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REVIEW ARTICLE

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Accurate vibrational energy spectra and dissociation energies of some diatomic electronic states

Abstract An algebraic method (AM) used to study the full vibrational spectra of diatomic systems, and an analytical formula used to calculate accurate molecular dissociation energies are applied to study the full vibrational spectra and molecular dissociation energies of some electronic states of homonuclear and heteronuclear diatomic molecules and diatomic ions. Studies show that the AM method and the analytical expression are reliable and economical physical methods for studying full vibrational spectra and molecular dissociation energies of diatomic electronic systems theoretically. They are particularly useful for those diatomic systems whose high-lying vibrational energies may not be available.

Keywords diatomic molecules, molecular ions, vibrational spectrum, dissociation energy, algebraic method

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1 Introduction

Molecular vibrational energies, especially accurate high-lying vibrational energies, have very important significance for investigating molecular long-rang interactions and reaction dynamics in dissociation regions. Studies show that the process of chemical reactions not only depends on the system energies, but also on the energy forms. Thus, studying molecular excited states may help to selectively provide effective energies for the reaction systems, such that molecular electronic-vibrational-rotational states are in favor of chemical reactions towards the anticipated routes [1, 2]. Molecular high-lying vibrational (rotational) excited data are also important for studying molecular scattering [3]. In recent decades, many theoretical and experimental studies on vibrational energies of many diatomic electronic states have been made. However, due to the limitations of experimental conditions and techniques, studies on high-lying vibrational energies, especially those near molecular dissociation limits, are rather limited. Therefore, it is still very important to study full vibrational energy spectra of diatomic molecules [1].

The dissociation energy of stable diatomic electronic states plays a significant role in atomic and molecular physics, chemical physics, thermodynamics, molecular spectroscopy and molecular collision physics [4]. Precise knowledge of dissociation energies is particularly important to the spectroscopy of long-range molecules, the light coupling ionization, the ultra-fine pre-dissociation process and the collision physics between ultra-cold atoms. For example, the binding energy (dissociation energy) of transition from the highest vibrational energy to rotationless ground state level determines the *s*-wave scattering length which gives the low-energy elastic-scattering cross section that is relevant to Bose-Einstein condensation of cold atoms. Accurate molecular dissociation energies must be known in investigations of molecular potentials either using quantum mechanics or analytical potential method. In chemical reactions, correct dissociation energy of each molecular state may help one to understand chemical reaction route, re-

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action mechanism and reaction products.

However, it is usually difficult to directly measure dissociation energy. Only few works of direct measurements on dissociation energy have been reported. For example, in 1996, Jones *et al.* [4] obtained accurate dissociation energy of the ground state of Na_2 using three kinds of laser-induced fluorescence spectroscopies. There have been no reports about direct measurements on dissociation energies of molecular electronic excited states, and usually these dissociation energies are indirectly obtained [5]. Theoretically, due to limitations of ab initio method itself, it is difficult to obtain accurate dissociation energies for most of molecular electronic states. The computational process of accurate ab initio studies is usually very complicated, even if for the ground state of simplest molecule H_2, the molecular wave function for calculating accurate dissociation energy contains many constituents and many correction terms [6]. Therefore, it is also necessary to study new physical method for obtaining molecular dissociation energy.

This study uses a new tactic which combines the advantages of accurate experimental measurements and solid theoretical tool to study the full vibrational spectrum $\{E_v\}$, and uses an analytical parameter-free formula to evaluate molecular dissociation energy for a group of stable diatomic electronic states. Section 2 describes the method. Section 3 presents the results and discussions. Section 4 concludes this study.

2 Methods

2.1 Algebraic method (AM) for full vibrational spectra of diatomic molecules

For a stable diatomic molecular electronic state, the nonrelativistic analytical expression of vibrational energy of nuclear motion is obtained using second perturbation theory as [7]:

$$\begin{aligned}E_v &= \omega_0 + (\omega_e + \omega_{e0})\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2 \\ &+\omega_e y_e\left(v+\frac{1}{2}\right)^3 + \omega_e z_e\left(v+\frac{1}{2}\right)^4 \\ &+\omega_e t_e\left(v+\frac{1}{2}\right)^5 + \omega_e s_e\left(v+\frac{1}{2}\right)^6 \\ &+\omega_e r_e\left(v+\frac{1}{2}\right)^7 + \cdots \end{aligned} \tag{1}$$

Comparing with Herzberg's energy expression [8]:

$$\begin{aligned}E_v &= \omega_e\left(v+\frac{1}{2}\right) - \omega_e x_e\left(v+\frac{1}{2}\right)^2 \\ &+\omega_e y_e\left(v+\frac{1}{2}\right)^3 + \omega_e z_e\left(v+\frac{1}{2}\right)^4 \\ &+\omega_e t_e\left(v+\frac{1}{2}\right)^5 + \omega_e s_e\left(v+\frac{1}{2}\right)^6 \\ &+\omega_e r_e\left(v+\frac{1}{2}\right)^7 + \cdots \end{aligned} \tag{2}$$

ω_0 and ω_{e0} are new small quantities, but they are not neglectable in calculating high-lying rovibrational energies. ω_0 is the vibrational constants of the zero order of $(v+1/2)$, ω_{e0} is the correction term to harmonic vibrational constant ω_e of the first order of $(v+1/2)$. Comparing Eq. (1) with Dunham's energy expression [9]:

$$E_{vJ} = \sum_l \sum_m Y_{lm}\left(v+\frac{1}{2}\right)^l [J(J+1)]^m \tag{3}$$

One has

$$\begin{cases} Y_{00} = \omega_0; \quad Y_{10} = (\omega_e + \omega_{e0}) \\ Y_{20} = -\omega_e x_e; \quad Y_{30} = \omega_e y_e \\ Y_{40} = \omega_e z_e; \quad Y_{50} = \omega_e t_e \\ Y_{60} = \omega_e s_e; \quad Y_{70} = \omega_e r_e \end{cases} \tag{4}$$

The algebraic method (AM) proposed by Sun *et al.* [7] is started by rewriting the vibrational energy expressions in Eq. (1) into a matrix form:

$$AX = E \tag{5}$$

where the vector matrix X of vibrational spectroscopic constants and the energy matrix E are

$$X = \begin{pmatrix} \omega_0 \\ \omega_e' \\ -\omega_e x_e \\ \omega_e y_e \\ \vdots \\ \omega_e r_e \end{pmatrix}, \quad E = \begin{pmatrix} E_v \\ E_{v+i} \\ E_{v+j} \\ \vdots \\ E_{v+s} \end{pmatrix}, \quad v = 0, 1, 2, \cdots \tag{6}$$

and the matrix element of the 8×8 coefficient matrix A is $A_{vk} = (v+1/2)^k$, $k = 0, 1, 2, \cdots, 7$. In the vector matrix X, $\omega_e' = \omega_e + \omega_{e0}$.

Although modern experimental techniques and accurate quantum methods have difficulty obtaining high-lying vibrational energies, especially those near the dissociation limit regions, they can usually obtain an accurate energy subset $[E_v]$ for most stable diatomic electronic systems. For a given electronic state, provided that m

accurate energies in energy subset $[E_v]$ are known, one may choose 8 of the m known energies to form the vibrational energy matrix E. There are $N = C_m^8$ groups of choices. Solving Eq. (5) without using any mathematical approximation and physical model, and substituting the obtained N sets of vibrational spectroscopic constants $\{\omega_0, \omega_e + \omega_{e0}, -\omega_e x_e, \omega_e y_e, \omega_e z_e, \omega_e t_e, \omega_e s_e, \omega_e r_e\}$ into Eq. (1) respectively, N sets of vibrational spectrum $\{E_v\}$ will be generated. One can always find a spectrum $\{E_v\}$ which best satisfies the following physical requirements:

$$\left.\frac{\mathrm{d}E_v}{\mathrm{d}v}\right|_{v=v_{\max}} = 0 \tag{7}$$

$$\overline{\Delta E(e,c)} = \sqrt{\frac{1}{m}\sum_{v=0}^{m-1}\left|E_{v,\exp} - E_{v,cal}\right|^2} \to 0 \tag{8}$$

$$\Delta E_{v_{\max},v_{\max}-1} = E_{v_{\max}} - E_{v_{\max}-1} \to \text{Small enough} \tag{9}$$

$$D_e^{\exp t} - E_{v_{\max}} \to \text{Small enough} \tag{10}$$

$$E_{v_{\max}} < D_e^{cal} < D_e^{\exp t} \tag{11}$$

$$D_e^{cal} \approx E_{v_{\max}} + \frac{\Delta E^2_{v_{\max},v_{\max}-1}}{\Delta E_{v_{\max},v_{\max}-2} - \Delta E_{v_{\max},v_{\max}-1}} \tag{12}$$

$$0 < E_{\text{rror}} = \frac{D_e^{\exp t} - D_e^{cal}}{\Delta E_{v_{\max},v_{\max}-1}} \lesssim 1 \tag{13}$$

The so determined vibrational spectroscopic constants should be the best physical representation of the true vibrational information for a specified molecular system, and the resulting vibrational energies form a full vibrational spectrum $\{E_v\}$ containing all correct vibrational energies. This AM spectrum is obtained by combining a limited number of accurate experimental energies with the advantages of standard algebraic computation subjecting to a set of physical converging conditions.

2.2 Formula for dissociation energies of diatomic molecules

A parameter-free analytical formula for dissociation energies of stable diatomic electronic states has been proposed recently by Sun *et al.* [10, 11]. A brief outline is given below. LeRoy and Bernstein studied the relationship among asymptotic potential $V(R)$, vibrational energy E_v and dissociation energy D_e of a stable diatomic system [12,13]. When near molecular dissociation limit, they obtained [12]

$$D_e = E_v - \frac{n+2}{2n}\cdot\frac{{E'_v}^2}{E''_v} \tag{14}$$

which is the analytical expression for dissociation energy D_e. They further approximated the first order derivative E'_v of vibrational energy by [13]

$$E'_v = \frac{\mathrm{d}E_v}{\mathrm{d}v} \approx \frac{1}{2}\left(E_{v+1} - E_{v-1}\right) + \cdots \tag{15}$$

and shown [12]

$$\frac{E'_v}{E''_v} = -\left(\pi\hbar\right)^{-1}\left(\frac{1}{2}\mu C_2\right)^{\frac{1}{2}} \tag{16}$$

One may substitute Eq. (15) and Eq. (16) into Eq. (14), and get

$$D_e = E_v + \frac{1}{2}\cdot\frac{n+2}{2n}\left(E_{v+1} - E_{v-1}\right)\left(\pi\hbar\right)^{-1}\left(\frac{1}{2}\mu C_2\right)^{\frac{1}{2}} \tag{17}$$

Eq. (17) is an alternative expression of Eq. (14). In LeRoy and Bernstein's studies [12, 13], a nonlinear least squares fitting was applied to solve Eq. (14) or Eq. (17) to calculate the molecular dissociation energy by using a set of experimental vibrational energies E_v and a group of initial trial values of dispersion coefficient C_2, asymptotic exponent n and D_e. However, it is not trivial for one to choose a reasonable initial values of C_2, n and D_e. The molecular dissociation energies fitted using these initial values sometimes may have notable errors. Therefore, the LB formula in Eq. (14) has not been widely used.

Based on the LB formula, a new analytical formula for dissociation energy D_e which is independent of dispersive coefficient C_n and asymptotic exponent n can be obtained. Apparently, the vibrational states in Eq. (17) should be those near the molecular dissociation limit, otherwise, the resulting dissociation energies from Eq. (17) will have big errors. Therefore, one may take $v + 1 = v_{\max}$ and Eq. (17) becomes

$$D_e^{cal} = E_{v_{\max}-1} + \frac{1}{2}\cdot\frac{n+2}{2n}\left(E_{v_{\max}} - E_{v_{\max}-2}\right) \cdot\left(\pi\hbar\right)^{-1}\left(\frac{1}{2}\mu C_2\right)^{\frac{1}{2}} \tag{18}$$

Eq. (18) is used to calculate the molecular dissociation energies using the three highest vibrational energies by Ren *et al.* for some electronic states of N_2 molecule [14]. Their study only uses the known values of n and C_2 without using numerical fitting. However, the n and C_2 values of many electronic states are unknown, so Eq. (18) is also hardly applicable.

In order to obtain an analytical expression of dissociation energies which is free of parameters C_2 and n, one may take $v = v_{\max}$ and then Eq. (17) becomes

$$D_e^{cal} = E_{\upsilon_{\max}} + \frac{1}{2} \cdot \frac{n+2}{2n} (E_{\upsilon_{\max}+1} - E_{\upsilon_{\max}-1}) \cdot (\pi\hbar)^{-1} \left(\frac{1}{2}\mu C_2\right)^{\frac{1}{2}} \tag{19}$$

Subtracting Eq. (18) from Eq. (19) gets

$$C_2^{1/2} = 2\pi\hbar \frac{2n}{n+2} \left(\frac{2}{\mu}\right)^{1/2} \cdot \frac{\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}}{\Delta E_{\upsilon_{\max},\upsilon_{\max}-2} - \Delta E_{\upsilon_{\max}+1,\upsilon_{\max}-1}} \tag{20}$$

Substituting Eq. (20) into Eq. (19), one has

$$D_e^{cal} \approx E_{\upsilon_{\max}} + (E_{\upsilon_{\max}+1} - E_{\upsilon_{\max}-1}) \cdot \frac{\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}}{\Delta E_{\upsilon_{\max},\upsilon_{\max}-2} - \Delta E_{\upsilon_{\max}+1,\upsilon_{\max}-1}} \tag{21}$$

Since $E_{\upsilon_{\max}}$ is the maximum vibrational energy of a diatomic electronic state, $E_{\upsilon_{\max}+1}$ is a "virtual" energy which is not physical and is numerically slightly smaller than $E_{\upsilon_{\max}}$. When $E_{\upsilon_{\max}+1} - E_{\upsilon_{\max}-1}$ is negative, it may cause an unphysical result $D_e^{cal} < E_{\upsilon_{\max}}$. In order to satisfy $D_e^{cal} > E_{\upsilon_{\max}}$, the second term of Eq. (21) must be greater than zero. So one may replace $E_{\upsilon_{\max}+1}$ with $E_{\upsilon_{\max}}$, and Eq. (21) becomes

$$D_e^{cal} \approx E_{\upsilon_{\max}} + \frac{\Delta E^2_{\upsilon_{\max},\upsilon_{\max}-1}}{\Delta E_{\upsilon_{\max},\upsilon_{\max}-2} - \Delta E_{\upsilon_{\max},\upsilon_{\max}-1}} \tag{22}$$

where

$$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1} = E_{\upsilon_{\max}} - E_{\upsilon_{\max}-1}$$

$$\Delta E_{\upsilon_{\max},\upsilon_{\max}-2} = E_{\upsilon_{\max}} - E_{\upsilon_{\max}-2}$$

Eq. (22) is the new analytical formula for molecular dissociation energy suggested recently [10, 11]. It indicates that one may obtain the correct molecular dissociation energy D_e^{cal} of a stable diatomic electronic state using its three highest vibrational energies $E_{\upsilon_{\max}}$, $E_{\upsilon_{\max}-1}$ and $E_{\upsilon_{\max}-2}$. Since the right hand side of Eq. (15) is always smaller than the left hand side by a very small quantity, the generated D_e^{cal} in Eq. (22) will be a little smaller than the correct experimental dissociation energy $D_e^{\exp t}$, namely

$$D_e^{cal} < D_e^{\exp t} \tag{23}$$

If Eq. (23) is violated, the three highest vibrational energies used to calculate D_e^{cal} have errors. Since Eq. (22) should use the three accurate highest vibrational energies, it may also be used as a physical criterion judging whether the full vibrational spectrum of a diatomic electronic state is well converged and it is so used in Eq. (12).

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3 Results and discussion

3.1 Applications to homonuclear diatomic molecules

The improved computational program of the AM method is used to study the vibrational spectroscopic constants and the full vibrational spectra, respectively, for 10 diatomic molecular electronic states of ^{6}Li$_2$, Na$_2$, K$_2$ and Br$_2$ molecules: the $1^1\Pi_g$ state of ^{6}Li$_2$; the $X^1\Sigma_g^+$, $2^3\Sigma_g^+$, $4^3\Sigma_g^+$, $2^1\Pi_g$ and $2^3\Pi_g$ states of Na$_2$; the $X^1\Sigma_g^+$, $2^1\Pi_g$ and $3^3\Pi_g$ states of K$_2$; and the $X^1\Sigma_g^+$ state of Br$_2$. The dissociation energies of the above electronic states are calculated using Eq. (22) and their three highest AM vibrational energies, respectively.

The vibrational spectroscopic constants from references and the AM method of these electronic states are listed in Table 1. It can be seen that the harmonic vibrational constant ω_e from the AM method has an excellent agreement with those from the references, the inharmonic vibrational constant $\omega_e x_e$ from the AM method agrees with those from references for most of the molecular electronic states, and some high-lying vibrational spectroscopic constants of several electronic states are not available in literatures. If one uses the literature low-lying vibrational spectroscopic constants to calculate all vibrational energies of these electronic states, the obtained high-lying vibrational energies would not be converged to their dissociation energies correctly and have big errors or are even incorrect.

For the above molecular electronic states, the known experimental vibrational energies, the full AM vibrational energies calculated using the AM vibrational spectroscopic constants and the theoretical vibrational energies calculated using the literature vibrational spectroscopic constants are listed in Table 2, respectively. For each electronic state, the 8 experimental energies chosen in the AM method are marked in bold face. Since the vibrational information and the measurement error contained in different experimental data are different, it is necessary to choose 8 energies which contain the most useful vibrational information and the smallest errors from a set of known experimental vibrational energies by applying a group of physical criteria in Eqs. (7)−(13) that judge the convergence of the calculation in the AM studies. Thus, the so obtained AM vibrational spectra not only reproduce known experimental energies, but also generate all unknown high-lying vibrational energies. Using the three highest AM vibrational energies and the analytical expression in Eq. (22), the correct molecular dissociation energies can be calculated.

