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Accurate studies of dissociation energies and vibrational energies on alkali metals*

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This paper studies full vibrational spectra $\{E_v\}$ and molecular dissociation energies D_e by using conventional least-squares (LS) fitting and an algebraic method (AM) proposed recently for 10 diatomic electronic states of $^7Li_2$, Na_2, NaK and NaLi molecules based on some known experimental vibrational energies in a subset $[E_v^{expt}]$ respectively. Studies show that: (1) although both the full AM spectrum $\{E_v^{AM}\}$ and the LS spectrum $\{E_v^{LS}\}$ can reproduce the known experimental energies in $[E_v^{expt}]$, the $\{E_v^{AM}\}$ is superior to the $\{E_v^{LS}\}$ in that the high-lying AM vibrational energies which may not be available experimentally have better or much better accuracy than those LS counterparts in $\{E_v^{LS}\}$, and so is the AM dissociation energy D_e^{AM}; (2) the main source of the errors in the data obtained by using the LS fitting is that the fitting which is just a pure mathematical process does not use any physical criteria that must be satisfied by the full vibrational spectrum, while the AM method does. This study suggests that when fitting or solving a physical equation using a set of source data, it is important not only to apply a proper mathematical tool, but also to use correct physical criteria which measure the physical properties of the data, kick out those data having bigger errors, and impose conditional convergence on the numerical process.

Keywords: least-squares method, algebraic method, vibrational energy, dissociation energy

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1. Introduction

In many experimental and/or theoretical physical studies, numerical fitting has been extensively used to fit some limited physical data to a physical law or a theoretical formula or an experience model which is an analytical representation of the physical nature embedded in these source data. For example, although molecular vibrational spectra $\{E_v\}$ of diatomic molecular systems are important physical quantities in many physical studies such as molecular structure, collision physics, plasma physics, low temperature physics, and astrophysics etc.,[1−6] most experimental studies can only obtain an energy subset $[E_v]$ of the full vibrational spectra $\{E_v\}$ of a diatomic system because of the limitations in experimental technologies and/or experimental conditions.[7] Similarly most quantum mechanical studies on vibrational spectrum for many molecular electronic systems don't give reliable high-lying vibrational energies near molecular dissociation limit because of the errors introduced in the one-electron model and the Born-Oppenheimer approximation[8]. To obtain those high-lying vibrational energies and/or an analytical numerical representation of known vibrational energies of an electronic system, people used to apply a mathematical fitting procedure such as least-squares (LS) fitting on a set of known energies to a physical law in Eq.(1). The fitted LS energies E_v^{LS} can usually reproduce the known input energies E_v^i, however, the high-lying E_v^{LS} have some errors or even wrong values, and the $E_{v_{max}}^{LS}$ may converge to a wrong dissociation limit for many diatomic electronic states as shown later.

Sun and co-workers proposed an algebraic method (AM)[9−11] to obtain correct full vibrational spectrum $\{E_v\}$ for a diatomic molecular electronic system recently. The AM uses standard algebraic method and a set of physical criteria which must be satisfied by vibrational spectrum based on a known accurate experimental or theoretical vibrational energy subset $[E_v]$. This study uses the AM and the LS fitting procedure on some diatomic molecular electronic states, finds the main source of the differences between the full vibrational spectra $\{E_v^{AM}\}$ and $\{E_v^{LS}\}$, and suggests that when fitting or solving a physical equation using a set

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of physical source data to extract accurate physical information, it is not only necessary to choose a proper mathematical tool, but also is important to use correct physical criteria as a judgement to select the best result out of all possible numerical solutions.

Section 2 briefly introduces the AM method,[9−11] Section 3 studies the full vibrational spectra $\{E_\upsilon\}$ and molecular dissociation energies $D_{\rm e}$ for 10 electronic states of diatomic molecules $^7Li_2$, Na_2, NaK and NaLi, and Section 4 summarizes this study.

