

Based on equation (1), the following formula has been obtained after the promotion by Sun's group

$$V_{\text{VAECM}(4)}(R) = V_{\text{HMS4}}(R) + \Lambda(R)[V_{\text{HMS4}}(R) - V_M(R)], \quad (2)$$

where the prior  $V_{\text{VAECM}}(R)$  has been substituted by the  $V_{\text{VAECM}(4)}(R)$ . In equation (1)  $V_{\text{HMS}}(R)$  corresponds to the HMS potential [33] and  $V_M(R)$  is the Morse potential. In equation (2), for the sake of improving the behavior near the dissociation energy, the  $V_{\text{HMS}}(R)$  has been replaced by the  $V_{\text{HMS4}}(R)$  with  $N = 4$

$$V_M(R) = D_e[e^{-2\beta x} - 2e^{-\beta x}], \quad (3)$$

$$V_{\text{HMS4}}(R) = -D_e \left( 1 + \sum_{n=1}^N a_n x^n \right) e^{-a_1 x}, \quad N = 4. \quad (4)$$

In the formula above,  $D_e$  is the dissociation energy, and  $x = R - R_e$ , where  $R$  is intermolecular nuclear distance,  $R_e$  corresponds equilibrium position of intermolecular nuclear distance. The expression for  $\beta$  is

$$\beta = (f_2 / (2D_e))^{1/2}, \quad (5)$$

where

$$f_2 = \mu \omega_e^2. \quad (6)$$

The equations (7)–(11) are used to calculate potential expansion coefficients  $a_n$ , and the vibration force constants  $f_n$  with the definitions of  $f_0 = -D_e$ ,  $f_1 = 0$ ,  $N = 4$ ,  $a_5 = 0$ . Using second-order perturbation theory, one can get equations (12)–(14)

$$a_n = -\frac{1}{D_e} \sum_{m=0}^n \frac{f_{n-m}}{m!(n-m)!} a_1^m, \quad n \geq 2, \quad (7)$$

$$D_e a_1^5 - 10f_2 a_1^3 - 10f_3 a_1^2 - 5f_4 a_1 - f_5 = 0, \quad (8)$$

$$a_2 = \frac{1}{2D_e} (D_e a_1^2 - f_2), \quad (9)$$

$$a_3 = \frac{1}{6D_e} (D_e a_1^3 - 3f_2 a_1 - f_3), \quad (10)$$

$$a_4 = \frac{1}{24D_e} (D_e a_1^4 - 6f_2 a_1^2 - 4f_3 a_1 - f_4), \quad (11)$$

$$\omega_e x_e = \frac{5f_3^2}{48\omega_e \alpha^3} - \frac{f_4}{16\alpha^2} + \frac{217f_5^2}{92160\omega_e \alpha^5}, \quad (12)$$

$$\omega_e y_e = -\frac{17f_4^2}{2304\omega_e \alpha^4} - \frac{7f_3 f_5}{288\omega_e \alpha^4}, \quad (13)$$

$$\alpha_e = -\frac{1}{2\mu\alpha R_e^4} \left( 3 + \frac{175}{8\alpha^2 R_e^4} \right) - \frac{f_3}{2\alpha^3 R_e^3} \left( 1 + \frac{95}{8\alpha^2 R_e^4} \right) + \frac{335f_4}{384\alpha^5 R_e^6} - \frac{19f_5}{96\alpha^5 R_e^5}, \quad (14)$$

where  $\alpha = \mu\omega_e$ , ( $D_e$ ,  $R_e$ ,  $\omega_e$ ,  $\omega_e x_e$ ,  $\alpha_e$ ) are molecular constants,  $\mu$  is the reduced mass.