It can be seen from Table 2 that for all electronic states

Table 1 Vibrational spectroscopic constants of some homonuclear diatomic electronic states (units: cm^{-1}).

State		ω_0	ω_{e0}	ω'_e	$\omega_e x_e$	$10^2\omega_e y_e$	$10^3\omega_e z_e$	$10^4\omega_e t_e$	$10^5\omega_e s_e$	$10^{10}\omega_e r_e$
Na_2-$X^1\Sigma_g^+$	AM	0.021023	−0.062917	159.0397	0.678027	−1.138707	0.69889	−0.21684	0.027278	−12.7149
	Ref. [15]			159.10257	0.718973	−0.180519	−0.010512	−0.006247	0.000397	−0.504721
Na_2-$2^3\Sigma_g^+$	AM	−0.003800	0.0017843	126.6867	0.46007	0.3787032	−0.182047	0.0420875	−0.0050906	1.891539
	Ref. [17]			126.685	0.4590	0.3479	−0.1466	0.02651	−0.002216	
Na_2-$4^3\Sigma_g^+$	AM	0.0072901	−0.011535	122.4514	0.484609	0.250506	0.139898	−0.16572	0.056966	−76.10584
	Ref. [18]			122.4630	0.49140	0.431	−0.0994			
Na_2-$2^1\Pi_g$	AM	0.0185437	0.000145	102.44037	0.349919	0.1261816	−0.089326	0.021823	−0.0035549	1.6628479
	Ref. [20]			102.4403	0.3498	0.122	−0.0825	0.0170	−0.002036	
Na_2-$2^3\Pi_g$	AM	−0.052227	0.0005236	94.35047	0.377076	0.209147	−0.0238595	0.0026541	−0.000316	0.143898
	Ref. [21]			94.35	0.3760	0.191	−0.0134			
K_2-$2^1\Pi_g$	AM	0.0110091	−0.0002709	55.5290	0.124129	−0.22382	0.0047904	−0.0032962	0.0011145	−1.46798
	Ref. [22]			55.5292	0.124256	−0.220272				
K_2-$3^3\Pi_g$	AM	0.00793014	0.00022604	73.21323	0.24374	−0.0092443	0.010872	−0.0065520	0.0019703	−2.34190
	Ref. [23]			73.213	0.244					
K_2-$X^1\Sigma_g^+$	AM	−0.024602	−0.004205	92.3935	0.32429	−0.066026	−0.01814	0.0069048	−0.0015186	0.92018115
	Ref. [25]			92.397660	0.324847	−0.07808	0.009327	−0.00561		
Br_2-$X^1\Sigma_g^+$	AM	−0.0068187	−0.0002544	325.31404	1.078597	−0.201478	−0.0140481	−0.0022033	−0.00007323	−0.2738711
	Ref. [28]			325.31419	1.078688	−0.19942	−0.01618	−0.00110	−0.00035245	
$^6Li_2$-$1^1\Pi_g$	AM	0.092346	0.083960	100.27698	2.0043	1.6249	−1.4806	0.576458	−0.065339	8.6358
	Ref. [29]			100.193	1.9480	Unknown	0.85	−1.19	0.644	−1410

Note: for the AM values: $\omega'_e = \omega_e + \omega_{e0}$; for values from references: $\omega'_e = \omega_e$.

Table 2 Vibrational energies of some homonuclear diatomic electronic states (energy units: cm^{-1}).

	$\text{Na}_2\text{-}X^1\Sigma_g^+$				$\text{Na}_2\text{-}2^3\Sigma_g^+$		
υ	$E_\upsilon^{\exp t}$[16]	E_υ^{AM}	E_υ^{Theo}[15]	υ	$E_\upsilon^{\exp t}$[17]	E_υ^{AM}	E_υ^{Theo}[17]
0	79.3700	79.3074	79.3713	0	**63.2250**	63.2250	63.2282
1	**237.0200**	237.0200	237.0300	1	**189.0030**	189.0030	189.0058
2	**393.2300**	393.2300	393.2342	2	**313.8900**	313.8900	313.8926
3	**547.9600**	547.9600	547.9723	3	**437.9010**	437.9010	437.9033
4	**701.2200**	701.2200	701.2324	4	561.0480	561.0478	561.0494
5	852.9900	853.0096	853.0022	5	683.3390	683.3393	683.3401
6	1003.2600	1003.3203	1003.2686	6	**804.7820**	804.7820	804.7826
7	1152.0100	1152.1367	1152.0180	7	925.3810	925.3803	925.3815
8	1299.2300	1299.4388	1299.2362	8	1045.1400	1045.1368	1045.1403
9	1444.9000	1445.2030	1444.9080	9	1164.0600	1164.0523	1164.0603
10	1589.0100	1589.4033	1589.0176	10	1282.1420	1282.1267	1282.1418
11	1731.5400	1732.0122	1731.5482	...	...	...	...
12	1872.4700	1873.0017	1872.4823	35	3946.7920	3946.7126	3946.7891
13	2011.7900	2012.3440	2011.8011	36	4040.8210	4040.7819	4040.8161
14	2149.4700	2150.0115	2149.4848	37	**4133.7470**	4133.7470	4133.7414
15	2285.5000	2285.9778	2285.5128	38	4225.5460	4225.5798	4225.5386
16	2419.8500	2420.2173	2419.8630	39	4316.1880	4316.2491	4316.1787
17	2552.5000	2552.7058	2552.5122	40	4405.6410	4405.7210	4405.6296
18	**2683.4200**	2683.4200	2683.4359	41	4493.8700	4493.9581	4493.8555
19	2812.5900	2812.3378	2812.6083	42	4580.8340	4580.9197	4580.8171
20	2939.5800	2939.4376	2940.0019	43	4666.4920	4666.5615	4666.4712
...	...	...	...	44	4750.7940	4750.8353	4750.7699
41	5137.0200	5136.2118	5136.9852	45	**4833.6890**	4833.6890	4833.6607
42	5214.5100	5214.0326	5214.4766	46	4915.1190	4915.0663	4915.0857
43	5289.0000	5288.8012	5288.9770	47	4995.0200	4994.9064	4994.9818
44	**5360.4100**	5360.4100	5360.3971	48	5073.3240	5073.1442	5073.2797
45	5428.6400	5428.7502	5428.6433	49	5149.9550	5149.7098	5149.9036
46	5493.6100	5493.7127	5493.6173	50	5224.8300	5224.5284	5224.7712
47	**5555.1900**	5555.1900	5555.2164	51	5297.8590	5297.5202	5297.7924
48	5613.2900	5613.0779	5613.3326	52	5368.9460	5368.6003	5368.8696
49	5667.8000	5667.2775	5667.8533	53	5437.9830	5437.6786	5437.8969
50	5718.6300	5717.6973	5718.6599	54	5504.8570	5504.6595	5504.7596
51	5765.6500	5764.2560	5765.6288	55	**5569.4420**	5569.4420	5569.3335
52	5808.7600	5806.8852	5808.6301	56		5631.9196	5631.4846
53	5847.8600	5845.5321	5847.5280	57		5691.9800	5691.0686
54	5882.8500	5880.1633	5882.1803	58		5749.5055	5747.9300
55	5913.6700	5910.7684	5912.4381	...		...	...
56	5940.2900	5937.3634	5938.1455	67		6130.8928	6105.2801
57	5962.6900	5959.9958	5959.1394	68		6155.3377	6123.5007
58	5980.9600	5978.7486	5975.2491	69		6175.5807	6136.3816
59	5995.2500	5993.7452	5986.2960	70		6191.4391	6143.5845
60	6005.8500	6005.1553	5992.0934	71		6202.7255	6144.7511
61	**6013.2000**	6013.2000	5992.4457	72		6209.2485	
62	6017.9700	6018.1580		73		6210.8129	
63		6020.3721		74			
$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	4.7700	2.2141	0.3523	$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	64.5850	1.5644	1.1666
D_e^{cal}		6021.3608	5992.4671	D_e^{cal}		6211.1880	6144.9400
$D_e^{\exp t}$	6022.0300 [4]			$D_e^{\exp t}$	6211.50 [17]		
$\Delta D_e\%$		0.01157	0.4909	$\Delta D_e\%$		0.005024	1.07156
E_{rror}		0.3022	83.9140	E_{rror}		0.1995	57.0546

Note: $E_\upsilon^{\exp t}$ is experimental energy; E_υ^{AM} is the AM vibrational energy; E_υ^{Theo} is vibrational energy calculated using spectroscopic constants from corresponding references; $\Delta E_{\upsilon_{\max},\upsilon_{\max}-1} = E_{\upsilon_{\max}} - E_{\upsilon_{\max}-1}$; $D_e^{\exp t}$ is experimental dissociation energy; D_e^{cal} is theoretical dissociation energy calculated using Eq. (22); $\Delta D_e\% = 100 \times (D_e^{\exp t} - D_e^{cal})/D_e^{\exp t}$; $E_{rror} = (D_e^{\exp t} - D_e^{cal})/\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$.

Table 2 (Continued)

	Na_2-$4^3\Sigma_g^+$				Na_2-$2^1\Pi_g$		
υ	$E_\upsilon^{\exp t}$[18]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[18]	υ	$E_\upsilon^{\exp t}$[20]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[20]
0	61.1090	61.1121	61.1092	0	**51.1514**	51.1514	51.1328
1	**182.6030**	182.6030	182.6029	1	**152.8956**	152.8956	152.8771
2	**303.1500**	303.1500	303.1497	2	**253.9489**	253.9489	253.9305
3	422.7700	422.7713	422.7707	3	**354.3151**	354.3151	354.2968
4	541.4830	541.4846	541.4846	4	453.9964	453.9964	453.9782
5	659.3060	659.3063	659.3078	5	552.9937	552.9937	552.9757
6	**776.2510**	776.2510	776.2540	6	651.3066	651.3066	651.2889
7	892.3320	892.3306	892.3350	7	748.9337	748.9337	748.9164
8	1007.5560	1007.5546	1007.5598	8	**845.8726**	845.8726	845.8558
9	1121.9310	1121.9297	1121.9353	9	942.1202	942.1200	942.1040
10	**1235.4600**	1235.4600	1235.4658	10	1037.6722	1037.6720	1037.6569
11	**1348.1470**	1348.1470	1348.1533	11	1132.5241	1132.5239	1132.5098
12	**1459.9900**	1459.9900	1459.9974	12	1226.6705	1226.6703	1226.6573
13	1570.9860	1570.9861	1570.9955	13	**1320.1053**	1320.1053	1320.0935
14	1681.1320	1681.1306	1681.1422	14	1412.8219	1412.8224	1412.8117
15	1790.4180	1790.4168	1790.4301	15	1504.8134	1504.8144	1504.8050
16	**1898.8360**	1898.8360	1898.8493	16	1596.0718	1596.0735	1596.0656
17	2006.3720	2006.3778	2006.3875	17	1686.5891	1686.5914	1686.5853
18	2113.0120	2113.0291	2113.0299	18	1776.3562	1776.3590	1776.3551
19	2218.7400	2218.7742	2218.7595	19	1865.3636	1865.3665	1865.3656
20	2323.5350	2323.5932	2323.5567	20	1953.6012	1953.6032	1953.6066
21	2427.3750	2427.4617	2427.3999	21	**2041.0577**	2041.0577	2041.0669
22	2530.2370	2530.3486	2530.2647	22	2127.7212	2127.7175	2127.7346
23	2632.0940	2632.2149	2632.1244	23	2213.5789	2213.5693	2213.5970
24	2732.9170	2733.0110	2732.9502	24	2298.6167	2298.5982	2298.6399
25	**2832.6740**	2832.6740	2832.7105	25	2382.8193	2382.7886	2382.8481
26	2931.3320	2931.1249	2931.3717	26	2466.1700	2466.1232	2466.2050
27		3028.2643	3028.8975	27	2548.6508	2548.5832	2548.6924
28		3123.9688	3125.2494	28	2630.2415	2630.1485	2630.2904
29		3218.0852	3220.3864	29	2710.9205	2710.7971	2710.9772
30		3310.4259	3314.2653	30	2790.6637	2790.5050	2790.7289
31		3400.7620	3406.8403	31	2869.4448	2869.2465	2869.5193
32		3488.8166	3498.0634	32	2947.2350	2946.9937	2947.3193
33		3574.2570	3587.8840	33	3024.0024	3023.7164	3024.0975
34		3656.6864	3676.2493	34	3099.7124	3099.3822	3099.8189
35		3735.6342	3763.1040	35	3174.3266	3173.9561	3174.4454
36		3810.5462	3848.3906	36	3247.8032	3247.4005	3247.9353
37		3880.7731	3932.0489	37	3320.0965	3319.6752	3320.2427
38		3945.5585	4014.0166	38	3391.1562	3390.7369	3391.3175
39		4004.0259	4094.2289	39	3460.9275	3460.5397	3461.1049
40		4055.1648	4172.6186	40	3529.3508	3529.0343	3529.5453
41		4097.8151	4249.1162	41	3596.3608	3596.1685	3596.5736
42		4130.6510	4323.6496	42	**3661.8866**	3661.8866	3662.1189
43		4152.1636	4396.1446	43	3725.8512	3726.1298	3726.1042
44		4160.6424	4466.5244	44		3788.8359	3788.4460
45			4534.7100	45		3849.9390	3849.0538
...			...	...		...	...
63			5282.3705	60		4518.5443	4461.6709
64			5290.6618	61		4542.1800	4474.6525
65			5294.6758	62		4562.5680	4482.8097
66				63		4579.5855	4485.8369
67				64		4593.1083	
68				65		4603.0107	
69				66		4609.1661	
70				67		4611.4471	
$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	98.6580	8.4789	4.0140	$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	63.9646	2.2810	3.0272
D_e^{cal}		4163.9842	5296.6190	D_e^{cal}	3788.291	4612.2923	4486.9603
$D_e^{\exp t}$	4164.0000 [19]			$D_e^{\exp t}$	4612.7000 [20]		
$\Delta D_e\%$		0.0003785	−27.2003	$\Delta D_e\%$		0.008838	2.7259
E_{rror}		0.001859	−282.1672	E_{rror}		0.1787	41.5366

Table 2 (Continued)

Na$_2$-2$^3\Pi_g$				K$_2$-2$^1\Pi_g$			
υ	$E_\upsilon^{\exp t}$[21]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[21]	υ	$E_\upsilon^{\exp t}$[22]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[22]
0	**47.029**	47.029	47.0812	0	**27.7442**	27.7442	27.7333
1	**140.632**	140.632	140.6854	1	83.0178	83.0177	83.0068
2	**233.499**	233.499	233.5543	2	**138.0229**	138.0229	138.0120
3	325.643	325.642	325.6989	3	192.7466	192.7465	192.7356
4	417.072	417.070	417.1295	4	**247.1754**	247.1754	247.1644
5	507.798	507.796	507.8565	5	301.2963	301.2963	301.2853
6	**597.829**	597.829	597.8896	6	355.0960	355.0959	355.0849
7	687.176	687.178	687.2384	7	408.5612	408.5611	408.5501
8	775.848	775.854	775.9120	8	461.6788	461.6788	461.6677
9	863.854	863.863	863.9194	9	514.4356	514.4356	514.4244
10	951.202	951.216	951.2692	10	**566.8183**	566.8183	566.8071
11	1037.900	1037.920	1037.9695	11	618.8137	618.8138	618.8024
12	1123.956	1123.983	1124.0283	12	670.4086	670.4087	670.3972
13	1209.378	1209.411	1209.4532	13	721.5898	721.5899	721.5784
14	1294.174	1294.213	1294.2515	14	772.3441	772.3441	772.3326
15	1378.349	1378.395	1378.4301	15	**822.6582**	822.6582	822.6466
16	1461.911	1461.964	1461.9957	16	**872.5189**	872.5189	872.5072
17	1544.866	1544.925	1544.9546	17	921.9131	921.9130	921.9013
18	1627.220	1627.284	1627.3128	18	970.8274	970.8274	970.8156
19	1708.978	1709.047	1709.0759	19	**1019.2488**	1019.2488	1019.2368
20	1790.147	1790.219	1790.2493	20	1067.1639	1067.1640	1067.1518
21	1870.730	1870.805	1870.8380	21	1114.5596	1114.5597	1114.5474
22	1950.732	1950.809	1950.8468	22	**1161.4226**	1161.4226	1161.4103
23	2030.159	2030.237	2030.2800	23		1207.7392	1207.7273
24	2109.013	2109.091	2109.1416	24		1253.4959	1253.4852
25	2187.299	2187.376	2187.4355	25		1298.6789	1298.6708
26	2265.021	2265.095	2265.1651	26		1343.2741	1343.2708
27	2342.180	2342.251	2342.3334	27		1387.2671	1387.2721
28	2418.780	2418.847	2418.9431	28		1430.6432	1430.6615
29	2494.823	2494.886	2494.9969	...		...	...
30	2570.312	2570.370	2570.4968	42		1962.7988	1966.4548
...	...	...	...	43		1994.4587	1999.0787
42	3433.237	3433.239	3433.6293	44		2025.0887	2030.8792
43	**3501.560**	3501.560	3501.9764	45		2054.6406	2061.8431
44	**3569.323**	3569.323	3569.7657	46		2083.0615	2091.9570
45	3636.525	3636.524	3636.9945	47		2110.2933	2121.2080
46	3703.162	3703.161	3703.6598	48		2136.2729	2149.5826
47	3769.231	3769.230	3769.7583	49		2160.9308	2177.0677
48	**3834.727**	3834.727	3835.2864	50		2184.1914	2203.6501
49	3899.648	3899.648	3900.2399	51		2205.9720	2229.3166
50	3963.989	3963.989	3964.6147	52		2226.1823	2254.0539
51	4027.744	4027.745	4028.4062	53		2244.7240	2277.8488
52	**4090.910**	4090.910	4091.6093	54		2261.4900	2300.6882
53		4153.480	4154.2188	55		2276.3638	2322.5587
...		...	...	56		2289.2186	2343.4473
98		6256.628	6209.3708	57		2299.9172	2363.3406
99		6287.180	6233.4236	58		2308.3106	2382.2254
100		6317.222	6256.2728	59		2314.2374	2400.0886
101		6346.792	6277.8975	60		2317.5231	2416.9169
102		6375.929	6298.2768	61		2317.9793	2432.6971
103			6317.3893	62			2447.4159
...			...	...			...
113			6433.9158	71			2529.9459
114			6437.5931	72			2533.3247
115			6439.7224	73			2535.4969
116			6440.2782	74			2536.4491
$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	63.166	29.1375	0.5558	$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	46.8630	0.4562	0.9522
D_e^{cal}		6404.641	6440.4233	D_e^{cal}		2318.0426	2536.8665
$D_e^{\exp t}$	6406.2 [21]			$D_e^{\exp t}$	2318.0900 [22]		
$\Delta D_e\%$		0.02433	−0.5342	$\Delta D_e\%$		0.002045	−9.4378
E_{rror}		0.05350	−61.5748	E_{rror}		0.1038	−229.7550