2. Algebraic method for accurate vibrational energy spectrum

The non-relativistic analytical expression of the vibrational energy of nuclear motion for a stable diatomic molecular electronic state is obtained by Sun *et al* using second order perturbation theory as[9]

$$\begin{aligned} E_\upsilon =&\omega_0+(\omega_{\rm e0}+\omega_{\rm e})\left(\upsilon+\frac{1}{2}\right)-\omega_{\rm e}x_{\rm e}\left(\upsilon+\frac{1}{2}\right)^2\\ &+\omega_{\rm e}y_{\rm e}\left(\upsilon+\frac{1}{2}\right)^3+\omega_{\rm e}z_{\rm e}\left(\upsilon+\frac{1}{2}\right)^4\\ &+\omega_{\rm e}t_{\rm e}\left(\upsilon+\frac{1}{2}\right)^5+\omega_{\rm e}s_{\rm e}\left(\upsilon+\frac{1}{2}\right)^6\\ &+\omega_{\rm e}r_{\rm e}\left(\upsilon+\frac{1}{2}\right)^7+\cdots, \end{aligned} \tag{1}$$

where ω_0 and $\omega_{\rm e0}$ are new terms in comparison with Herzberg's energy expression.[12] ω_0 is the vibrational constant for the zeroth order of $\left(\upsilon+\frac{1}{2}\right)$, $\omega_{\rm e0}$ is the correction term to the harmonic vibrational constant $\omega_{\rm e}$ for the first order of $\left(\upsilon+\frac{1}{2}\right)$. Although both ω_0 and $\omega_{\rm e0}$ are small quantities, they are not negligible in calculating excited rovibrational energies. The algebraic method (AM) is started by rewriting the correct vibrational energy expression in Eq.(1) into a matrix form

$$AX=E, \tag{2}$$

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

$$X=\begin{pmatrix}\omega_0\\ \omega'_{\rm e}\\ -\omega_{\rm e}x_{\rm e}\\ \vdots\\ \omega_{\rm e}r_{\rm e}\end{pmatrix},$$

$$E=\begin{pmatrix}E_\upsilon\\ E_{\upsilon+i}\\ E_{\upsilon+j}\\ \vdots\\ E_{\upsilon+s}\end{pmatrix},\quad \upsilon=0,1,2,\ldots, \tag{3}$$

and the matrix element of the 8×8 coefficient matrix A is $A_{\upsilon k}=\left(\upsilon+\frac{1}{2}\right)^k$, $k=0,1,2,\ldots,7$. In Eq.(3), $\omega'_{\rm e}=\omega_{\rm e}+\omega_{\rm e0}$.

The accurate experimental vibrational energies satisfying the physical law expressed in Eq.(1) contain almost all important physical vibrational information and all important quantum effects such as the electron–electron correlation, spin–orbit coupling, electron–nuclei coupling, nuclei–nuclei coupling, electromagnetic effect, and relativistic effect etc. For many diatomic molecular electronic systems, an energy subset $[E_\upsilon]$ of the full vibrational energy spectrum $\{E_\upsilon\}$ can be obtained experimentally. One may choose 8 of the m known energies in the subset $[E_\upsilon]$ at a time to solve Eq.(2) using standard AM. There are $N=C_m^8$ groups of energies. The N sets of vibrational constants $[X]$ can be generated by solving Eq.(2) N times. An accurate solution X which best satisfies the following physical requirements may always be found from the N sets of constants:

$$\frac{{\rm d}E_\upsilon}{{\rm d}\upsilon}\,|_{\upsilon=\upsilon_{\max}}=0, \tag{4}$$

$$\overline{\Delta E(e,c)}=\sqrt{\frac{1}{m}\sum_{\upsilon=0}^{m-1}|E_{\upsilon,\rm exp}-E_{\upsilon,\rm cal}|^2}\to 0, \tag{5}$$

$$\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}=E_{\upsilon_{\max}}-E_{\upsilon_{\max}-1}\to\text{small enough}, \tag{6}$$

$$D_{\rm e}^{\rm expt}-E_{\upsilon_{\max}}\to\text{small enough}, \tag{7}$$

$$E_{\upsilon_{\max}}<D_{\rm e}^{\rm expt}, \tag{8}$$

$$D_{\rm e}^{\rm cal}\cong E_{\upsilon_{\max}}+\frac{\Delta E^2_{\upsilon_{\max},\upsilon_{\max}-1}}{\Delta E_{\upsilon_{\max},\upsilon_{\max}-2}-\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}}, \tag{9}$$

$$0<E_{\rm rror}=\frac{D_{\rm e}^{\rm expt}-D_{\rm e}^{\rm cal}}{\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}}\lesssim 1. \tag{10}$$