Finally, the expression for the variational function  $\Lambda(R)$  [30, 31] is following

$$\Lambda(R) = \lambda \left( \frac{x}{R} \right)^{N-2} [1 - e^{-x\lambda^2/R_e}], \quad N \geq 3, \quad (15)$$

Where  $\lambda$  is a variational parameter, so the  $\Lambda(R)$  is a variational function, in addition, the  $\Lambda(R)$  and its  $k$  derivatives  $\Lambda^{(k)}(R)$  are zero at  $R = R_e$

$$\Lambda(R) = \Lambda^{(k)}(R_e) = 0, \quad k = 1, 2, \dots, N-2. \quad (16)$$

The  $V_{\text{VAECM}(4)}(R)$  in equation (1) meets these physical conditions

$$V_{\text{VAECM}(4)}(R)_{R=R_e} = -D_e, \quad (17)$$

$$V_{\text{VAECM}(4)}(R)_{R \rightarrow \infty} \rightarrow \text{const.}, \quad (18)$$

$$V_{\text{VAECM}(4)}(R)_{R \rightarrow 0} = \infty. \quad (19)$$

In order to improve the reliability of the PECs especially for the long-range part correlating to the dissociation limit, the full vibrational energies  $\{E_v\}$ , for which high-lying data are lacking experimentally for many cases of diatomic molecules, are essential parameters. Here, we are using the variational algebra method (VAM) [36] to determine the full vibration energies  $\{E_v^{\text{VAM}}\}$  and dissociation energy  $D_e^{\text{VAM}}$ . To offset the probable error hidden in experimental data, a tiny quantity  $\delta E$  is an essential part of data analysis and is added to each vibrational energy. This can be expressed in matrix form [36]

$$AX = E + \delta E = E', \quad (20)$$

where

$$X = \begin{pmatrix} \omega_0 \\ \omega_e' \\ -\omega_e x_e \\ \omega_e y_e \\ \vdots \end{pmatrix}, \quad E' = \begin{pmatrix} E_{v1} + \delta E_{v1} \\ E_{v2} + \delta E_{v2} \\ (E_{v3} + \delta E_{v3}) \\ \vdots \\ E_{vm} + \delta E_{vm} \end{pmatrix}, \quad \delta E_{vi} \rightarrow \text{small enough.} \quad (21)$$

To determine full vibration energies converging the dissociation limit, we took into account the fact that the VAM values must best satisfy the following physical criteria of equations (22)–(26)

$$\overline{\Delta E(\text{expt, cal})} = \sqrt{\left[ \frac{1}{m} \sum_{v=0}^{m-1} |E_{v,\text{expt}} - E_{v,\text{cal}}|^2 \right]} \rightarrow 0, \quad (22)$$

$$\Delta E_{v_{\text{max}}, v_{\text{max}}-1} = E_{v_{\text{max}}} - E_{v_{\text{max}}-1} \rightarrow \text{small enough}, \quad (23)$$

$$E_{v_{\text{max}}} \leq D_e, \quad (24)$$

$$D_e^{\text{cal}} \cong E_{v_{\text{max}}} + \Delta E_{v_{\text{max}}-v_{\text{max}}-1}^2 / (\Delta E_{v_{\text{max}}, v_{\text{max}}-2} - \Delta E_{v_{\text{max}}, v_{\text{max}}-1}), \quad (25)$$

$$0 < \text{Error} = \frac{D_e^{\text{expt}} - D_e^{\text{cal}}}{\Delta E_{v_{\text{max}}, v_{\text{max}}-1}} \leq 1. \quad (26)$$

In the above physical criteria, ‘expt’ represents experimental data, and ‘cal’ represents data calculated by the VAM method. Briefly, the potential energy function  $V_{\text{AECM}}(R)$  of the electronic state analyzed by the  $V_{\text{AECM}}(4)$  method is described as