Table 2 (Continued)

K_2-$3^3\Pi_g$				K_2-$X^1\Sigma_g^+$			
υ	$E_\upsilon^{\exp t}$[23]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[23]	υ	$E_\upsilon^{\exp t}$[25,26]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[25]
0	**36.5536**	36.5536	36.5455	0	**46.0910**	46.0910	46.1175
1	**109.2791**	109.2791	109.2705	1	**137.8337**	137.8337	137.8630
2	181.5163	181.5166	181.5075	2	**228.9214**	228.9214	228.9520
3	253.2654	253.2658	253.2565	3	319.3490	319.3494	319.3801
4	324.5262	324.5267	324.5175	4	409.1120	409.1128	409.1430
5	395.2989	395.2993	395.2905	5	498.2055	498.2065	498.2363
6	465.5833	465.5837	465.5755	6	**586.6251**	586.6251	586.6557
7	535.3796	535.3798	535.3725	7	674.3662	674.3632	674.3966
8	604.6876	604.6877	604.6815	8	761.4238	761.4152	761.4542
9	**673.5075**	673.5075	673.5025	9	847.7932	847.7755	847.8234
10	**741.8391**	741.8391	741.8355	10	933.4691	933.4383	933.4989
11	809.6826	809.6825	809.6805	11	1018.4461	1018.3979	1018.4749
12	**877.0378**	877.0378	877.0375	12	1102.7183	1102.6484	1102.7449
13	943.9049	943.9049	943.9065	13	1186.2796	1186.1837	1186.3022
14	1010.2837	1010.2837	1010.2875	14	1269.1237	1268.9979	1269.1393
15	1076.1744	1076.1744	1076.1805	15	1351.2436	1351.0848	1351.2481
16	**1141.5768**	1141.5768	1141.5855	16	1432.6323	1432.4379	1432.6196
17	1206.4911	1206.4910	1206.5025	17	1513.2822	1513.0508	1513.2440
18	**1270.9171**	1270.9171	1270.9315	18	1593.1857	1592.9167	1593.1109
19	1334.8550	1334.8550	1334.8724	19	1672.3346	1672.0286	1672.2086
20	1398.3046	1398.3048	1398.3254	20	1750.7204	1750.3794	1750.5245
21	1461.2661	1461.2665	1461.2904	21	1828.3344	1827.9613	1828.0450
22	1523.7393	1523.7399	1523.7674	...	...	...	...
23	1585.7244	1585.7250	1585.7564	35	2828.0559	2827.9793	2818.9794
24	**1647.2212**	1647.2212	1647.2574	36	**2892.7620**	2892.7620	2881.9799
25	1708.2299	1708.2281	1708.2704	37	2956.4958	2956.5747	2943.7631
26		1768.7448	1768.7954	38	3019.2404	3019.3980	3004.2865
27		1828.7699	1828.8324	...	...	...	...
28		1888.3018	1888.3814	48	3587.9945	3588.2807	3529.1484
29		1947.3380	1947.4424	49	3638.5189	3638.6802	3572.3029
30		2005.8752	2006.0154	50	**3687.7899**	3687.7899	3613.4888
31		2063.9095	2064.1004	51	3735.7802	3735.5807	3652.6287
32		2121.4355	2121.6974	52	3782.4614	3782.0233	3689.6416
33		2178.4466	2178.8064	...	...	...	...
34		2234.9347	2235.4274	62	4170.4476	4165.9553	3922.6025
35		2290.8898	2291.5604	63	4200.6362	4195.7152	3929.9090
36		2346.3000	2347.2054	64	4229.1242	4223.8163	3933.8464
37		2401.1507	2402.3624	65	4255.8796	4250.2431	3934.2865
38		2455.4248	2457.0314	66	4280.8722	4274.9828	
39		2509.1020	2511.2124	67	4304.0744	4298.0261	
40		2562.1586	2564.9054	68	4325.4624	4319.3671	
41		2614.5669	2618.1104	69	4345.0175	4339.0042	
...		...	...	70	4362.7287	4356.9399	
60		3377.4390	3536.2853	71	4378.5958	4373.1818	
61		3402.7724	3579.7303	72	4392.6339	4387.7427	
62		3425.1052	3622.6873	73	4404.8772	4400.6414	
63		3444.1620	3665.1563	74	4415.3572	4411.9028	
64		3459.6439	3707.1373	75	4424.1717	4421.5586	
65		3471.2271	3748.6303	76	4431.4103	4429.6480	
66		3478.5612	3789.6353	77	4437.1978	4436.2181	
67		3481.2678	3830.1523	78	4441.6829	4441.3244	
68			3870.1813	79	**4445.0317**	4445.0317	
...			...	80	**4447.4144**	4447.4144	
148			5491.3811	81	4448.9822	4448.5575	
149			5491.8821				
150			5491.8951				
$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	61.0087	2.7066	0.0130	$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	1.5678	1.1431	0.4401
D_e^{cal}		3482.2667	5491.8954	D_e^{cal}		4449.1058	3934.3357
$D_e^{\exp t}$	3482.6649 [24]			$D_e^{\exp t}$	4450.7479 [27]		
$\Delta D_e\%$		0.0114	−57.6923	$\Delta D_e\%$		0.03690	11.6028
E_{rror}		0.1471	−154596.4566	E_{rror}		1.4366	1173.3974

Table 2 (Continued)

Br_2-$X^1\Sigma_g^+$				$^6\mathrm{Li}_2$-$1^1\Pi_g$			
υ	$E_\upsilon^{\exp t}$[28]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[28]	υ	$E_\upsilon^{\exp t}$[29]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[29]
0	**162.3803**	162.3803	162.3872	0	**49.7317**	49.7317	49.6095
1	485.5306	485.5305	485.5374	1	**146.0459**	146.0459	145.9100
2	**806.5050**	806.5050	806.5118	2	**238.4594**	238.4594	238.3306
3	1125.2909	1125.2909	1125.2977	3	327.0141	327.0126	326.8885
4	**1441.8750**	1441.8750	1441.8818	4	411.7278	411.7261	411.5987
5	1756.2437	1756.2436	1756.2504	5	**492.6062**	492.6062	492.4702
6	2068.3828	2068.3827	2068.3895	6	569.6484	569.6502	569.5046
7	2378.2777	2378.2776	2378.2844	7	**642.8506**	642.8506	642.6960
8	2685.9132	2685.9131	2685.9199	8	712.2075	712.1997	712.0313
9	2991.2737	2991.2735	2991.2804	9	777.7147	777.6931	777.4912
10	3294.3429	3294.3427	3294.3496	10	839.3712	839.3331	839.0498
11	3595.1037	3595.1035	3595.1104	11	897.1830	897.1313	896.6734
12	3893.5386	3893.5384	3893.5453	12	951.1660	951.1114	950.3168
13	4189.6294	4189.6292	4189.6360	13	1001.3503	1001.3111	999.9168
14	4483.3568	4483.3567	4483.3634	14	**1047.7834**	1047.7834	1045.3823
15	4774.7011	4774.7010	4774.7076	15	1090.5330	1090.5983	1086.5801
16	5063.6415	5063.6415	5063.6480	16	1129.6891	1129.8429	1123.3159
17	**5350.1565**	5350.1565	5350.1630	17	1165.3644	1165.6225	1155.3092
18	5634.2235	5634.2235	5634.2299	18	1197.6943	1198.0599	1182.1623
19	5915.8189	5915.8189	5915.8252	19	1226.8346	1227.2952	1203.3219
20	**6194.9181**	6194.9181	6194.9243	20	1252.9594	1253.4850	1218.0331
21	6471.4954	6471.4953	6471.5015	21	1276.2570	1276.8014	1225.2847
22	6745.5237	6745.5236	6745.5297	22	1296.9258	1297.4296	
23	7016.9750	7016.9749	7016.9807	23	1315.1698	1315.5668	
24	7285.8196	7285.8194	7285.8250	24	1331.1938	1331.4193	
25	7552.0265	7552.0265	7552.0317	25	**1345.1999**	1345.1999	
26	**7815.5635**	7815.5635	7815.5684	26	1357.3833	1357.1247	
27	**8076.3966**	8076.3966	8076.4010	27	1367.9295	1367.4097	
28	8334.4900	8334.4901	8334.4940	28	1377.0130	1376.2670	
29	**8589.8067**	8589.8067	8589.8100	29	1384.7955	1383.9005	
30		8842.3071	8842.3101	30	1391.4262	1390.5014	
31		9091.9502	9091.9531	31	1397.0421	1396.2431	
32		9338.6929	9338.6961	32	1401.7693	1401.2766	
33		9582.4896	9582.4942	33	**1405.7241**	1405.7241	
34		9823.2930	9823.3001	34	1409.0156	1409.6736	
35		10061.0529	10061.0644	35		1413.1725	
36		10295.7168	10295.7352	36		1416.2213	
37		10527.2297	10527.2585	37		1418.7661	
38		10755.5336	10755.5773	38		1420.6922	
39		10980.5677	10980.6322	39		1421.8159	
40		11202.2680	11202.3609	40		1421.8772	
41		11420.5676	11420.6984	41			
42		11635.3959	11635.5763	42			
43		11846.6789	11846.9236	43			
44		12054.3389	12054.6656	44			
45		12258.2944	12258.7245	45			
...		...	...	46			
72		15923.8481	15976.2899	47			
73		15968.1895	16027.5889	48			
74		16003.7145	16070.8421	49			
75		16030.1056	16105.8014	50			
76		16047.0320	16132.2099	51			
77		16054.1489	16149.8026	52			
78			16158.3051	53			
$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	255.3167	7.1169	8.5025	$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	3.2915	0.0613	7.2516
D_e^{cal}		16057.1413	16162.4143	D_e^{cal}		1421.8806	1228.8592
$D_e^{\exp t}$	16057.16 [28]			$D_e^{\exp t}$	1421.9800 [29]		
$\Delta D_e\%$		0.00012	−0.6554	$\Delta D_e\%$		0.006999	13.5811
E_{rror}		0.0026	−12.3792	E_{rror}		1.6235	26.6315

of these homonuclear diatomic molecules, the obtained AM dissociation energies D_e^{cal} agree very well with the experimental values $D_e^{\exp t}$. The percent error of D_e^{cal} (AM) from $D_e^{\exp t}$ is less than 1 %. For example, for the K$_2$-$2^1\Pi_g$ electronic state, Zhao *et al.* [22] gave 23 experimental energies in 1997, the maximum vibrational energy $E_{\upsilon_{\max}=22}^{\exp t}$ is 1161.4226 cm^{-1} which is 1156.5674 cm^{-1} smaller than the experimental dissociation energy $D_e^{\exp t}$(=2318.0900 cm^{-1}). However, the full AM vibrational spectrum of this electronic state obtained using the AM method contains 62 vibrational energies with the maximum vibrational energy $E_{\upsilon_{\max}=61}^{\mathrm{AM}}$(=2317.9793 cm^{-1}) which is only 0.1107 cm^{-1} less than experimental dissociation energy $D_e^{\exp t}$. Substituting the three highest AM vibrational energies into Eq. (22), the obtained AM dissociation energy D_e^{cal} is 2318.0426 cm^{-1}. The percent error between D_e^{cal} and $D_e^{\exp t}$ is only 0.002 045%. The accuracy of the AM energy spectrum uniquely depends on that of the experimental energies. If the experimental energies are accurate enough, the obtained vibrational spectroscopic constants are accurate. Consequently, the resulting AM vibrational spectrum will reproduce the known experimental energies, generate all high-lying vibrational energies including those in the dissociation region and produce correct dissociation energies.

It is also seen from Table 2 that the theoretical vibrational spectrum $\{E_\upsilon^{\mathrm{Theo}}\}$ obtained using the literature vibrational spectroscopic constants usually reproduce the known experimental energies, but the generated high-lying vibrational energies may have errors, or may even be wrong. For example, for the $3^3\Pi_g$ electronic state of K$_2$, Ref. [23] gives 26 experimental energies. However, the number of vibrational energies obtained by using the literature spectroscopic constants from Ref. [23] is 151, and the maximum vibrational energy $E_{\upsilon_{\max}=150}^{\mathrm{Theo}}=$ 5491.8951 cm^{-1}, which severely violates Eq. (11). In order to make a direct comparison, Fig. 1 plots the known (incomplete) experimental energies $[E_\upsilon^{\exp t}]$, the AM vibrational spectrum $\{E_\upsilon^{\mathrm{AM}}\}$, the theoretical vibrational spectrum $\{E_\upsilon^{\mathrm{Theo}}\}$evaluated using vibrational constants from reference and the RKR potential curves for the state. Similar figures for K$_2$-$2^1\Pi_g$ and Na$_2$-$4^3\Sigma_g^+$ states are also plotted in Fig. 2 and Fig. 3, respectively. However, for some electronic states, the maximum vibrational energies $E_{\upsilon_{\max}}^{\mathrm{Theo}}$ obtained using the literature spectroscopic constants are smaller or much smaller than their dissociation energies $D_e^{\exp t}$ (like the Na$_2$-$2^3\Sigma_g^+$ and the K$_2$-$X^1\Sigma_g^+$ electronic states), or are not converged (such as the HgI-$X^2\Sigma^+$ electronic state in Table 4). This is because many experimental spectroscopic constants are obtained by fitting Dunham's or Herzberg's energy expression on known experimental energies. The fitting process not only obtains vibrational information of each energy, but also takes different errors contained in each experimental energy. The resulting spectroscopic constants are contaminated someway by these errors. The high-lying vibrational energies evaluated using the fitted vibrational constants might be poor or very poor, especially those near the dissociation limit. However, although the AM method also uses known experimental energies, it doesn't use any mathematic fitting and physical approximation and instead selects the best physical

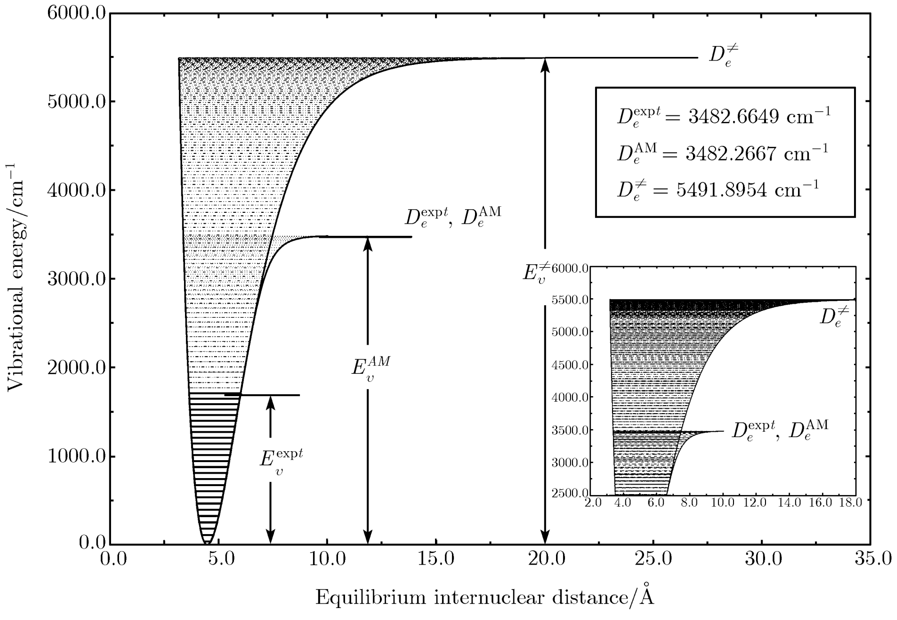

Fig. 1 RKR potentials, vibrational spectra $\{E_\upsilon^{\exp t}\}$, $\{E_\upsilon^{\mathrm{AM}}\}$ and $\{E_\upsilon^{\mathrm{Theo}} = E_\upsilon^{\neq}\}$ of K$_2$-$3^3\Pi_g$ state.