The so determined vibrational constants X should be one of the best physical representations of the true vibrational information for a specified molecular system, and the resulting full vibrational energy spectrum $\{E_\upsilon^{\rm AM}\}$ is the best energy representation. The AM stated above solves Eq.(2) without using any mathematical approximation, any physical model and any test trial functions.

Equation (9) is a new analytical expression suggested recently by Sun and coworkers to evaluate accurate molecular dissociation energy D_e^{cal}, and is derived based on LeRoy and Bernstein's energy expression.[2] Equation (9) shows that, for a stable diatomic electronic state, if three accurate highest vibrational energies $E_{v_{max}}$, $E_{v_{max}-1}$, $E_{v_{max}-2}$ are known, then accurate molecular dissociation energy of this state can be obtained. However, if the three highest vibrational energies have certain errors or are incorrect, the dissociation energy obtained using Eq.(9) would have notable error or be wrong. Therefore, Eq.(9) may work as a good physical criterion to judge the quality and the convergence of the full vibrational spectrum $\{E_v\}$ and the corresponding spectroscopic constants.

3. Application and discussion

The LS fitting method and the AM method are used to study the vibrational spectroscopic constants respectively for 10 diatomic molecular electronic states of $^7Li_2$, Na_2, NaK and NaLi molecules: the $3^3\Sigma_g^+$, $1^1\Pi_g$, $2^3\Pi_g$ states of $^7Li_2$, the $b^3\Pi_u$ and $2^3\Pi_g$ states of Na_2, the $c^3\Sigma^+$, $B^1\Pi$ and $d^3\Pi$ states of NaK, and the $X^1\Sigma^+$ and $A^1\Sigma^+$ states of NaLi. The full AM vibrational spectra $\{E_v^{AM}\}$ and the full LS spectra $\{E_v^{LS}\}$ are then evaluated using Eq.(1). Theoretical dissociation energies of the above states are also calculated using Eq.(9). The vibrational spectroscopic constants of these states evaluated using these two methods are given in Table 1, together with those from references. In Table 1, AM corresponds to the 8 vibrational spectroscopic constants generated using the AM method, LS(1) are the m spectroscopic constants obtained using the LS fitting and all known vibrational energies in order to reproduce those counterparts given in references which are also obtained using the LS method,[13−15] and LS(2) are the 8 spectroscopic constants obtained using the LS fitting and all known vibrational energies.

The LS(1) vibrational spectroscopic constants of the $b^3\Pi_u$ and $2^3\Pi_g$ states of Na_2, and the $d^3\Pi$ state of NaK in Table 1 excellently agree with the literature data which are also obtained using the LS method respectively. The LS(1) energies $\{E_v^{LS(1)}\}$ generated using LS(1) constants agree very well with the literature energies $\{E_v^{ref}\}$ obtained using the vibrational constants of each reference for these three states in Table 2, and so do the LS(2) energies $\{E_v^{LS(2)}\}$. The lower ones of these calculated energies $\{E_v^{LS(1)}\}$, $\{E_v^{LS(2)}\}$ and $\{E_v^{ref}\}$ have good agreement with known experimental energies in the subset $[E_v^{expt}]$. However, the high-lying vibrational energies of the spectra $\{E_v^{LS(1)}\}$, $\{E_v^{LS(2)}\}$ and $\{E_v^{ref}\}$ of the $b^3\Pi_u$ and $2^3\Pi_g$ states of Na_2 do not converge to correct dissociation energies respectively. The calculated LS spectra of the $b^3\Pi_u$ state have 15 energies less than the AM spectrum $\{E_v^{AM}\}$, and the LS spectra of the $2^3\Pi_g$ state have