- (1) Based on the exact subset of known experimental measurements  $\{E_v^{\text{expt}}\}$  of the alkali metal dimer systems, a full list of molecular constants  $\{\omega_0, \omega_e, \omega_e x_e, \omega_e y_e, \dots\}$  and vibrational energies  $\{E_v^{\text{VAM}}\}$  is provided using the VAM method.
- (2) By substituting the obtained spectral constants ( $f_2, f_3, f_4, f_5$ ) into equations (6), (12)–(14), the vibration dynamic constants can be calculated. Moreover, the expansion coefficient can be solved by substituting the molecular constants ( $D_e, R_e, \mu, \omega_e, \omega_e x_e, \alpha_e$ ) into equations (7)–(11).
- (3) If the variational parameter  $\lambda$  is assigned with an initial value, a tentative  $V_{\text{VAECM}(4)}(\lambda, R)$  potential energy function will be obtained, which will be substituted into the radial Schrodinger equation of nuclear motion and solved by the normalized Numerov numerical method to obtain a set of vibrational energies  $\{E_v^\lambda\}$ . The  $V_{\text{AECM}}$  potential is calculated based on the data of VAM as the convergence criterion, while VAM is derived based on experimental data, so our results are reliable. By comparing the theoretical vibrational energies  $\{E_v^\lambda\}$  with VAM energies  $\{E_v^{\text{VAM}}\}$ , the variational parameter  $\lambda$  value is further adjusted.
- (4) Repeat step (3) until  $|E_v^\lambda - E_v^{\text{VAM}}|$  reaching a certain convergence accuracy, then it can be determined that the parameter  $\lambda$  is the corresponding data to the potential energy function, the final converged analytical potential  $V_{\text{VAECM}(4)}(R)$  can be derived.

Here, the EHFAC2U [24, 25] model is used for comparison, and the general expression of the EHFAC2U function is

$$V = V_{\text{EHF}}(R) + V_{dc}(R), \quad (27)$$

**Table 1.** The spectroscopic constants for  $4^1\Pi$  electronic state of  $\text{Na}^{85}\text{Rb}$  (in  $\text{cm}^{-1}$ ).

Constant	$\omega_0$	$\omega'_e$	$-\omega_e x_e$	$10^2 \omega_e y_e$	$10^5 \omega_e z_e$
Expt. [5]	-0.0238	73.721	-0.5195	0.302	
This work	-0.02399	73.79541	-0.53415	0.42345	-3.60016
Reference [15]		69.20			
Reference [16]		69.66	-0.3477		

\* The spectral constant  $\omega_0$  and Dunham constant  $Y_{00}$  correspond as follow:  $Y_{00} = \omega_0$ , and it is calculated from  $Y_{00} = [Y_{01} + Y_{20}]/4 - [Y_{11}Y_{10}/12Y_{01}] + [Y_{11}Y_{10}/12Y_{01}]^2/Y_{01}$  [38].

**Table 2.** The VAM vibrational energies and experimental data for  $4^1\Pi$  electronic state of  $\text{Na}^{85}\text{Rb}$  (in  $\text{cm}^{-1}$ ).

$v$	$E_v^{\text{expt}}[5]$	$E_v^{\text{VAM}}$	$v$	$E_v^{\text{VAM}}$	$v$	$E_v^{\text{VAM}}$
0	36.707	36.607	27	1692.737	54	2802.977
1		109.348	28	1743.418	55	2832.483
2	181.079	181.057	29	1793.404	56	2861.000
3		251.759	30	1842.696	57	2888.506
4	321.476	321.476	31	1891.291	58	2914.976
5		390.230	32	1939.190	59	2940.385
6	458.043	458.043	33	1986.391	60	2964.708
7		524.934	34	2032.889	61	2987.918
8	590.925	590.923	35	2078.681	62	3009.988
9		656.029	36	2123.762	63	3030.891
10	720.268	720.268	37	2168.126	64	3050.596
11		783.658	38	2211.767	65	3069.075
12	846.215	846.215	39	2254.678	66	3086.296
13		907.954	40	2296.850	67	3102.227
14	968.913	968.888	41	2338.274	68	3116.837
15		1029.032	42	2378.940	69	3130.091
16	1088.505	1088.397	43	2418.837	70	3141.956
17		1146.995	44	2457.953	71	3152.397
18	1205.137	1204.838	45	2496.276	72	3161.377
19		1261.934	46	2533.792	73	3168.860
20	1318.954	1318.293	47	2570.487	74	3174.809
21		1373.923	48	2606.346	75	3179.184
22		1428.831	49	2641.353	76	3181.946
23		1483.023	50	2675.490	77	3183.055
24		1536.506	51	2708.740		
25		1589.284	52	2741.084		
26		1641.360	53	2772.503		
$D_e^{\text{expt}}$	3183.500					
$D_e^{\text{VAM}}$						3183.500