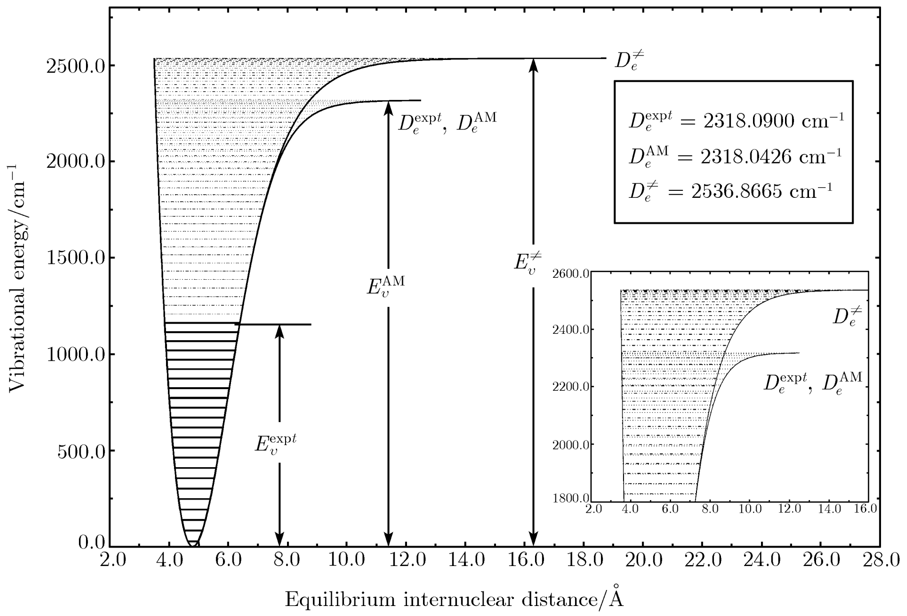

Fig. 2 RKR potentials, vibrational spectra $\{E_v^{\mathrm{exp}\,t}\}$, $\{E_v^{\mathrm{AM}}\}$ and $\{E_v^{\mathrm{Theo}} = E_v^{\neq}\}$ of K$_2$-$2^1\Pi_g$ state.

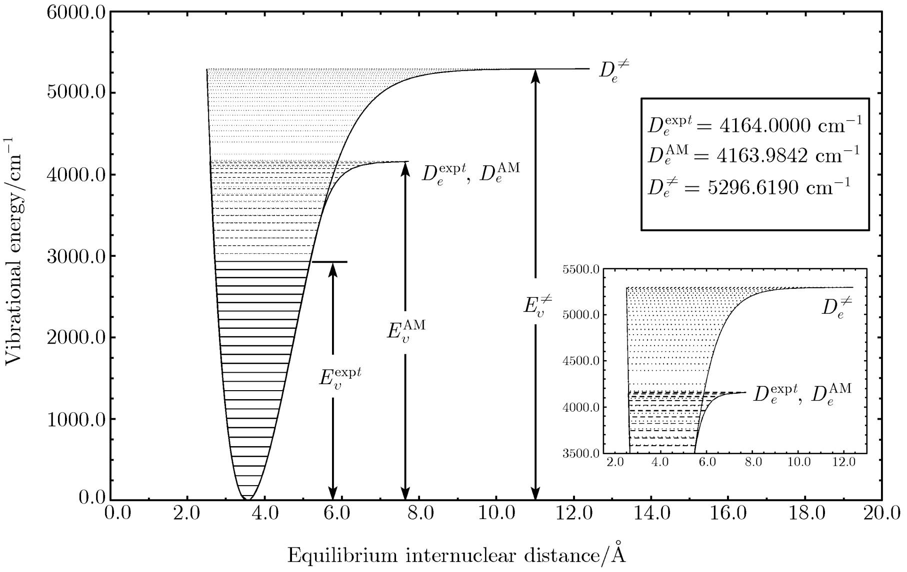

Fig. 3 RKR potentials, vibrational spectra $\{E_v^{\mathrm{exp}\,t}\}$, $\{E_v^{\mathrm{AM}}\}$ and $\{E_v^{\mathrm{Theo}} = E_v^{\neq}\}$ of Na$_2$-$4^3\Sigma_g^+$ state.

representation of the known energies by using a group of physical criteria. This is the reason why AM spectroscopic constants and AM energies are different from those obtained by numerical fitting in literatures.

$0 < E_{rror} \lesssim 1$ is an useful empirical criterion judging the correctness of the calculated theoretical dissociations D_e^{cal}. It is seen from Table 2 that all E_{rror} (AM) except for K$_2$-$X^1\Sigma_g^+$ and ^{6}Li$_2$- $1^1\Pi_g$ states satisfy this criterion. For K$_2$- $X^1\Sigma_g^+$ and ^{6}Li$_2$-$1^1\Pi_g$ states, E_{rror} (AM) are slightly greater than 1. This is because the high-lying vibrational energies near dissociation energies are so dense that the last energy difference $\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$ is too small. Furthermore, all AM energy spectra of these states satisfy other criteria of Eqs. (7)−(13). However, for the theoretical vibrational spectra $\{E_v^{\mathrm{Theo}}\}$ obtained using the corresponding literature spectroscopic constants, all E_{rror} do not satisfy this criterion.

3.2 Applications to heteronuclear diatomic molecules

Compared with homonuclear diatomic molecules, the atoms in heteronuclear diatomic molecules have different electronegativity, so these molecules usually behave with a certain polarity. The molecules formed from the

Table 3 Vibrational spectroscopic constants of some heteronuclear diatomic electronic states (units: cm^{-1}).

State		ω_0	ω_{e0}	ω_e'	$\omega_e x_e$	$10^2\omega_e y_e$	$10^3\omega_e z_e$	$10^4\omega_e t_e$	$10^5\omega_e s_e$	$10^{10}\omega_e r_e$
^{6}LiH-$C^1\Sigma^+$	AM	−0.515720	−0.02006	298.589438	2.266664	−1.938807	1.473193	−0.641465	0.181673	−211.73108
	Ref. [30]			298.6094	2.28241	−1.420	0.6859	−0.0768		
^{7}LiD-$C^1\Sigma^+$	AM	−0.279411	0.006189	221.017362	1.106709	−2.127916	1.087604	−0.303092	0.049589	−35.294536
	Ref. [30]			221.0111	1.1045	−2.13	1.051084	−0.270	0.039236	−24.62
NaK-$X^1\Sigma^+$	AM	−0.397735	0.377996	124.371066	0.583750	0.855376	−0.490562	0.119412	−0.01502	7.128175
	Ref. [31]			123.993	0.3045					
NaRb-$a^3\Sigma^+$	AM	−0.020088	−0.001270	18.858075	0.407865	−0.882283	0.320799	−0.106381	0.052329	−97.176108
	Ref. [33]			18.85934	0.408976	−0.83564	0.21918			
NaLi-$B^1\Pi$	AM	0.984898	0.167710	209.797806	10.036900	20.164335	3.776662	−5.605986	3.359488	−7315.215651
	Ref. [35]			209.630	9.97945	20.5438				
KRb-$2^1\Pi$	AM	−0.057862	0.017184	51.717286	0.428821	−0.181252	−0.238627	0.144994	−0.037285	16.534392
	Ref. [36]			51.70004	0.420405	−0.37896				
CsH-$X^1\Sigma^+$	AM	0.246151	2.886377	882.976354	12.100722	−8.488510	24.449209	−21.236131	9.047087	−15470.640475
	Ref. [37]			880.09	13.676	19.723	−5.6323			
RbH-$X^1\Sigma^+$	AM	0.582503	−0.556885	936.631173	13.804228	−5.172669	21.696606	−21.345715	10.858210	−22291.366046
	Ref. [38]			937.188	14.173	6.97				
ICl-$A^3\Pi(1)$	AM	−0.086933	−0.144726	210.855331	2.012744	−6.305891	5.547201	−3.634316	0.986696	−901.439938
	Ref. [39]			211.0	2.12	−2.4	0.2			
ClF-$A(^3\Pi_1)$	AM	−0.539845	1.576180	362.806180	9.100703	13.3128959	−79.572733	85.969592	−41.593014	79665.704687
	Ref. [40]			361.23	7.74	−36	10			
CO-$X^1\Sigma^+$	AM	0.186086	0.011508	2169.811450	13.287185	1.026494	0.081821	−0.001608	−0.000629	−2.144089
	Ref. [41]			2169.8	13.3					
HgI-$X^2\Sigma^+$	AM	0.004464	−0.011111	126.059945	1.264354	1.384285	−1.251220	0.026326	0.089098	−117.277653
	Ref. [42]			126.071	1.2704	1.5899	−1.5785	0.27681		

Note: for the AM values: $\omega_e' = \omega_e + \omega_{e0}$; for values from references: $\omega_e' = \omega_e$.

Table 4 Vibrational energies of some heteronuclear diatomic electronic states (energy units: cm^{-1}).

^{6}LiH-$C^1\Sigma^+$				^{7}LiD-$C^1\Sigma^+$			
υ	$E_\upsilon^{\exp t}$[30]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[30]	υ	$E_\upsilon^{\exp t}$[30]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[30]
0	**148.2100**	148.2100	148.7324	0	**109.9500**	109.9500	110.2268
1	**442.2100**	442.2100	442.7342	1	**328.6900**	328.6900	328.9647
2	**731.5400**	731.5400	732.0626	2	545.0500	545.0542	545.3303
3	**1016.1400**	1016.1400	1016.6635	3	**758.9600**	758.9600	759.2397
4	1295.9700	1295.9701	1296.4966	4	970.3500	970.3428	970.6272
5	1571.0100	1571.0062	1571.5353	5	1179.1700	1179.1537	1179.4425
6	1841.2400	1841.2367	1841.7649	6	1385.3700	1385.3566	1385.6488
7	**2106.6600**	2106.6600	2107.1823	7	1588.9400	1588.9268	1589.2207
8	2367.2700	2367.2826	2367.7949	8	1789.8600	1789.8486	1790.1421
9	2623.0900	2623.1180	2623.6196	9	1988.1300	1988.1140	1988.4053
10	2874.1600	2874.1861	2874.6818	10	2183.7300	2183.7214	2184.0091
11	3120.4900	3120.5128	3121.0147	11	2376.6800	2376.6741	2376.9577
12	**3362.1300**	3362.1300	3362.6585	12	**2566.9800**	2566.9800	2567.2598
13	3599.1300	3599.0761	3599.6589	13	**2754.6500**	2754.6500	2754.9275
14	3831.5400	3831.3959	3832.0668	14	2939.7000	2939.6980	2939.9758
15	4059.4100	4059.1412	4059.9370	15	**3122.1400**	3122.1400	3122.4218
16	4282.8000	4282.3706	4283.3274	16	3302.0100	3301.9941	3302.2843
17	4501.7700	4501.1498	4502.2981	17	3479.3100	3479.2797	3479.5833
18	4716.3800	4715.5507	4716.9105	18	3654.0600	3654.0179	3654.3399
19	4926.7000	4925.6510	4927.2263	19	3826.3000	3826.2307	3826.5755
20	5132.7800	5131.5322	5133.3066	20	3996.0400	3995.9417	3996.3126
21	5334.6800	5333.2780	5335.2110	21	4163.3000	4163.1751	4163.5737
22	5532.4700	5530.9709	5532.9966	22	4328.1000	4327.9563	4328.3818
23	5726.1900	5724.6888	5726.7174	23	4490.4800	4490.3119	4490.7604
24	5915.9000	5914.5000	5916.4227	24	4650.4600	4650.2690	4650.7329
25	6101.6300	6100.4576	6102.1569	25	4808.0500	4807.8557	4808.3232
26	6283.4300	6282.5920	6283.9583	26	4963.2800	4963.1004	4963.5553
27	6461.3300	6460.9031	6461.8581	27	5116.1800	5116.0320	5116.4535
28	**6635.3500**	6635.3500	6635.8795	28	5266.7700	5266.6792	5267.0421
29	6805.5100	6805.8400	6806.0368	29	**5415.0700**	5415.0700	5415.3453
30	6971.8100	6972.2157	6972.3346	30	5561.1100	5561.2314	5561.3869
31	**7134.2400**	7134.2400	7134.7666	31	5704.9100	5705.1882	5705.1905
32	7292.7900	7291.5801	7293.3151	32	5846.5000	5846.9625	5846.7784
33		7443.7886	7447.9496	33	5985.8900	5986.5722	5986.1719
...		...	...	...	...	...	...
41		8366.9714	8535.5971	41	7023.5800	7025.0878	7023.8583
42		8422.0328	8651.1077	42	7143.5700	7144.5144	7143.8518
43		8455.5334	8761.5064	43	**7261.3200**	7261.3200	7261.5972
44		8463.8865	8866.5635	44	7376.7500	7375.3336	7377.0316
45			8966.0260	45		7486.3456	7490.0733
...			...	...		...	...
49			9301.9889	55		8346.1456	8451.0518
50			9368.7900	56		8393.2480	8523.6320
51			9427.9301	57		8429.4933	8590.0580
52			9478.9647	58		8453.5280	8649.6375
53			9521.4186	59		8463.8421	8701.5908
54			9554.7845	60			8745.0431
55			9578.5224	61			8779.0165
56			9592.0583	62			8802.4212
57			9594.7838	63			8814.0466
$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	158.5500	8.3531	2.7255	$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	115.4300	10.3141	11.6254
D_e^{cal}		8465.9692	9595.3326	D_e^{cal}		8468.2682	8819.8211
$D_e^{\exp t}$	8466.1600 [30]			$D_e^{\exp t}$	8468.2700 [30]		
$\Delta D_e\%$		0.0023	−13.3748	$\Delta D_e\%$		0.00002	−4.1514
E_{rror}		0.0228	−414.2963	E_{rror}		0.0002	−30.2399

Note: $E_\upsilon^{\exp t}$ is experimental energy; E_υ^{AM} is the AM vibrational energy; $E_\upsilon^{\mathrm{Theo}}$ is vibrational energy calculated using spectroscopic constants from corresponding references; $\Delta E_{\upsilon_{\max},\upsilon_{\max}-1} = E_{\upsilon_{\max}} - E_{\upsilon_{\max}-1}$; $D_e^{\exp t}$ is experimental dissociation energy; D_e^{cal} is theoretical dissociation energy calculated using Eq. (22); $\Delta D_e\% = 100 \times (D_e^{\exp t} - D_e^{cal})/D_e^{\exp t}$; $E_{rror} = (D_e^{\exp t} - D_e^{cal})/\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$.

Table 4 (Continued)

NaK-$X^1\Sigma^+$				NaRb-$a^3\Sigma^+$			
υ	$E_\upsilon^{\exp t}$[31]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[31]	υ	$E_\upsilon^{\exp t}$[34]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[33]
0	61.8525	61.6429	61.9204	0	**9.3059**	9.3059	9.3264
1	**184.8719**	184.8719	185.3044	1	**27.3211**	27.3211	27.3417
2	306.9035	306.9971	308.0794	2	**44.4497**	44.4497	44.4702
3	427.9362	428.0492	430.2454	3	**60.6520**	60.6520	60.6723
4	547.9607	548.0502	551.8024	4	**75.8939**	75.8939	75.9137
5	666.9685	667.0150	672.7504	5	90.1461	90.1465	90.1651
6	**784.9517**	784.9517	793.0893	6	103.3850	103.3860	103.4029
7	901.9025	901.8633	912.8193	7	115.5918	115.5937	115.6083
8	1017.8127	1017.7481	1031.9403	8	126.7534	126.7558	126.7681
9	1132.6736	1132.6006	1150.4523	9	136.8617	136.8639	136.8743
10	1246.4759	1246.4119	1268.3553	10	145.9138	145.9152	145.9240
11	1359.2098	1359.1710	1385.6493	11	**153.9122**	153.9122	153.9198
12	**1470.8646**	1470.8646	1502.3343	12	160.8647	160.8632	160.8692
13	1581.4291	1581.4779	1618.4103	13	166.7841	166.7818	166.7854
14	1690.8914	1690.9949	1733.8773	14	171.6889	171.6870	171.6866
15	1799.2389	1799.3989	1848.7353	15	**175.6023**	175.6023	175.5962
16	1906.4586	1906.6726	1962.9843	16	178.5532	178.5551	178.5431
17	2012.5365	2012.7983	2076.6243	17	**180.5756**	180.5756	180.5612
18	2117.4582	2117.7582	2189.6553	18		181.6950	181.6898
19	2221.2086	2221.5345	2302.0773	19		181.9440	181.9736
20	2323.7720	2324.1093	2413.8903	20			
21	2425.1318	2425.4647	2525.0943	21			
22	2525.2708	2525.5829	2635.6893	22			
23	2624.1708	2624.4462	2745.6753	23			
24	2721.8129	2722.0366	2855.0523	24			
25	2818.1771	2818.3360	2963.8203	25			
26	2913.2427	2913.3259	3071.9793	26			
27	**3006.9875**	3006.9875	3179.5293	27			
28	3099.3888	3099.3012	3286.4703	28			
29	3190.4221	3190.2466	3392.8023	29			
30	3280.0624	3279.8023	3498.5252	30			
31	3368.2829	3367.9458	3603.6392	31			
32	3455.0559	3454.6531	3708.1442	32			
33	3540.3523	3539.8987	3812.0402	33			
...	...	...	...	34			
40	4093.3629	4093.1302	4522.2602	35			
41	4165.6383	4165.5162	4621.2842	36			
42	**4236.1128**	4236.1128	4719.6992	37			
43	4304.7424	4304.8710	4817.5052	38			
...	...	...	...	39			
55	4965.4505	4965.7392	5943.6751	40			
56	5005.1126	5005.2561	6033.5641	41			
57	**5042.0991**	5042.0991	6122.8441	42			
58	5076.3471	5076.2182	6211.5151	43			
...	...	...	...	44			
63	5204.8512	5204.6638	6645.7351	45			
64	5221.8767	5221.7920	6730.7521	46			
65	**5236.0782**	5236.0782	6815.1601	47			
66	**5247.5570**	5247.5570	6898.9591	48			
67		5256.2815	6982.1491	49			
68		5262.3253	7064.7301	50			
69		5265.7846	7146.7020	51			
70		5266.7808	7228.0650	52			
71			7308.8190	53			
...			...	54			
201			12621.2031	55			
202			12622.1781	56			
203			12622.5440	57			
$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	11.4788	0.9962	0.3660	$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	2.0224	0.2489	0.2838
D_e^{cal}		5267.0677	12622.6814	D_e^{cal}		181.9993	182.0450
$D_e^{\exp t}$	5268.1000 [32]			$D_e^{\exp t}$	182.0000 [33]		
$\Delta D_e\%$		0.01959	−139.3479	$\Delta D_e\%$		0.00035908	−0.00025
E_{rror}		1.0362	−20079.4758	E_{rror}		0.0026	−0.1584