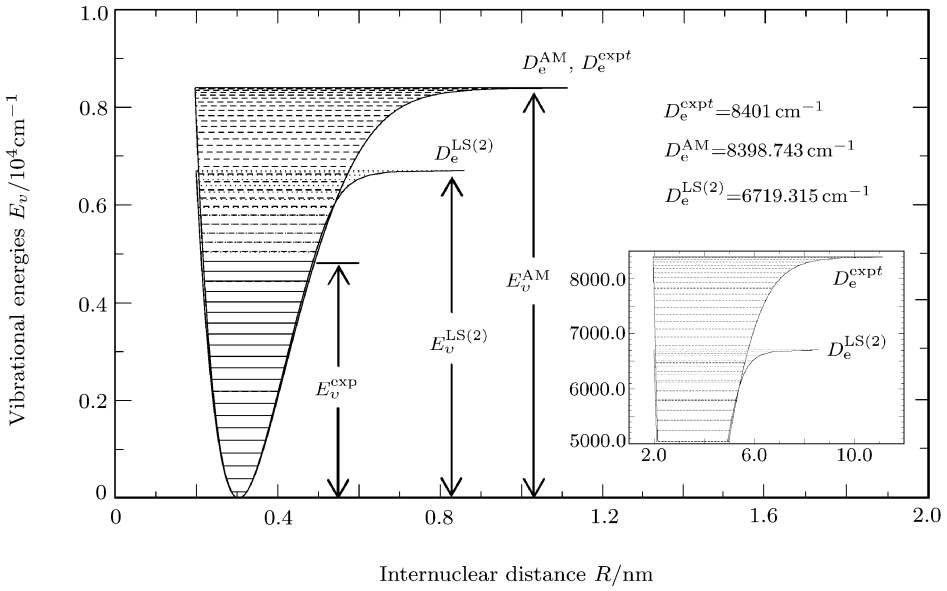


Fig.1. RKR potential, vibrational energies $[E_v^{expt}]$, $\{E_v^{LS(2)}\}$, $\{E_v^{AM}\}$ for the $3^3\Sigma_g^+$ state of $^7Li_2$ molecule.

Table 1

Table 1. (Continued)

Table 2. Vibrational energies* and dissociation energies of some diatomic molecular electronic states of $^7Li_2$, Na_2, NaK and NaLi molecules (energies are in cm^{-1}).