Note. Bold italics are used in the calculation of the VAM method and bold type is dissociation energy; in addition, the experimental dissociation energy is  $3183.5 \pm 0.1 \text{ cm}^{-1}$  [5].

where the extended Hartree–Fock energy model is expressed as

$$V_{\text{EHF}} = -DR^{-1} \left( 1 + \sum_{i=1}^m b_i x^i \right) \exp[-\gamma(x)x]. \quad (28)$$

The  $D$ ,  $b_i$  and  $\gamma_i$  ( $i = 0 - 2$ ) are the parameters. And the  $\gamma(x)$  is

$$\gamma(x) = \gamma_0[1 + \gamma_1 \tanh(\gamma_2 x)] \quad (29)$$

and the dynamical correlation item in equation (27) is

$$V_{dc} = - \sum_{m=6,8,10,\dots} C_m \chi_m(R) R^{-m} \quad (30)$$

$$V_{dc} = -\chi_6(R) C_6 R^{-6} \left[ 1 + \sum_{m=8,10} \xi_m \frac{\chi_m(R)}{\chi_6(R)} R^{6-m} \right], \quad (31)$$

where the damping function  $\chi_m$  is determined by the relation:

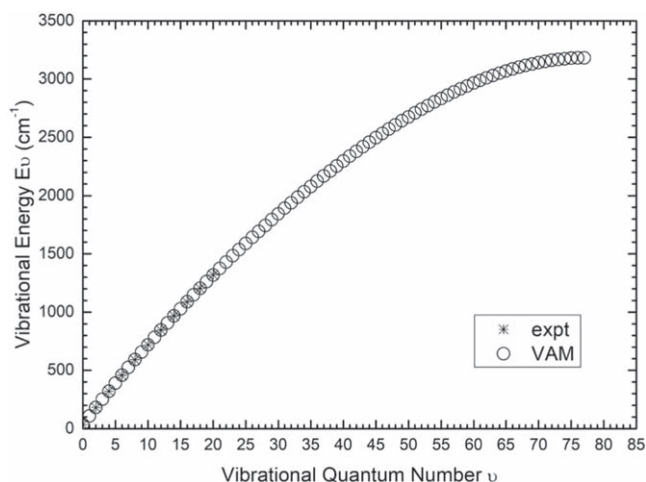
$$\chi_m = \left[ 1 - \exp \left( -A_m \frac{R}{\rho} - B_m \frac{R^2}{\rho^2} \right) \right]^m \quad (32)$$

with the auxiliary functions  $A_m = 16.36606 \text{ m}^{-0.70172}$  and  $B_m = 17.19338 \exp(-0.09574 \text{ m})$ .  $\rho (= 5.5 + 1.25R_0)$  is the scaling factor.  $R_0$  denotes the squared radii for the

**Table 3.** Some important parameters of the VAECM(4) potential for  $4^1\Pi$  electronic state of  $\text{Na}^{85}\text{Rb}$ , force constants  $f_n$ , expansion coefficients  $a_n$  and variational parameter  $\lambda$ .