Table 4 (Continued)

NaLi-$B^1\Pi$				KRb-$2^1\Pi$			
v	$E_v^{\exp t}$[35]	E_v^{AM}	E_v^{Theo}[35]	v	$E_v^{\exp t}$[36]	E_v^{AM}	E_v^{Theo}[36]
0	**103.4000**	103.4000	102.3458	0	25.6990	25.6933	25.7446
1	293.7000	293.7944	292.6846	1	**76.5460**	76.5460	76.5919
2	**466.0000**	466.0000	464.9134	2	126.5180	126.5189	126.5643
3	**621.3000**	621.3000	620.2649	3	**175.5930**	175.5930	175.6390
4	761.0000	760.9684	759.9717	4	**223.7470**	223.7470	223.7933
5	886.3000	886.2581	885.2664	5	270.9590	270.9584	271.0045
6	**998.4000**	998.4000	997.3817	6	**317.2040**	317.2040	317.2498
7	1098.6000	1098.6101	1097.5501	7	362.4610	362.4608	362.5065
8	**1188.1000**	1188.1000	1187.0044	8	**406.7060**	406.7060	406.7519
9	1268.0000	1268.0877	1266.9771	9	**449.9170**	449.9170	449.9632
10	1339.8000	1339.8055	1338.7008	10	492.0720	492.0715	492.1176
11	**1404.5000**	1404.5000	1403.4083	11	**533.1470**	533.1470	533.1925
12	1463.4000	1463.4217	1462.3321	12	573.1190	573.1204	573.1652
13	**1517.8000**	1517.8000	1516.7048	13	**611.9670**	611.9670	612.0128
14	**1568.8000**	1568.8000	1567.7591	14		649.6601	649.7126
15	1617.8000	1617.4573	1616.7276	15		686.1696	686.2419
16		1664.5872	1664.8429	16		721.4608	721.5780
17		1710.6650	1713.3378	17		755.4933	755.6981
18		1755.6727	1763.4446	18		788.2191	788.5795
19		1798.9097	1816.3963	19		819.5816	820.1994
20		1838.7627	1873.4252	20		849.5131	850.5351
21		1872.4318	1935.7642	21		877.9337	879.5640
22		1895.6089	2004.6457	22		904.7488	907.2631
23		1902.1046	2081.3024	23		929.8472	933.6098
24			2166.9671	24		953.0990	958.5814
25			2262.8722	25		974.3535	982.1551
26			2370.2504	26		993.4364	1004.3082
27			2490.3344	27		1010.1483	1025.0179
...			...	28		1024.2612	1044.2616
99			124430.9485	29		1035.5170	1062.0164
100			128807.8799	30		1043.6244	1078.2596
...			...	31		1048.2565	1092.9685
199			1275845.1055	32		1049.0485	1106.1204
200			1296715.5671	33			1117.6925
...			...	34			1127.6621
599			40802820.82	35			1136.0064
600			41012928.20	36			1142.7027
...			not converged	37			1147.7283
				38			1151.0605
				39			1152.6764
$\Delta E_{v_{\max},v_{\max}-1}$	49.0000	6.4957		$\Delta E_{v_{\max},v_{\max}-1}$	38.8480	0.7919	1.6159
D_e^{cal}		1903.9250		D_e^{cal}		1049.1838	1153.4600
$D_e^{\exp t}$	1904.3000 [35]			$D_e^{\exp t}$	1050.0000 [36]		
$\Delta D_e\%$		0.0197		$\Delta D_e\%$		0.0777	−9.8533
E_{rror}		0.0577		E_{rror}		1.0306	−64.0255

Table 4 (Continued)

	CsH-$X^1\Sigma^+$				RbH-$X^1\sum^+$		
υ	$E_\upsilon^{\exp t}$[37]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[37]	υ	$E_\upsilon^{\exp t}$[38]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[38]
0	**438.7000**	438.7000	436.6503	0	465.3200	465.4419	465.0595
1	1297.4000	1297.3062	1290.0012	1	**1374.3900**	1374.3900	1374.1280
2	**2131.5000**	2131.5000	2117.6118	2	**2255.7400**	2255.7400	2255.4778
3	**2941.5000**	2941.5000	2920.3951	3	3109.7900	3109.7920	3109.5271
4	3727.7000	3727.6655	3699.1291	4	**3936.9500**	3936.9500	3936.6941
5	**4490.4000**	4490.4000	4454.4564	5	4737.6600	4737.6471	4737.3970
6	5230.2000	5230.0935	5186.8845	6	**5512.3100**	5512.3100	5512.0540
7	5947.2000	5947.0936	5896.7857	7	6261.3400	6261.3511	6261.0833
8	**6641.7000**	6641.7000	6584.3972	8	6985.1700	6985.1765	6984.9031
9	7314.2000	7314.1729	7249.8209	9	**7684.2000**	7684.2000	7683.9316
10	7964.7000	7964.7479	7893.0237	10	**8358.8500**	8358.8500	8358.5871
11	8593.6000	8593.6503	8513.8372	11	**9009.5600**	9009.5600	9009.2876
12	**9201.1000**	9201.1000	9111.9579	12	**9636.7300**	9636.7300	9636.4514
13	**9787.3000**	9787.3000	9686.9470	13		10240.6483	10240.4967
14	**10352.4000**	10352.4000	10238.2306	14		10821.3623	10821.8417
15		10896.4280	10765.0997	15		11378.4868	11380.9046
16		11419.1818	11266.7099	16		11910.9392	11918.1036
17		11920.0720	11742.0820	17		12416.5900	12433.8569
18		12397.9104	12190.1012	18		12891.8164	12928.5827
19		12850.6335	12609.5178	19		13330.9502	13402.6992
20		13274.9559	12998.9469	20		13725.6060	13856.6246
21		13665.9440	13356.8684	21		14063.8804	14290.7771
22		14016.5026	13681.6268	22		14329.4100	14705.5749
23		14316.7673	13971.4319	23		14500.2777	15101.4362
24		14553.3944	14224.3578	24		14547.7550	15478.7792
25		14708.7397	14438.3439	25			15838.0221
26		14759.9204	14611.1940	26			16179.5831
27			14740.5771	27			16503.8804
28			14824.0267	28			16811.3322
29			14858.9413	29			17102.3567
30				30			17377.3721
31				31			17636.7966
32				32			17881.0484
33				33			18110.5457
34				34			18325.7067
35				...			...
36				41			19465.5461
37				42			19581.0719
38				43			19686.0252
39				44			19780.8242
40				45			19865.8871
41				46			19941.6321
42				47			20008.4774
43				48			20066.8412
44				49			20117.1417
45				50			20159.7971
46				51			20195.2256
47				52			20223.8454
48				53			20246.0747
49				54			20262.3317
50				55			20273.0346
51				56			20278.6016
52				57			20279.4509
$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	565.1000	51.1807	34.9146	$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	627.1700	47.4773	0.8493
D_e^{cal}		14776.7826	14873.5493	D_e^{cal}		14560.9470	20279.5805
$D_e^{\exp t}$	14805.0001 [37]			$D_e^{\exp t}$	14580.0000 [38]		
$\Delta D_e\%$		0.1906	-0.4630	$\Delta D_e\%$		0.1307	-39.0918
E_{rror}		0.5513	-1.9633	E_{rror}		0.4013	-6710.9072

Table 4 (Continued)

	ICl-$A^3\Pi(1)$			ClF -$A(^3\Pi_1)$		
υ	$E_\upsilon^{\exp t}$[39]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[39]	$E_\upsilon^{\exp t}$[40]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[40]
0	**104.8300**	104.8300	104.9670	**178.6000**	178.6000	178.6356
1	**311.4800**	311.4800	311.6500	**523.3000**	523.3000	523.2656
2	**513.6700**	513.6700	513.8828	849.5000	849.3109	849.4657
3	711.2400	711.2061	711.5310	1155.6000	1155.3672	1155.5557
4	904.0500	903.9404	904.4650	1440.1000	1440.0080	1440.0957
5	1091.9200	1091.7468	1092.5600	**1701.9000**	1701.9000	1701.8857
6	1274.7000	1274.5019	1275.6960	**1940.0000**	1940.0000	1939.9657
7	1452.2100	1452.0713	1453.7578	**2153.6000**	2153.6000	2153.6157
8	**1624.3000**	1624.3000	1626.6350	2342.4000	2342.2929	2342.3557
9	1790.7800	1791.0077	1794.2220	**2505.9000**	2505.9000	2505.9457
10	1951.4800	1951.9872	1956.4180	**2644.4000**	2644.4000	2644.3857
11	2106.1800	2107.0061	2113.1270	**2757.9000**	2757.9000	2757.9158
12	2254.6600	2255.8118	2264.2578		2846.6883	2847.0158
13	2396.6800	2398.1380	2409.7240		2911.4096	2912.4058
14	2532.0800	2533.7138	2549.4440		2953.4018	2955.0458
15	2660.5900	2662.2739	2683.3410		2975.2364	2976.1358
16	2782.0100	2783.5701	2811.3430		2981.5000	2977.1158
17	2896.1200	2897.3822	2933.3828			
18	3002.6600	3003.5310	3049.3980			
19	3101.4700	3101.8887	3159.3311			
20	**3192.3900**	3192.3900	3263.1291			
21	3275.3200	3275.0413	3360.7441			
22	3350.2000	3349.9280	3452.1329			
23	**3417.2200**	3417.2200	3537.2571			
24	3476.6200	3477.1744	3616.0831			
25	3528.9000	3530.1349	3688.5821			
26	3574.6900	3576.5276	3754.7301			
27	3614.9300	3616.8532	3814.5079			
28	3649.7900	3651.6743	3867.9011			
29	3680.1200	3681.5979	3914.9001			
30	3706.5200	3707.2527	3955.5001			
31	**3729.2600**	3729.2600	3989.7011			
32	3748.7500	3748.1990	4017.5079			
33	3765.1600	3764.5649	4038.9301			
34	**3778.7200**	3778.7200	4053.9821			
35	3789.6300	3790.8368	4062.6831			
36		3800.8335	4065.0571			
37		3808.3007				
38		3812.4188				
$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	10.9100	4.1180	2.3740	113.5	6.2636	0.9800
D_e^{cal}		3814.6898	4065.7049		2983.2968	2977.1613
$D_e^{\exp t}$	3814.7000 [39]			2988.4000 [40]		
$\Delta D_e\%$		0.00025	-6.5799		0.1708	0.3760
E_{rror}		0.0025	-105.7305		0.8147	11.4679

Table 4 (Continued)

	CO-$X^1\Sigma^+$				HgI -$X^2\Sigma^+$		
υ	$E_\upsilon^{\exp t}$[41]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[41]	υ	$E_\upsilon^{\exp t}$[42]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[42]
0	1081.7710	1081.7713	1081.5750	0	**62.7200**	62.7200	62.7198
1	**3225.0422**	3225.0422	3224.7751	1	**186.2900**	186.2900	186.2940
2	**5341.8334**	5341.8334	5341.3751	2	**307.4200**	307.4200	307.4270
3	**7432.2104**	7432.2104	7431.3752	3	426.1400	426.1346	426.1454
4	9496.2408	9496.2407	9494.7752	4	542.4400	542.4312	542.4465
5	11533.9939	11533.9934	11531.5753	5	656.3000	656.2817	656.3010
6	13545.5404	13545.5396	13541.7753	6	767.6500	767.6352	767.6568
7	15530.9533	15530.9520	15525.3754	7	876.4300	876.4205	876.4423
8	17490.3067	17490.3051	17482.3754	8	982.5600	982.5495	982.5694
9	19423.6767	19423.6752	19412.7754	9	**1085.9200**	1085.9200	1085.9372
10	21331.1407	21331.1397	21316.5755	10	**1186.4200**	1186.4200	1186.4351
11	**23212.7777**	23212.7777	23193.7755	11	1283.9300	1283.9308	1283.9461
12	25068.6679	25068.6695	25044.3756	12	1378.3300	1378.3309	1378.3502
13	26898.8930	26898.8967	26868.3756	13	**1469.5000**	1469.5000	1469.5279
14	28703.5355	28703.5418	28665.7757	14	1557.3300	1557.3224	1557.3631
15	30482.6787	30482.6882	30436.5757	15	1641.7100	1641.6910	1641.7468
16	32236.4070	32236.4198	32180.7758	16	1722.5300	1722.5105	1722.5802
17	33964.8049	33964.8212	33898.3758	17	1799.7200	1799.7008	1799.7782
18	35667.9573	35667.9770	35589.3758	18	**1873.2000**	1873.2000	1873.2726
19	37345.9491	37345.9719	37253.7759	19	1942.9300	1942.9672	1943.0153
20	38998.8648	38998.8901	38891.5759	20	2008.8800	2008.9845	2008.9820
21	40626.7883	40626.8155	40502.7760	21	2071.0500	2071.2589	2071.1751
22	42229.8025	42229.8308	42087.3760	22	2129.4800	2129.8239	2129.6273
23	43807.9889	43808.0175	43645.3760	23	2184.2400	2184.7399	2184.4049
24	45361.4276	45361.4555	45176.7761	24	2235.4100	2236.0944	2235.6108
25	46890.1961	46890.2224	46681.5761	25	2283.1600	2284.0015	2283.3884
26	48394.3696	48394.3934	48159.7762	26	2327.6600	2328.6006	2327.9244
27	49874.0201	49874.0408	49611.3762	27	2369.1400	2370.0539	2369.4523
28	51329.2161	51329.2333	51036.3762	28	2407.9000	2408.5442	2408.2559
29	52760.0222	52760.0357	52434.7763	29	**2444.2700**	2444.2700	2444.6724
30	54166.4980	54166.5079	53806.5763	30	2478.6400	2477.4414	2479.0956
31	55548.6983	55548.7049	55151.7763	31		2508.2738	2511.9798
32	56906.6718	56906.6757	56470.3764	32		2536.9807	2543.8422
33	58240.4610	58240.4628	57762.3764	33		2563.7659	2575.2673
34	59550.1010	59550.1016	59027.7765	34		2588.8136	2606.9092
35	**60835.6192**	60835.6192	60266.5765	35		2612.2782	2639.4958
36	62097.0343	62097.0342	61478.7765	36		2634.2717	2673.8314
37	**63334.3553**	63334.3553	62664.3766	37		2654.8508	2710.8005
38	**64547.5809**	64547.5809	63823.3766	38		2674.0016	2751.3710
39	65736.6981	65736.6978	64955.7766	39		2691.6233	2796.5972
40	66901.6811	66901.6805	66061.5767	40		2707.5102	2847.6238
41	**68042.4899**	68042.4899	67140.7767	41		2721.3321	2905.6885
42		69159.0726	68193.3767	42		2732.6130	2972.1258
43		70251.3594	69219.3768	43		2740.7080	3048.3702
44		71319.2643	70218.7768	44		2744.7783	3135.9593
45		72362.6837	71191.5768	45			3236.5376
46		73381.4941	72137.7769	46			3351.8592
47		74375.5520	73057.3769	...			...
48		75344.6915	73950.3769	99			130870.5039
...		...	...	100			138746.5033
75		90599.2280	88006.5776	...			...
76		90659.1287	88154.7776	199			6348139.1947
77		90671.4085	88276.3776	200			6520603.4458
78			88371.3777	...			...
79			88439.7777	599			1942672955.45
80			88481.5777	600			1959262216.28
81			88496.7777	...			not converged
$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	1140.8088	12.2798	15.2000	$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	34.3700	4.0703	
D_e^{cal}		90673.9259	88502.3050	D_e^{cal}		2746.8250	
$D_e^{\exp t}$	90674.0000 [41]			$D_e^{\exp t}$	2750.0000 [42]		
$\Delta D_e\%$		0.00008172	2.3950	$\Delta D_e\%$		0.1155	
E_{rror}		0.0060	142.8744	E_{rror}		0.7800	

atoms with large electronegative difference usually have ionic bonds. In this situation, certain potential barriers may exist in the long-range asymptotic region, which will result in a maximum vibrational energy that would be greater than the molecular dissociation energy. This energy does not exceed the maximum value of the potential behavior. For those molecules having a potential barrier, the maximum vibrational energy criterion in Eq. (11) will become $E_{\upsilon_{\max}} < D_e^{\exp t} + E_{\rm bar}$, and the potential barrier $E_{\rm bar}$ is the difference between the maximum value of the potential barrier and the dissociation limit. For many stable heteronuclear systems which have no potential barriers, the AM method can be directly used to study full vibrational spectra and then the analytical expression in Eq. (22) can be used to calculate their dissociation energies.

In this section, the vibrational spectroscopic constants and full vibrational spectra are studied for 12 heteronuclear diatomic electronic states without having noticeable potential barriers: ^{6}LiH-$C^1\Sigma^+$, ^{6}LiD-$C^1\Sigma^+$, NaK-$X^1\Sigma^+$, NaRb-$a^3\Sigma^+$, NaLi-$B^1\Pi$, KRb-$2^1\Pi$, CsH-$X^1\Sigma^+$, RbH-$X^1\Sigma^+$, ICl-$A^3\Pi(1)$, ClF-$A(^3\Pi_1)$, CO-$X^1\Sigma^+$, and HgI-$X^2\Sigma^+$ states. Their dissociation energies D_e^{cal} are calculated using the analytical expression in Eq. (22). The AM vibrational spectroscopic constants and vibrational spectra of these electronic states are listed in Table 3 and Table 4, respectively.