	$Na_2 - b^3\Pi_u$					$Na_2 - 2^3\Pi_g$				
υ	$E_\upsilon^{expt[13]}$	$E_\upsilon^{ref[13]}$	$E_\upsilon^{LS(1)}$	$E_\upsilon^{LS(2)}$	E_υ^{AM}	$E_\upsilon^{expt[14]}$	$E_\upsilon^{ref[14]}$	$E_\upsilon^{LS(1)}$	$E_\upsilon^{LS(2)}$	E_υ^{AM}
0	76.979	76.979	76.979	76.979	76.979	47.029	47.081	47.029	47.029	47.029
1	230.233	230.234	230.233	230.233	230.233	140.632	140.685	140.632	140.632	140.632
2	382.534	382.535	382.534	382.534	382.533	233.499	233.554	233.500	233.500	233.499
3	533.879	533.881	533.879	533.879	533.878	325.643	325.699	325.643	325.643	325.642
4	684.269	684.271	684.269	684.269	684.269	417.072	417.130	417.072	417.072	417.070
5	833.703	833.705	833.703	833.703	833.703	507.798	507.857	507.798	507.798	507.796
6	982.180	982.183	982.180	982.180	982.180	597.829	597.890	597.829	597.829	597.829
7	1129.700	1129.702	1129.700	1129.700	1129.700	687.176	687.238	687.176	687.176	687.178
8	1276.260	1276.263	1276.260	1276.260	1276.261	775.848	775.912	775.848	775.848	775.854
9	1421.861	1421.865	1421.861	1421.861	1421.862	863.854	863.919	863.854	863.854	863.863
10	1566.501	1566.505	1566.501	1566.501	1566.502	951.202	951.269	951.202	951.202	951.216
11	1710.179	1710.182	1710.179	1710.179	1710.179	1037.900	1037.970	1037.900	1037.900	1037.920
12	1852.892	1852.895	1852.892	1852.892	1852.892	1123.956	1124.028	1123.956	1123.956	1123.983
13	1994.639	1994.642	1994.639	1994.639	1994.639	1209.378	1209.453	1209.378	1209.378	1209.411
14	2135.418	2135.421	2135.418	2135.418	2135.418	1294.174	1294.252	1294.174	1294.174	1294.213
15	2275.227	2275.230	2275.227	2275.227	2275.226	1378.349	1378.430	1378.349	1378.349	1378.395
16	2414.062	2414.065	2414.062	2414.063	2414.062	1461.911	1461.996	1461.911	1461.911	1461.964
17	2551.922	2551.925	2551.922	2551.922	2551.921	1544.866	1544.955	1544.866	1544.866	1544.925
18	2688.803	2688.805	2688.803	2688.803	2688.802	1627.220	1627.313	1627.220	1627.220	1627.284
19	2824.701	2824.703	2824.701	2824.701	2824.700	1708.978	1709.076	1708.978	1708.978	1709.047
20	2959.612	2959.614	2959.613	2959.613	2959.612	1790.147	1790.249	1790.147	1790.147	1790.219
21	3093.534	3093.535	3093.534	3093.534	3093.534	1870.730	1870.838	1870.730	1870.730	1870.805
22	3226.460	3226.461	3226.460	3226.460	3226.460	1950.732	1950.847	1950.732	1950.732	1950.809
23	3358.386	3358.386	3358.386	3358.386	3358.387	2030.159	2030.280	2030.159	2030.159	2030.237
24	3489.307	3489.307	3489.307	3489.307	3489.308	2109.013	2109.142	2109.013	2109.013	2109.091
25	3619.216	3619.216	3619.217	3619.216	3619.218	2187.299	2187.436	2187.300	2187.299	2187.376
26	3748.109	3748.109	3748.109	3748.109	3748.111	2265.021	2265.165	2265.021	2265.021	2265.095
27	3875.978	3875.978	3875.978	3875.978	3875.980	2342.180	2342.333	2342.180	2342.180	2342.251
28	4002.816	4002.816	4002.816	4002.816	4002.818	2418.780	2418.943	2418.780	2418.780	2418.847
29	4128.616	4128.615	4128.616	4128.616	4128.617	2494.823	2494.997	2494.823	2494.823	2494.886
30	4253.369	4253.369	4253.369	4253.369	4253.369	2570.312	2570.497	2570.312	2570.312	2570.370
31	4377.068	4377.067	4377.068	4377.068	4377.065	2645.247	2645.445	2645.248	2645.248	2645.300
32	4499.702	4499.702	4499.702	4499.702	4499.696	2719.632	2719.842	2719.632	2719.632	2719.679
33	4621.263	4621.262	4621.263	4621.263	4621.251	2793.466	2793.690	2793.466	2793.466	2793.507
34	4741.739	4741.739	4741.739	4741.739	4741.722	2866.750	2866.989	2866.751	2866.751	2866.786
35	4861.121	4861.122	4861.121	4861.121	4861.095	2939.486	2939.740	2939.486	2939.486	2939.516
36	4979.397	4979.398	4979.397	4979.397	4979.361	3011.673	3011.943	3011.673	3011.673	3011.697
37	5096.554	5096.557	5096.554	5096.554	5096.507	3083.311	3083.599	3083.311	3083.311	3083.330
38	5212.581	5212.584	5212.581	5212.581	5212.519	3154.399	3154.706	3154.399	3154.399	3154.414
39	5327.463	5327.468	5327.463	5327.463	5327.385	3224.937	3225.263	3224.937	3224.937	3224.948
40	5441.187	5441.194	5441.187	5441.187	5441.091	3294.924	3295.271	3294.924	3294.924	3294.931
41	5553.739	5553.747	5553.739	5553.739	5553.621	3364.358	3364.727	3364.358	3364.358	3364.362
42	5665.102	5665.111	5665.102	5665.102	5664.962	3433.237	3433.629	3433.237	3433.237	3433.239
43	5775.260	5775.272	5775.260	5775.260	5775.096	3501.560	3501.976	3501.560	3501.560	3501.560
44	5884.198	5884.212	5884.198	5884.198	5884.008	3569.323	3569.766	3569.323	3569.323	3569.323
45	5991.897	5991.914	5991.897	5991.897	5991.680	3636.525	3636.995	3636.525	3636.525	3636.524
46	6098.338	6098.358	6098.338	6098.338	6098.096	3703.162	3703.660	3703.162	3703.162	3703.161
47	6203.503	6203.527	6203.503	6203.503	6203.236	3769.231	3769.758	3769.231	3769.231	3769.230
48	6307.372	6307.399	6307.372	6307.372	6307.083	3834.727	3835.286	3834.727	3834.727	3834.727
49	6409.924	6409.955	6409.924	6409.924	6409.616	3899.648	3900.240	3899.648	3899.648	3899.648
50	6511.137	6511.172	6511.137	6511.137	6510.817	3963.989	3964.615	3963.989	3963.989	3963.989
51	6610.988	6611.028	6610.989	6610.988	6610.664	4027.744	4028.406	4027.744	4027.744	4027.745
52	6709.455	6709.500	6709.456	6709.456	6709.138	4090.910	4091.609	4090.910	4090.910	4090.910
53	6806.514	6806.564	6806.514	6806.514	6806.216		4154.219	4153.480	4153.481	4153.480
54	6902.138	6902.194	6902.138	6902.138	6901.878		4216.229	4215.449	4215.450	4215.448
55	6996.302	6996.364	6996.302	6996.302	6996.101		4277.635	4276.812	4276.813	4276.809
56	7088.979	7089.047	7088.979	7088.979	7088.862		4338.429	4337.561	4337.563	4337.557
57	7180.140	7180.216	7180.140	7180.140	7180.140		4398.605	4397.691	4397.694	4397.684
58		7269.841	7269.758	7269.758	7269.911		4458.156	4457.194	4457.198	4457.185
59		7357.892	7357.801	7357.801	7358.151		4517.076	4516.063	4516.069	4516.052
60		7444.339	7444.239	7444.239	7444.838		4575.356	4574.291	4574.298	4574.278