Parameter	$10^3 f_2 / E_h a_0^{-2}$	$10^3 f_3 / E_h a_0^{-3}$	$10^2 f_4 / E_h a_0^{-4}$	$10 f_5 / E_h a_0^{-5}$	$a_1 / a_0^{-1}$	$a_2 / a_0^{-2}$	$a_3 / a_0^{-3}$	$a_4 / a_0^{-4}$	$\lambda$
Value	3.730610	-1.441467	6.612664	9.236990	2.817457	3.840435	3.381772	1.971844	-1.6

\* $E_h$  (hartree) = 219474.63067  $\text{cm}^{-1}$ .

**Figure 1.** The comparison between the calculated vibrational energies and the experimental ones. '\*' = experimental data; 'O' = VAM data.

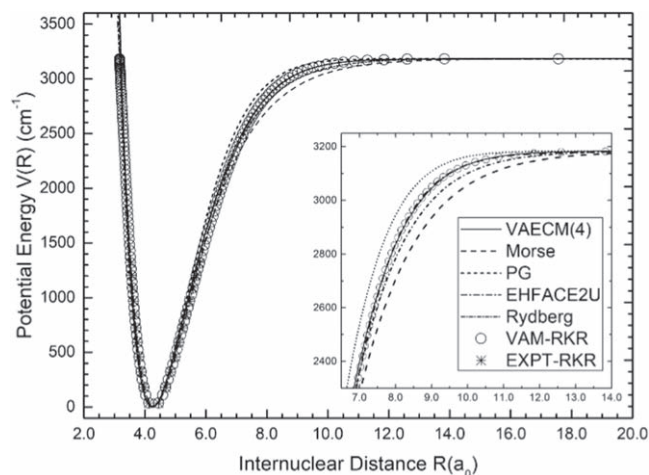
outermost electrons [37].  $\xi_m = C_m / C_6 = \kappa_m R_0^{1.57(m-6)/2}$  ( $m = 8, 10$ ) are the ratios. For the system considered here, the least-squares fitting procedure has been performed to yield these parameters of EHFACE2U potential.

### 3. Results and discussion

This study presents the full VAM vibrational energies of vibrational quantum numbers range from 0 to 77, and the analytical potential energy function  $V_{\text{VAECM}(4)}(R)$  for the  $4^1\Pi$  electronic state of  $\text{Na}^{85}\text{Rb}$  molecule by using Sun's VAECM (4) method. The theoretical calculation data obtained by other methods in this paper and the experimental data from literatures are listed together in the tables.

The obtained vibrational constants  $\{\omega_0, \omega_e, \omega_e x_e, \omega_e y_e, \omega_e z_e\}$  are displayed in table 1, with the values from Bang *et al* [5], Korek *et al* [15], and Chaieb *et al* [16] shown for comparison. And the results are in good agreement.

Bang *et al* did only get a part of the low-lying vibration energy spectrum, and the highest vibrational energy  $E_{v=20}^{\text{expt}}$  ( $= 1318.954 \text{ cm}^{-1}$ ) [5] was much smaller than experimental dissociation energy, so we have used the VAECM method to calculate unknown high-lying energies and dissociation energy. Substitute the vibrational constants into equation (20), the full VAM vibrational energies  $\{E_v^{\text{VAM}}\}$  that are found to be in reasonable agreement with the experimental values can be determined. Evidence to data comparison, as shown in table 2 in which the experimental values considered in the VAM procedure are in bold italic,

**Figure 2.** APEFs for the  $\text{Na}^{85}\text{Rb}-4^1\Pi$  electronic state: '---' = Morse potential; '.....' = PG potential; '- · - · - ·' = EHFACE2U potential; '- · - · - ·' = Rydberg potential; '\*' = experimental data; 'O' = VAM data; and '- · - ·' = VAECM(4) potential with  $\lambda = -1.6$ .

gives the energy difference  $|E_v^{\text{VAM}} - E_v^{\text{expt}}|$  in the range of  $0-0.67 \text{ cm}^{-1}$ . Moreover, two overlapping vibrational spectra are displayed in figure 1, indicating that the VAM energies  $\{E_v^{\text{VAM}}\}$  have a reasonable approach to the dissociation limit. And, the VAM-RKR data can be performed as input in the least-squares fitting for the EHFACE2U potential.