It can be seen from Table 3 and Table 4 that, for the

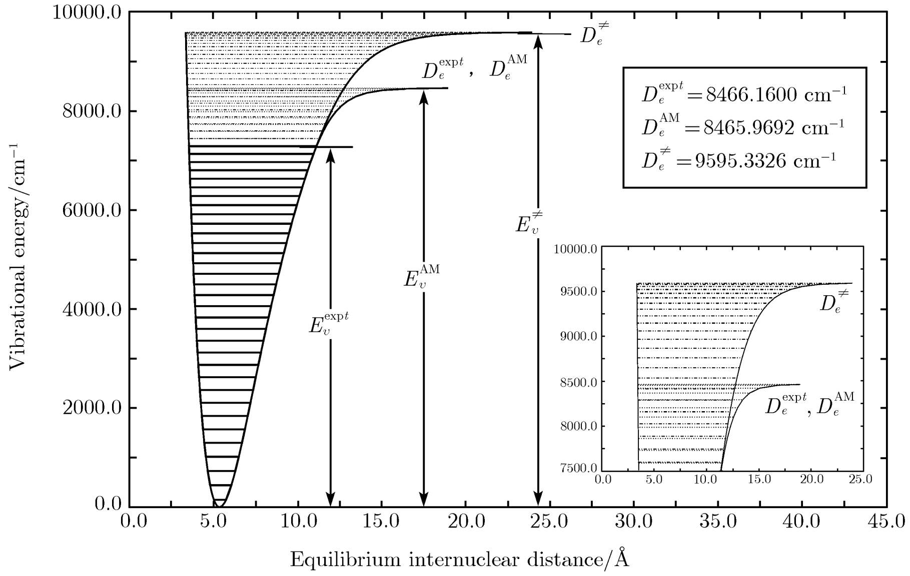

Fig. 4 RKR potentials, vibrational spectra $\{E_\upsilon^{\exp t}\}$, $\{E_\upsilon^{\rm AM}\}$ and $\{E_\upsilon^{\rm Theo} = E_\upsilon^{\neq}\}$ of ^{6}LiH-$C^1\Sigma^+$ state.

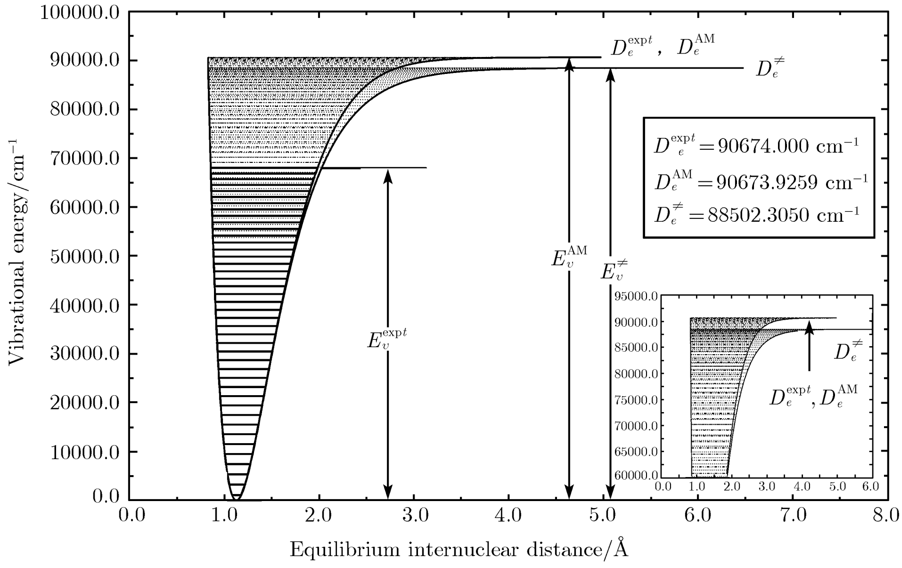

Fig. 5 RKR potentials, vibrational spectra $\{E_\upsilon^{\exp t}\}$, $\{E_\upsilon^{\rm AM}\}$ and $\{E_\upsilon^{\rm Theo} = E_\upsilon^{\neq}\}$ of CO-$X^1\Sigma^+$ state.

above heteronuclear diatomic electronic states, the qualities of the AM vibrational spectroscopic constants and vibrational spectra are the same as those of homonuclear molecules. The full AM vibrational spectra not only reproduce known experimental energies, but also correctly generate all unknown high-lying vibrational energies. The percent errors between D_e^{cal} and $D_e^{\exp t}$ are all less than 1 %. The greatest is 0.1906 % (CsH-$X^1\Sigma^+$ state), and the smallest is only 0.000 081 72 % (CO-$X^1\Sigma^+$ state).

Table 4 also lists the theoretical vibrational spectrum $\{E_\upsilon^{\rm Theo}\}$ calculated using vibrational spectroscopic constants from references. Most of these spectra do not correctly represent the vibrational information of high-lying vibrational states near molecular dissociation limit for corresponding electronic systems. In order to make a direct comparison, the AM vibrational spectra $\{E_\upsilon^{\rm AM}\}$, theoretical vibrational spectra $\{E_\upsilon^{\rm Theo}\}$ obtained using the literature spectroscopic constants of ^{6}LiH-$C^1\Sigma^+$ and CO-$X^1\Sigma^+$ states and their RKR potential curves are plotted in Fig. 4 and Fig. 5, respectively.

3.3 Application to diatomic molecular ions

The vibrational spectroscopic constants and full vibrational spectra of BeH$^+$-$X^1\Sigma^+$, CO$^+$-$X^2\Sigma^+$, O_2^+-$A^2\Pi_u$, F_2^+-$X^2\Pi_g$ and $\mathrm{Li}_2^+ - X^2\Sigma_g^+$ states are studied using the AM method. The results are listed in Table 5 and Table 6, respectively.

It is seen from Table 6 that, the AM vibrational spectra $\{E_\upsilon^{\rm AM}\}$ of the above electronic states of some diatomic molecular ions reproduce the known experimental energies or quantum theoretical vibrational energies (Li_2^+- $X^2\Sigma_g^+$ state) and correctly generate all high-lying vibrational energies which may be difficult to obtain experimentally or theoretically. All the AM vibrational spectra satisfy the physical criteria in Eqs. (7)−(13). Therefore the AM vibrational spectrum $\{E_\upsilon^{\rm AM}\}$ is the correct full vibrational spectra of a given diatomic ionic system. For example, for the O_2^+-$A^2\Pi_u$ electronic state, Coxon *et al.* [48] observed the second negative band system of the $A^2\Pi_u \rightarrow X^2\Pi_g$ transition of O_2^+ ion and 16 vibrational energies of the O_2^+-$A^2\Pi_u$ state are fitted based on the positions of spectroscopic lines in each spectrum band. Using this set of vibrational energies, 29 AM vibrational energies are obtained using the AM method. The maximum AM vibrational energy $E_{\upsilon_{\max}=28}^{\rm AM}$ is 14 168.285 0 cm^{-1} and the percent error of $E_{\upsilon_{\max}=28}^{\rm AM}$ from experimental dissociation energy $D_e^{\exp t}$(=14 195.352 0 cm^{-1}) is only 0.1907 %. Therefore, the AM spectroscopic constants and corresponding vibrational spectrum $\{E_\upsilon^{\rm AM}\}$ of this state can correctly represent the true vibrational information of this system. The relative percent error of the AM dissociation energy D_e^{cal}(=14 181.4705 cm^{-1}) from experimental dissociation energy $D_e^{\exp t}$ is 0.0978 % which is within the error between different experimental measurements.

Li_2^+ is one of the simplest diatomic molecular ions except for H_2^+. Although it has been the object of many experimental and theoretical studies, there has been no experimental report on the accurate vibrational energies of the Li_2^+-$X^2\Sigma_g^+$ state. Schmidt-Mink *et al.* [46] used self-consistent field configuration interaction (SCF-CI) with core polarization potentials (CPP), including closed-shell correlation effect, to obtain a theoretical subset $[E_\upsilon^{\rm Theo}]$ of the vibrational spectrum of this state. Since the kinetic energy of nuclear motion is large and the coupling interaction between electrons and nuclei is not negligible when Li_2^+ is in high-lying vibrational motion, there will be a notable error due to the breakdown of the Born-Oppenheimer approximation if the SCF-CPP is used to calculate high-lying vibrational energies. Therefore, Schmidt-Mink only obtained some energies of its vibrational spectrum $\{E_\upsilon\}$. The highest vibrational energy $E_{\upsilon_{\max}=57}^{\rm SCF\text{-}CPP}$ (=9929 cm^{-1}) is 535 cm^{-1} smaller than its experimental dissociation energy $D_e^{\exp t}$(=10 464 cm^{-1}) [44]. The 58 SCF-CPP theoretical energies of this state are used for the AM study, and the obtained AM vibrational spectrum reproduces those SCF-CPP vibrational energies and generates all high-lying vibrational energies which are not given by the SCF-CPP method. The maximum vibrational energy $E_{\upsilon_{\max}=72}^{\rm AM}$(=10 463.690 1 cm^{-1}) is only 0.3099 cm^{-1} smaller than the experimental dissociation energy $D_e^{\exp t}$.

For the BeH$^+$-$X^1\Sigma^+$ and CO$^+$-$X^2\Sigma^+$ states, the relative errors E_{rror} are 1.3516 and 1.0622, respectively. This is because their ($D_e^{\exp t}$-D_e^{cal}) and $\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$ have comparable values.

The vibrational spectra $\{E_\upsilon^{\rm Theo}\}$ obtained using the literature spectroscopic constants are also listed in Table 6. These spectra may not represent the correct high-lying vibrational information of a given ionic system. For example, for the F_2^+-$X^2\Pi_g$ state, the vibrational spectrum $\{E_\upsilon^{\rm Theo}\}$ using spectroscopic constants from Ref. [43] gives 61 energies and has many wrong energies since υ=36. The obtained theoretical energy D_e^{cal}(=33 088.547 1 cm^{-1}) is much greater than its experimental dissociation energy $D_e^{\exp t}$(=27 472.840 9 cm^{-1}), namely, Eq. (11) is not satisfied. This indicates that this set of spectroscopic constants have notable physical deficiencies. However, the AM dissociation energy $D_e^{\rm AM}$(=27 412.628 5 cm^{-1}) is only 60 cm^{-1} smaller than the $D_e^{\exp t}$. The AM spectrum $\{E_\upsilon^{\rm AM}\}$ and the $\{E_\upsilon^{\rm Theo}\}$ are plotted

Table 5 Vibrational spectroscopic constants of some diatomic ionic electronic states (units: cm^{-1}).

State		ω_0	ω_{e0}	ω_e'	$\omega_e x_e$	
F_2^+-$X^2\Pi_g$	AM	−0.218974	15.593967	1088.894017	8.891354	
	Ref. [43]			1088.90	8.96	
CO^+-$X^2\Sigma^+$	AM	0.060234	−0.121836	2214.118151	15.114133	
	Ref. [44]			2214.24	15.164	
Li_2^+-$X^2\Sigma_g^+$	AM	0.936431	−0.938684	262.821311	1.377690	
	Ref. [45]			263.76	1.646	
O_2^+-$A^2\Pi_u$	AM	0.177826	0.512358	898.762301	13.639999	
	Ref. [44]			898.25	13.573	
BeH^+-$X^1\Sigma^+$	AM	0.804125	−1.782949	2219.916980	39.604013	
	Ref. [44]			2221.7	39.79	

State		$10^2\omega_e y_e$	$10^3\omega_e z_e$	$10^4\omega_e t_e$	$10^5\omega_e s_e$	$10^{10}\omega_e r_e$
F_2^+-$X^2\Pi_g$	AM	−4.571418	8.383869	−6.530651	2.280705	−2890.627816
	Ref. [43]					
CO^+-$X^2\Sigma^+$	AM	−0.659281	0.343076	−0.321043	0.128108	−203.001423
	Ref. [44]					
Li_2^+-$X^2\Sigma_g^+$	AM	−2.185801	1.053078	−0.220786	0.020462	−7.223862
	Ref. [45]					
O_2^+-$A^2\Pi_u$	AM	0.966998	−3.359792	4.296727	−1.819780	2159.436628
	Ref. [44]					
BeH^+-$X^1\Sigma^+$	AM	−18.982085	1.619065	−4.065573	−1.081074	6889.329655
	Ref. [44]					

Note: for the AM values: $\omega_e' = \omega_e + \omega_{e0}$; for values from references: $\omega_e' = \omega_e$.

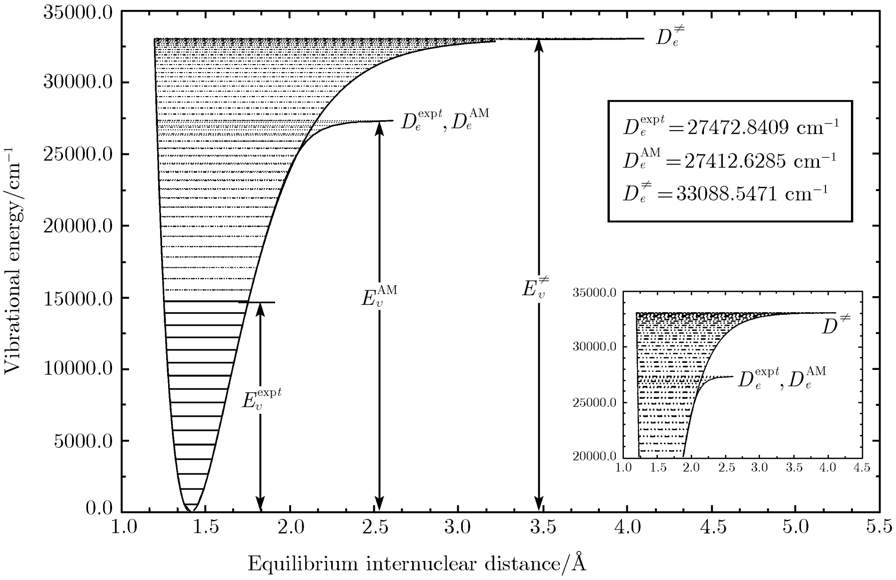

Fig. 6 RKR potentials, vibrational spectra $\{E_v^{\exp t}\}$, $\{E_v^{\mathrm{AM}}\}$ and $\{E_v^{\mathrm{Theo}} = E_v^{\neq}\}$ of F_2^+- $X^2\Pi_g$ state.

in Fig. 6 together with their RKR potential curves. It should be noted that there are only 16 experimental vibrational energies available for this state. If two or three more accurate energies are given experimentally, the accuracy of the full AM vibrational spectrum $\{E_v^{\mathrm{AM}}\}$ and the dissociation energy $D_e^{cal}(\mathrm{AM})$ would be better. A similar figure for CO-$X^2\Sigma^+$ state is shown in Fig. 7.

3.4 Influence of experimental energy subsets $[E_v]$ on the AM vibrational energy spectra

From the AM process of obtaining molecular full vibrational spectra, it can be seen that when constructing algebraic equation $A{\cdot}X = E$ using the known experimental energies, different input energies E have different influences on the obtained vibrational spectrum. That is to say, the correctness and accuracy of the AM vibrational spectrum are determined by those of the chosen experimental energies and the vibrational information thereof. On one hand, if there are many accurate experimental energies which contain enough vibrational information, the extracted vibrational spectroscopic constants using the AM method will be accurate, and so is the AM spectrum $\{E_v^{\mathrm{AM}}\}$. On the other hand, low-lying vibrational

Table 6 Vibrational energies of some diatomic ionic electronic states (energy units: cm^{-1}).

F_2^+-$X^2\Pi_g$				CO^+-$X^2\Sigma^+$			
υ	$E_\upsilon^{\exp t}$[43]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[43]	υ	$E_\upsilon^{\exp t}$[45]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[44]
0	**542.000**	542.0000	542.2100	0	**1103.340**	1103.340	1103.3290
1	**1613.000**	1613.0000	1613.1900	1	**3287.210**	3287.2100	3287.2410
2	**2666.000**	2666.0000	2666.2501	2	5440.800	5440.8000	5440.8250
3	3702.000	3700.9863	3701.3901	3	**7564.080**	7564.0800	7564.0810
4	**4718.000**	4718.0000	4718.6101	4	9657.020	9657.0215	9657.0090
5	5717.000	5717.1014	5717.9101	5	11719.590	11719.5957	11719.6090
6	6699.000	6698.3450	6699.2902	6	13751.770	13751.7725	13751.8810
7	7662.000	7661.7649	7662.7502	7	**15753.520**	15753.5200	15753.8250
8	8608.000	8607.3683	8608.2902	8	17724.800	17724.8045	17725.4409
9	9535.000	9535.1364	9535.9102	9	19665.590	19665.5903	19666.7289
10	10445.000	10445.0300	10445.6103	10	**21575.840**	21575.8400	21577.6889
11	**11337.000**	11337.0000	11337.3903	11	23455.510	23455.5149	23458.3209
12	**12211.000**	12211.0000	12211.2503	12	25304.580	25304.5752	25308.6249
13	**13067.000**	13067.0000	13067.1903	13	**27122.980**	27122.9800	27128.6009
14	**13905.000**	13905.0000	13905.2103	14	28910.690	28910.6871	28918.2490
15	14725.000	14725.0417	14725.3104	15	30667.650	30667.6526	30677.5690
16		15527.2168	15527.4904	16	**32393.830**	32393.8300	32406.5610
17		16311.6710	16311.7504	17	34089.160	34089.1683	34105.2250
18		17078.6014	17078.0904	18	**35753.610**	35753.6100	35773.5610
19		17828.2465	17826.5105	19		37387.0883	37411.5690
20		18560.8671	18557.0105	20		38989.5230	39019.2490
21		19276.7168	19269.5905	21		40560.8157	40596.6010
22		19976.0000	19964.2505	22		42100.8439	42143.6250
23		20658.8173	20640.9906	23		43609.4543	43660.3210
24		21325.0952	21299.8106	24		45086.4538	45146.6890
25		21974.5000	21940.7106	25		46531.6004	46602.7290
26		22606.3333	22563.6906	26		47944.5917	48028.4411
27		23219.4091	23168.7506	27		49325.0520	49423.8251
28		23811.9091	23755.8907	28		50672.5182	50788.8811
29		24381.2168	24325.1107	29		51986.4231	52123.6091
30		24923.7273	24876.4107	30		53266.0777	53428.0091
31		25434.6322	25409.7907	31		54510.6506	54702.0811
32		25907.6783	25925.2508	32		55719.1461	55945.8252
33		26334.8974	26422.7908	33		56890.3795	57159.2412
34		26706.3077	26902.4108	34		58022.9507	58342.3292
35		27009.5833	27364.1108	35		59115.2147	59495.0892
36		27229.6923	27807.8908	36		60165.2501	60617.5212
37		27348.5000	28233.7509	37		61170.8249	61709.6253
38			28641.6909	38		62129.3594	62771.4013
39			29031.7109	39		63037.8865	63802.8493
40			29403.8109	40		63893.0090	64803.9693
41			29757.9909	41		64690.8540	65774.7614
42			30094.2510	42		65427.0238	66715.2254
43			30412.5910	43		66096.5442	67625.3614
44			30713.0110	44		66693.8086	68505.1694
45			30995.5110	45		67212.5199	69354.6495
46			31260.0911	46		67645.6276	70173.8015
47			31506.7511	47		67985.2622	70962.6255
…			…	48		68222.6652	71721.1216
54			32731.6112	49		68348.1158	72449.2896
55			32834.9112	50		68350.8533	73147.1296
56			32920.2913	51			73814.6417
57			32987.7513	…			…
58			33037.2913	71			80796.0026
59			33068.9113	72			80826.6266
60			33082.6113	73			80826.9227
$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	820.000	118.8077	13.7000	$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	1664.45	2.7375	0.2961
D_e^{cal}		27412.6285	33088.5471	D_e^{cal}		68350.9131	80826.9256
$D_e^{\exp t}$	27472.8409 [43]			$D_e^{\exp t}$	68353.821 [44]		
$\Delta D_e\%$		0.2192	−20.4409	$\Delta D_e\%$		0.004254	−18.2479
E_{rror}		0.5068	−409.9056	E_{rror}		1.0622	−42124.6359

Note: $E_\upsilon^{\exp t}$ is experimental energy; E_υ^{AM} is the AM vibrational energy; $E_\upsilon^{\mathrm{Theo}}$ is vibrational energy calculated using spectroscopic constants from corresponding references; $\Delta E_{\upsilon_{\max},\upsilon_{\max}-1} = E_{\upsilon_{\max}} - E_{\upsilon_{\max}-1}$; $D_e^{\exp t}$ is experimental dissociation energy; D_e^{cal} is theoretical dissociation energy calculated using Eq. (22); $\Delta D_e\% = 100 \times (D_e^{\exp t} - D_e^{cal})/D_e^{\exp t}$; $E_{rror} = \Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$.

Table 6 (Continued)

Li_2^+-$X^2\Sigma_g^+$							
υ	$E_\upsilon^{\text{SCF-CPP}}$[46]	E_υ^{AM}	E_υ^{Theo}[46]	υ	$E_\upsilon^{\text{SCF-CPP}}$[46]	E_υ^{AM}	E_υ^{Theo}[46]
0	**132.00**	132.0000	131.4685	41	8270.00	8270.9799	8111.2169
1	**392.00**	392.0000	391.9365	42	8403.00	8403.6667	8236.7129
2	649.00	649.0767	649.1125	43	8532.00	8532.7726	8358.9169
3	903.00	903.1440	902.9965	44	8658.00	8658.2372	8477.8289
4	1154.00	1154.1351	1153.5885	45	**8780.00**	8780.0000	8593.4489
5	**1402.00**	1402.0000	1400.8886	46	**8898.00**	8898.0000	8705.7769
6	1646.00	1646.7036	1644.8966	47	9013.00	9012.1764	8814.8129
7	1887.00	1888.2234	1885.6126	48	9124.00	9122.4686	8920.5569
8	2125.00	2126.5483	2123.0366	49	9231.00	9228.8167	9023.0089
9	2360.00	2361.6763	2357.1686	50	9333.00	9331.1617	9122.1689
10	2592.00	2593.6130	2588.0086	51	9432.00	9429.4454	9218.0369
11	2820.00	2822.3705	2815.5566	52	9526.00	9523.6109	9310.6129
12	3046.00	3047.9656	3039.8126	53	9615.00	9613.6026	9399.8969
13	3268.00	3270.4189	3260.7766	54	9701.00	9699.3663	9485.8890
14	3488.00	3489.7534	3478.4486	55	9782.00	9780.8492	9568.5890
15	3704.00	3705.9935	3692.8286	56	**9858.00**	9858.0000	9647.9970
16	3918.00	3919.1642	3903.9167	57	9929.00	9930.7688	9724.1130
17	4128.00	4129.2903	4111.7127	58		9999.1068	9796.9370
18	4335.00	4336.3951	4316.2167	59		10062.9665	9866.4690
19	4540.00	4540.5006	4517.4287	60		10122.3013	9932.7090
20	4741.00	4741.6261	4715.3487	61		10177.0649	9995.6570
21	4939.00	4939.7881	4909.9767	62		10227.2116	10055.3130
22	**5135.00**	5135.0000	5101.3127	63		10272.6953	10111.6770
23	5327.00	5327.2713	5289.3567	64		10313.4690	10164.7490
24	5517.00	5516.6076	5474.1087	65		10349.4847	10214.5290
25	5703.00	5703.0105	5655.5687	66		10380.6921	10261.0170
26	5887.00	5886.4771	5833.7367	67		10407.0384	10304.2130
27	**6067.00**	6067.0000	6008.6127	68		10428.4670	10344.1170
28	6245.00	6244.5675	6180.1968	69		10444.9167	10380.7290
29	6419.00	6419.1633	6348.4888	70		10456.3209	10414.0491
30	6591.00	6590.7667	6513.4888	71		10462.6059	10444.0771
31	6759.00	6759.3526	6675.1968	72		10463.6901	10470.8131
32	6925.00	6924.8917	6833.6128	73			10494.2571
33	7087.00	7087.3506	6988.7368	74			10514.4091
34	7246.00	7246.6922	7140.5688	75			10531.2691
35	7402.00	7402.8756	7289.1088	76			10544.8371
36	7555.00	7555.8566	7434.3568	77			10555.1131
37	7704.00	7705.5880	7576.3128	78			10562.0971
38	7851.00	7852.0196	7714.9768	79			10565.7891
40	8134.00	8134.7713	7982.4289	80			10566.1891
$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$				$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	71.00	1.0842	0.4000
D_e^{cal}				D_e^{cal}		10463.8771	10566.2324
$D_e^{\exp t}$				$D_e^{\exp t}$	10464 [47]		
$\Delta D_e\%$				$\Delta D_e\%$		0.0012	−0.9770
E_{rror}				E_{rror}		0.1132	−255.5780

Note: $E_\upsilon^{\text{SCF-CPP}}$ is the theoretical vibrational energy from Ref. [46].

Table 6 (Continued)

	O_2^+-$A^2\Pi_u$				BeH^+-$X^1\Sigma^+$		
υ	$E_\upsilon^{\exp t}$[48]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[44]	υ	$E_\upsilon^{\exp t}$[50]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[44]
0	**446.150**	446.1500	445.7318	0	**1100.8380**	1100.8380	1100.9025
1	**1317.650**	1317.6500	1316.8358	1	**3240.9350**	3240.9350	3243.0224
2	2161.870	2161.8911	2160.7938	2	**5300.1270**	5300.1270	5305.5624
3	**2978.860**	2978.8600	2977.6058	3	**7277.2400**	7277.2400	7288.5223
4	3768.510	3768.5516	3767.2718	4	9171.0020	9171.0018	9191.9023
5	4530.980	4530.9867	4529.7918	5	**10979.9860**	10979.9860	11015.7022
6	**5266.220**	5266.2200	5265.1658	6	**12702.5610**	12702.5610	12759.9221
7	**5974.340**	5974.3400	5973.3938	7	**14336.8460**	14336.8460	14424.5621
8	6655.300	6655.4617	6654.4758	8	15880.6810	15880.6789	16009.6220
9	7309.910	7309.7133	7308.4118	9	**17331.5990**	17331.5990	17515.1020
10	7937.520	7937.2181	7935.2018	10	18686.8070	18686.8473	18941.0019
11	8538.630	8538.0726	8534.8458	11		19943.3896	20287.3218
12	9112.470	9112.3211	9107.3438	12		21097.9637	21554.0617
13	**9659.930**	9659.9300	9652.6958	13		22147.1562	22741.2217
14	**10180.760**	10180.7600	10170.9018	14		23087.5107	23848.8016
15	**10674.540**	10674.5400	10661.9618	15		23915.6720	24876.8015
16		11140.8419	11125.8758	16		24628.5697	25825.2214
17		11579.0584	11562.6438	17		25223.6434	26694.0614
18		11988.3843	11972.2658	18		25699.1153	27483.3213
19		12367.8029	12354.7418	19		26054.3107	28193.0012
20		12716.0785	12710.0718	20		26290.0329	28823.1011
21		13031.7552	13038.2558	21		26408.9940	29373.6210
22		13313.1646	13339.2938	22		26416.3052	29844.5609
23		13558.4426	13613.1858	23			30235.9208
24		13765.5558	13859.9318	24			30547.7008
25		13932.3404	14079.5318	25			30779.9007
26		14056.5525	14271.9858	26			30932.5206
27		14135.9327	14437.2938	27			31005.5605
28		14168.2850	14575.4558	28			
29			14686.4718	29			
30			14770.3418	30			
31			14827.0658	31			
32			14856.6438	32			
33			14859.0758	33			
34				34			
35				35			
36				36			
37				37			
$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	493.780	32.3523	2.4320	$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	1355.208	7.3112	73.0399
D_e^{cal}		14181.4705	14859.2758	D_e^{cal}		26416.7546	31040.5155
$D_e^{\exp t}$	14195.3520 [49]			$D_e^{\exp t}$	26426.6367 [44]		
$\Delta D_e\%$		0.0978	−4.6770	$\Delta D_e\%$		0.03739	−17.4616
E_{rror}		0.4291	−272.9950	E_{rror}		1.3516	−63.1693

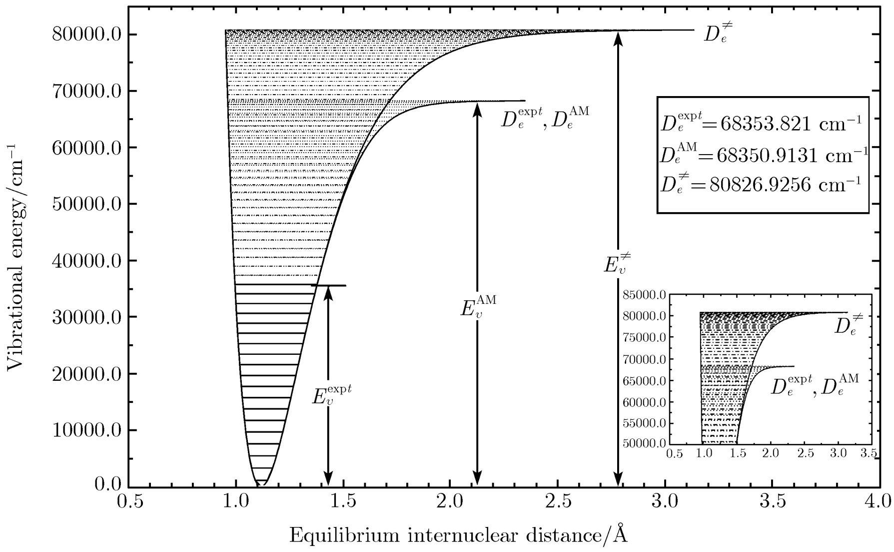

Fig. 7 RKR potentials, vibrational spectra $\{E_v^{\exp t}\}$, $\{E_v^{\mathrm{AM}}\}$ and $\{E_v^{\mathrm{Theo}} = E_v^{\neq}\}$ of CO$^+$- $X^2\Sigma^+$ state.

Table 7 Influence on vibrational spectroscopic constants of different energy subsets (different M) of NaRb-$a^3\Sigma^+$ state (units: cm^{-1}).

	ω_0	ω_{e0}	ω'^{*}_e	$\omega_e x_e$
Ref. [33]$^{\#}$	−0.02		18.85934	0.408976
$M =$ 11	−0.020255	−0.000693	18.858652	0.408476
12	−0.020307	−0.000506	18.858839	0.408690
13	−0.020220	−0.000799	18.858546	0.408394
14	−0.020312	−0.000488	18.858857	0.408711
15	−0.020178	−0.000916	18.858429	0.408327
16	−0.020516	0.000175	18.859521	0.409327
17	−0.020187	−0.000919	18.858426	0.408258
18	−0.020088	−0.001270	18.858075	0.407865

	$10^2\omega_e y_e$	$10^3\omega_e z_e$	$10^4\omega_e t_e$	$10^5\omega_e s_e$	$10^{10}\omega_e r_e$
Ref. [33]$^{\#}$	−0.83564	0.21918			
$M =$ 11	−0.855061	0.266152	−0.059251	0.038194	−99.206349
12	−0.844043	0.237377	−0.019625	0.010762	−24.050024
13	−0.856464	0.261081	−0.041633	0.020260	−38.580247
14	−0.842963	0.234558	−0.015741	0.008074	−16.684704
15	−0.856615	0.258124	−0.036778	0.017358	−32.577376
16	−0.820002	0.193587	0.021206	−0.008015	10.104350
17	−0.863150	0.276517	−0.058076	0.028218	−52.771303
18	−0.882283	0.320799	−0.106381	0.052329	−97.176108

* Note: M is the number of experimental vibrational energies in an energy subset $[E_v^{\exp t}]$.
For the AM values: $\omega'_e = \omega_e + \omega_{e0}$; for values from references: $\omega'_e = \omega_e$.

$^{\#}$ The spectroscopic constants in this reference are fitted using experimental energies.

energies usually contain more low-lying vibrational information and high-lying vibrational energies contain more high-lying vibrational information. If the excited vibrational states are not high enough, the high-lying vibrational information embedded in the input energies is limited. Therefore, the vibrational spectroscopic constants obtained using these energies may not well represent the true high-lying physical pictures and although the obtained full vibrational spectrum can assure the accuracy of low-lying vibrational energies, it may not give accurate high-lying vibrational energies. The more the number of correct high-lying experimental energies are used, the more accurate the high-lying AM vibrational energies will be. Therefore, we should choose 8 energies which contain more high-lying ones and best satisfy Eqs. (7)−(13) from all known energies.

As an example, the influence of different input energy combinations on AM vibrational spectroscopic constants

Table 8 Comparisons among the experimental and the AM vibrational energies from different experimental energy subsets (different M) for the NaRb -$a^3\Sigma^+$ state (energy units: cm^{-1}).

υ	Ref. [34]	M=18	M=17	M=16	M=15	M=14	M=13	M=12	M=11
0	9.3059	**9.3059**	**9.3059**	**9.3059**	**9.3059**	**9.3059**	**9.3059**	**9.3059**	**9.3059**
1	27.3211	**27.3211**	**27.3211**	**27.3211**	**27.3211**	**27.3211**	**27.3211**	**27.3211**	**27.3211**
2	44.4497	**44.4497**	**44.4497**	44.4496	44.4498	**44.4497**	44.4497	**44.4497**	**44.4497**
3	60.6520	**60.6520**	**60.6520**	**60.6520**	60.6521	60.6521	**60.6520**	60.6521	60.6521
4	75.8939	**75.8939**	75.8938	**75.8939**	75.8939	75.8939	75.8937	75.8939	75.8939
5	90.1461	90.1465	**90.1461**	90.1462	**90.1461**	**90.1461**	90.1459	**90.1461**	**90.1461**
6	103.3850	103.3860	103.3852	**103.3850**	103.3849	103.3849	103.3848	103.3849	103.3849
7	115.5918	115.5937	115.5924	**115.5918**	**115.5918**	**115.5918**	115.5917	**115.5918**	**115.5918**
8	126.7534	126.7558	126.7542	126.7534	126.7534	**126.7534**	**126.7534**	**126.7534**	**126.7534**
9	136.8617	136.8639	136.8626	**136.8617**	**136.8617**	136.8617	**136.8617**	136.8617	**136.8617**
10	145.9138	145.9152	145.9146	145.9141	**145.9138**	**145.9138**	**145.9138**	**145.9138**	**145.9138**
11	153.9122	**153.9122**	153.9127	153.9132	**153.9122**	153.9123	**153.9122**	**153.9122**	153.9117
12	160.8647	160.8632	160.8648	160.8664	160.8646	**160.8647**	**160.8647**	160.8644	160.8617
13	166.7841	166.7818	**166.7841**	166.7864	**166.7841**	166.7840	166.7843	166.7831	166.7738
14	171.6889	171.6870	**171.6889**	171.6908	171.6886	171.6880	171.6892	171.6856	171.6608
15	175.6023	**175.6023**	**175.6023**	**175.6023**	175.6011	175.5996	175.6022	175.5939	175.5365
16	178.5532	178.5551	178.5518	178.5481	178.5490	178.5463	178.5506	178.5345	178.4145
17	180.5756	**180.5756**	180.5684	180.5606	180.5640	180.5600	180.5660	180.5373	180.3055
18		181.6950	181.6863	181.6766	181.6814	181.6770	181.6827	181.6358	181.2148
19		181.9440	181.9411	181.9382	181.9393	181.9370	181.9380	181.8658	
$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	2.0224	0.2489	0.2548	0.2615	0.2579	0.2600	0.2553	0.2300	0.9093
D_e^{cal}		181.9993	181.9991	181.9994	181.9989	181.9975	181.9964	181.9140	181.6520
$D_e^{\exp t}$	182.0000 [32]								
$\Delta D_e\%$		3.5908E-04%	4.7177E-04%	2.8781E-04%	6.1455E-04%	1.3481E-03%	2.0015E-03%	4.7265E-02%	1.9117E-01%
E_{rror}		0.0026	0.0034	0.0020	0.0044	0.0095	0.0143	0.3740	0.3826

Note: Bold-faced values in each M are the 8 energies chosen in the AM method; $\Delta E_{\upsilon_{\max},\upsilon_{\max}-1} = E_{\upsilon_{\max}} - E_{\upsilon_{\max}-1}$; $D_e^{\exp t}$ is experimental dissociation energy; D_e^{cal} is the calculated theoretical dissociation energy using Eq. (22); $\Delta D_e\% = 100 \times (D_e^{\exp t} - D_e^{cal})/D_e^{\exp t}$; $E_{rror} = (D_e^{\exp t} - D_e^{cal})/\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$.