Then, the APEF can be derived through the vibrational constants, the full vibrational energies and dissociation energy obtained above. Potential energy curves for the  $4^1\Pi$  state of  $\text{Na}^{85}\text{Rb}$  molecule are presented in figure 2, with the VAECM (4) potential (with  $\lambda = -1.6$ ), Morse potential, PG potential, EHFACE2U potential, Rydberg potential, VAM-RKR potential, and EXPT-RKR potential shown for comparison. And, the potential minima are all shifted to zero. The force constants ( $f_2, f_3, f_4, f_5$ ), the expansion coefficients ( $a_1, a_2, a_3, a_4$ ) and the variational parameter  $\lambda$  of the VAECM (4) potential are listed in table 3. The numerical parameters of the EHFACE2U potential are collected in table 4.

As can be seen from figure 2, all potentials agree well with each other near equilibrium position and have quite similar potential wells, the main reason is the use of the same  $R_e$  and  $D_e$  values. One can also see from figure 2 that the VAECM (4) potential and EHFACE2U potential are found to lie fairly close to each other in whole potential region, which are in good agreement with the VAM-RKR potential and EXPT-RKR potential. However, the Morse potential and Rydberg potential deviate from the VAECM (4) potential and EHFACE2U potential with lower PECs between  $7.0 a_0$  and



**Table 4.** Numerical parameters for the EHFACE2U potential of Na<sup>85</sup>Rb molecule.

Parameter	$10^2D$	$\gamma_0$	$10\gamma_1$	$\gamma_2$	$b_1$	$b_2$
Value	5.85051169	2.03168760	4.72063605	1.26444920	2.32762223	3.33543528
$b_3$	$b_4$	$b_5$	$10b_6$	$10^4b_7$	$10b_8$	$10^2b_9$
3.93611038	3.21918563	1.92020474	6.06668696	6.05897360	1.47949967	6.97534180
$10^2b_{10}$	$10^3b_{11}$	$10C_6$	$10^3C_8$	$10^5C_{10}$	$R_0$	$R_e$
−3.47545458	6.45204905	5.99492253	6.55084452	8.08889973	19.880	4.23928144

Note. All values are in atomic units.

13.0  $a_0$ . The quite similar discrepancies happen on the PG potential curve, which is higher than the VAECM(4) potential and EHFACE2U potential in the region of  $5.5 a_0 < R < 12.5 a_0$ .

Overall, the results of VAECM(4) potential agree well with the available VAM-RKR data, EXPT-RKR data and theoretical EHFACE2U potential, which implies the present calculations are credible to investigate the  $4^1\Pi$  electronic state of NaRb molecule. Moreover, the EHFACE2U function used here is a promising model to check the VAECM(4) potential and is expected to be a good candidate to improve our VAECM function for the long range part near the asymptotic and dissociation region in future studies.

#### 4. Conclusions


In this work, the full vibrational energies of 78 levels and analytical potential energy function (APEF) for the excited electronic state of  $4^1\Pi$  symmetry has been calculated for the Na<sup>85</sup>Rb molecule in the range 2 – 20  $a_0$  through Sun's VAECM(4) method very similar to that used to describe successfully the other alkali metal dimers in our previous study. With the three highest VAM vibrational energies and improved vibrational constants, the VAM dissociation energy, the VAECM(4) potential energy curve and the vibrational force constants  $f_n$  of  $4^1\Pi$  electronic state have been calculated. The results of comparisons with other theoretical methods demonstrate that the VAECM(4) APEF can display a 'correct' curve to cover the description of the experiment and expand the range of ' $v$ ' in the segment of long-range interaction region of  $4^1\Pi$  electronic state. The results obtained in this study also provide valuable reference data for other areas of researches on Na<sup>85</sup>Rb.

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