Table 9 Vibrational energies of three diatomic electronic states whose vibrational spectra are not well converged due to the missing of accurate high-lying experimental energies (energy units: cm^{-1}).

	NaK-3$^1\Pi$				NaK-5$^1\Sigma^+$		
υ	$E_\upsilon^{\exp t}$[51]	E_υ^{AM}	E_υ^{Theo}[51]]	υ	$E_\upsilon^{\exp t}$[52]	E_υ^{AM}	E_υ^{Theo}[52]
0	**23.7279**	23.7279	23.7279	0	**56.5000**	56.5000	57.1331
1	**70.9059**	70.9059	70.9059	1	167.0590	167.0572	167.6929
2	117.6743	117.6743	117.6743	2	273.2840	273.2831	273.9182
3	**163.9858**	163.9858	163.9858	3	**375.7870**	375.7870	376.4216
4	209.7933	209.7933	209.7933	4	**475.0600**	475.0600	475.6949
5	255.0495	255.0495	255.0495	5	571.4870	571.4872	572.1228
6	299.7072	299.7072	299.7072	6	**665.3600**	665.3600	665.9965
7	343.7191	343.7191	343.7191	7	**756.8900**	756.8900	757.5274
8	**387.0381**	387.0381	387.0381	8	846.2220	846.2223	846.8612
9	**429.6169**	429.6169	429.6169	9	**933.4500**	933.4500	934.0909
10	471.4083	471.4083	471.4083	10	1018.6290	1018.6277	1019.2712
11	512.3652	512.3651	512.3652	11	1101.7870	1101.7857	1102.4316
12	552.4402	552.4401	552.4402	12	**1182.9430**	1182.9430	1183.5904
13	591.5861	591.5860	591.5861	13	1262.1180	1262.1198	1262.7684
14	629.7558	629.7557	629.7558	14	**1339.3490**	1339.3490	1340.0025
15	666.9020	666.9019	666.9020	15	1414.7030	1414.6866	1415.3596
16	702.9774	702.9774	702.9774	16		1488.2204	1488.9497
17	737.9350	737.9350	737.9350	17		1560.0772	1560.9405
18	**771.7274**	771.7274	771.7274	18		1630.4281	1631.5702
19	804.3074	804.3074	804.3074	19		1699.4913	1701.1619
20	835.6278	835.6278	835.6278	20		1767.5332	1770.1369
21	**865.6414**	865.6414	865.6414	. . .		. . .	. . .
22	**894.3010**	894.3010	894.3010	28		2318.4395	2393.5686
23		921.5595	921.5594	29		2393.6958	2498.9468
24		947.3699	947.3693	30		2471.1802	2616.3397
25		971.6852	971.6834	31		2550.8050	2748.1536
26		994.4585	994.4547	32		2632.2646	2897.0572
27		1015.6434	1015.6359	33		2714.9833	3065.9959
28		1035.1933	1035.1796	34		2798.0576	3258.2047
29		1053.0620	1053.0389	35		2880.1923	3477.2225
30		1069.2036	1069.1663	36		2959.6303	3726.9056
31		1083.5727	1083.5147	37		3034.0768	4011.4414
32		1096.1242	1096.0369	38		3100.6153	4335.3618
33		1106.8135	1106.6857	39		3155.6183	4703.5575
34		1115.5967	1115.4137	40		3194.6497	5121.2913
35		1122.4304	1122.1739	41		3212.3607	5594.2116
36		1127.2722	1126.9190	42			6128.3666
37		1130.0805	1129.6017	43			6730.2177
38		1130.8147	1130.1749	. . .			. . .
39				99			610709.0999
40				100			645961.4687
41				. . .			. . .
42				299			226798311.67
43				300			230760828.62
44				. . .			. . .
45				499			3163962159.16
46				500			3196500859.62
47				. . .			. . .
48							Not converged
$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	28.6596	0.7342	0.5732	$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$	75.3540	17.7110	
D_e^{cal}		1131.0066	1130.2974	D_e^{cal}		3220.3973	
$D_e^{\exp t}$	1290.90 [51]			$D_e^{\exp t}$	3277.90 [52]		
$\Delta D_e\%$		12.3861	12.4411	$\Delta D_e\%$		1.7543	
E_{rror}		217.7790	280.1893	E_{rror}		3.2467	

Note: $E_\upsilon^{\exp t}$ is experimental energies; E_υ^{AM} is the AM vibrational energies; E_υ^{Theo} is vibrational energies calculated using spectroscopic constants from corresponding references; $\Delta E_{\upsilon_{\max},\upsilon_{\max}-1} = E_{\upsilon_{\max}} - E_{\upsilon_{\max}-1}$; $D_e^{\exp t}$ is experimental dissociation energy; D_e^{cal} is theoretical dissociation energy calculated using Eq. (22); $\Delta D_e\% = 100 \times (D_e^{\exp t} - D_e^{cal})/D_e^{\exp t}$; $E_{rror} = (D_e^{\exp t} - D_e^{cal})/\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$.

Table 9 (Continued)

Rb_2-$1^1\Pi_g$				Rb_2-$1^1\Pi_g$			
υ	$E_\upsilon^{\exp t}$[53]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[53]	υ	$E_\upsilon^{\exp t}$[53]	E_υ^{AM}	$E_\upsilon^{\mathrm{Theo}}$[53]
0	**11.1130**	11.1130	11.1134	62	937.1750	937.1767	798.2343
1	33.1130	33.1109	33.1114	63	945.9380	945.9408	801.3223
2	54.8170	54.8144	54.8044	64	954.5350	954.5377	804.1053
3	76.2320	76.2293	76.1924	65	962.9660	962.9691	806.5833
4	97.3640	97.3609	97.2754	66	971.2340	971.2367	808.7563
5	118.2170	118.2145	118.0534	67	979.3400	979.3424	810.6243
6	138.7970	138.7952	138.5264	68	**987.2880**	987.2880	812.1873
7	159.1090	159.1075	158.6944	69		995.0752	813.4453
8	**179.1560**	179.1560	178.5574	70		1002.7060	814.3983
9	**198.9450**	198.9450	198.1154	71		1010.1822	815.0463
10	218.4770	218.4785	217.3684	72		1017.5057	815.3893
11	237.7590	237.7605	236.3164	73		1024.6784	815.4273
12	256.7920	256.7944	254.9594	74		1031.7022	
13	275.5810	275.5839	273.2974	75		1038.5790	
14	294.1290	294.1321	291.3304	76		1045.3105	
15	312.4390	312.4422	309.0584	77		1051.8988	
16	330.5140	330.5171	326.4814	78		1058.3456	
17	348.3560	348.3595	343.5994	79		1064.6526	
18	365.9690	365.9720	360.4124	80		1070.8217	
19	383.3540	383.3572	376.9204	81		1076.8545	
20	400.5150	400.5173	393.1234	82		1082.7526	
21	417.4520	417.4545	409.0214	83		1088.5177	
22	434.1690	434.1708	424.6144	84		1094.1510	
23	450.6670	450.6683	439.9024	85		1099.6541	
24	466.9740	466.9487	454.8854	86		1105.0282	
25	483.0130	483.0138	469.5634	87		1110.2744	
26	498.8650	498.8652	483.9364	88		1115.3937	
27	514.5040	514.5045	498.0044	89		1120.3870	
28	**529.9330**	529.9330	511.7674	90		1125.2550	
29	545.1520	545.1522	525.2254	91		1129.9982	
30	560.1640	560.1635	538.3784	92		1134.6170	
31	574.9680	574.9680	551.2264	93		1139.1114	
32	589.5670	589.5670	563.7694	94		1143.4814	
33	603.9620	603.9616	576.0074	95		1147.7267	
34	618.1530	618.1529	587.9404	96		1151.8466	
35	632.1420	632.1420	599.5684	97		1155.8404	
36	**645.9300**	645.9300	610.8914	98		1159.7067	
37	659.5180	659.5178	621.9094	99		1163.4442	
38	672.9060	672.9065	632.6224	100		1167.0511	
39	686.0970	686.0969	643.0303	101		1170.5252	
40	699.0900	699.0902	653.1333	102		1173.8638	
41	711.8870	711.8872	662.9313	103		1177.0643	
42	724.4890	724.4890	672.4243	104		1180.1230	
43	736.8960	736.8965	681.6123	105		1183.0363	
44	749.1100	749.1106	690.4953	106		1185.7998	
45	761.1320	761.1325	699.0733	107		1188.4089	
46	**772.9630**	772.9630	707.3463	108		1190.8582	
47	784.6030	784.6033	715.3143	109		1193.1418	
48	796.0550	796.0543	722.9773	110		1195.2534	
49	807.3180	807.3173	730.3353	111		1197.1859	
50	818.3940	818.3932	737.3883	112		1198.9318	
51	829.2840	829.2834	744.1363	113		1200.4827	
52	839.9900	839.9888	750.5793	114		1201.8296	
53	850.5120	850.5108	756.7173	115		1202.9628	
54	860.8510	860.8506	762.5503	116		1203.8719	
55	871.0100	871.0096	768.0783	117		1204.5456	
56	880.9900	880.9891	773.3013	118		1204.9718	
57	890.7910	890.7904	778.2193	119		1205.1377	
58	**900.4150**	900.4150	782.8323				
59	909.8640	909.8644	787.1403				
60	919.1390	919.1401	791.1433				
61	928.2420	928.2436	794.8413				
$\Delta E_{\upsilon_{\max},\upsilon_{\max-1}}$					7.9480	0.1659	0.0380
D_e^{cal}						1205.2023	815.4315
$D_e^{\exp t}$					1290.0000 [53]		
$\Delta D_e\%$						6.5735	36.7882
E_{rror}						511.1374	12488.9782

Table 10 Vibrational spectroscopic constants of three diatomic electronic states whose vibrational spectra are not well converged due to the missing accurate high-lying experimental energies (units: cm^{-1}).

State		ω_0	ω_{e0}	ω_e'	$\omega_e x_e$	
NaK-$3^1\Pi$	AM	0.000029	0.000053	47.542428	0.169446	
	Ref. [51]			47.5424	0.1694	
NaK-$5^1\Sigma^+$	AM	−0.628082	−0.014322	115.589770	2.738628	
	Ref. [52]			115.604	2.7484	
Rb$_2$-$1^1\Pi_g$	AM	0.001780	−0.004964	22.298048	0.151736	
	Ref. [53]			22.303	0.1525	

State		$10^2\omega_e y_e$	$10^3\omega_e z_e$	$10^4\omega_e t_e$	$10^5\omega_e s_e$	$10^{10}\omega_e r_e$
NaK-$3^1\Pi$	AM	−0.785374	−0.002396	0.001707	−0.000582	0.762866
	Ref. [51]	−0.787				
NaK-$5^1\Sigma^+$	AM	14.577973	−5.923787	0.638908	0.242531	−470.287722
	Ref. [52]	14.892	−6.4596	1.1411		
Rb$_2$-$1^1\Pi_g$	AM	0.104470	−0.011588	0.000583	0.000014	−0.015201
	Ref. [53]					

Note: for the AM values: $\omega_e' = \omega_e + \omega_{e0}$; for values from references: $\omega_e' = \omega_e$.

and vibrational spectra of NaRb-$a^3\Sigma^+$ state is given in Table 7 and Table 8, respectively. M represents the number of experimental energies listed in the 2nd column used in the energy subset $[E_\upsilon]_M$ in Table 8. One chooses 8 experimental energies which best satisfy the physical requirements in Eq. (7)−Eq. (13) from each energy subset (each M) and obtains the best AM vibrational spectrum for the corresponding subset using the AM method. For instance, the first 15 experimental energies in the 2nd column are included in the subset of M=15. In the 6th column of M=15, all AM vibrational energies are listed and the 8 energies used in the AM study are printed in bold face. One can see from Table 8 that except for M=16, as M is increasing (as more experimental energies are included in a subset), the values of $E_{\upsilon_{\max}}(M)$ and D_e^{cal} (M) are increasing and the values of the percent errors ΔD_e %(M) and the relative errors E_{error} (M) are decreasing. Therefore, the accuracy of the AM spectrum $\{E_\upsilon^{\mathrm{AM}}\}$ gets better as M increasing. For M=18, the last AM energy difference $\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$ is 0.2489 cm^{-1} and the difference between the maximum AM vibrational energy $E_{\upsilon_{\max}=19}$(=181.9440 cm^{-1}) and $D_e^{\exp t}$(=182.00 cm^{-1}) is only 0.056 cm^{-1}. Thus, the corresponding AM spectrum $\{E_\upsilon^{\mathrm{AM}}\}$ obtained from M=18 can be taken as the correct full vibrational spectrum for this state.

It should be noted that since the accuracy of the AM vibrational spectrum is uniquely determined by the accuracy of experimental energies, if the accuracies of the known experimental energies are not enough or if the given energies do not contain enough correct vibrational information, then the obtained AM vibrational spectrum would be less accurate or may even be wrong. For example, for the NaK-$3^1\Pi$ state in Table 9, Laub *et al.* [51] obtained 23 vibrational energies using optical-optical double resonance spectroscopy (OODR). The highest vibrational energy $E_{\upsilon_{\max}=22}^{\exp t}$(=894.3010 cm^{-1}) is 396.599 cm^{-1} smaller than the experimental dissociation energy $D_e^{\exp t}$(=1290.90 cm^{-1}). When this set of experimental energies is used on the AM study, one obtains 39 vibrational energies of which the maximum vibrational energy $E_{\upsilon_{\max}=38}$(=1130.8147 cm^{-1}) is still 160 cm^{-1} smaller than the $D_e^{\exp t}$. Therefore, this spectrum is not the best representation of the true vibrational spectrum of this state. If the experimental energies are more accurate or there are more high-lying experimental vibrational energies available, the quality of the obtained full AM vibrational spectrum would be much better. The AM vibrational spectra of the NaK-$5^1\Sigma^+$ and Rb$_2$-$1^1\Pi_g$ states are also listed in Table 9, which have similar results as those of NaK-$3^1\Pi$ state. The vibrational spectroscopic constants of these electronic states are listed in Table 10.

4 Summary

An algebraic method (AM) used to study the full vibrational energy spectra of diatomic systems proposed by Weiguo Sun *et al.* and an analytical formula used to calculate accurate molecular dissociation energies are described. At present, accurate vibrational energies near molecular dissociation limits for many diatomic electronic states may not be available experimentally or theoretically. The AM method and the new formula for dissociation energy are applied to study the vibrational spectroscopic constants, the full AM vibrational spectra and the molecular dissociation energies of some electronic states of some homonuclear and heteronuclear diatomic molecules and diatomic ions. Studies show that:

(1) For many diatomic molecular or ionic electronic states, although there are many results on their vibrational energies, the data of high-lying vibrational energies near dissociation limits are still sorely lacking. The AM method generates accurate vibrational spectroscopic constants and full vibrational spectrum for a diatomic electronic state by using some accurate experimental energies and a set of physical requirements satisfied by correct vibrational energies. The AM vibrational spectrum not only reproduces the known experimental energies, but also obtains all high-lying vibrational energies near dissociation limits which may be difficult to obtain experimentally.

(2) For some diatomic molecular or ionic electronic states, it may be difficult to obtain their accurate molecular (or ionic) dissociation energies using modern quantum methods and it is costly to obtain them experimentally. However, the parameter-free analytical expression we proposed recently is only the function of the three highest vibrational energies near the dissociation limit. Therefore, if we use the three accurate highest vibrational energies, the analytical formula will generate accurate molecular dissociation energies. The AM dissociation energies D_e^{AM} are in excellent agreement with the experimental dissociation energies $D_e^{\exp t}$ and the percent error of D_e^{AM} from $D_e^{\exp t}$ is only several thousandths or even several ten millionths.

In summary, the AM method, together with the analytical formula for dissociation energy, supplies a reliable and economical physical method to study the full vibrational spectrum and the molecular dissociation energy of a stable diatomic molecular and ionic system theoretically. This method is particularly useful for those diatomic systems whose high-lying vibrational energies may not be available experimentally. The parameter-free analytical formula also provides an effective physical tool to check the quality of any (experimental or theoretical) full vibrational spectrum.

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