* E_υ^{expt}: experimental energies. E_υ^{ref}: vibrational energies calculated using the spectroscopic constants from each corresponding reference. $E_\upsilon^{LS(1)}$: vibrational energies calculated using the LS(1) spectroscopic constants. $E_\upsilon^{LS(2)}$: vibrational energies calculated using the LS(2) spectroscopic constants. E_υ^{AM}: vibrational energies calculated using the AM spectroscopic constants.

Table 2. (*Continued*).

	$Na_2 - b^3\Pi_u$					$Na_2 - 2^3\Pi_g$				
υ	$E_\upsilon^{expt[13]}$	$E_\upsilon^{ref[13]}$	$E_\upsilon^{LS(1)}$	$E_\upsilon^{LS(2)}$	E_υ^{AM}	$E_\upsilon^{expt[14]}$	$E_\upsilon^{ref[14]}$	$E_\upsilon^{LS(1)}$	$E_\upsilon^{LS(2)}$	E_υ^{AM}
61		7529.148	7529.040	7529.040	7529.947		4632.988	4631.870	4631.879	4631.857
62		7612.289	7612.171	7612.171	7613.456		4689.966	4688.791	4688.803	4688.780
63		7693.725	7693.597	7693.597	7695.339		4746.279	4745.045	4745.061	4745.041
64		7773.422	7773.284	7773.284	7775.574		4801.920	4800.625	4800.645	4800.631
65		7851.344	7851.195	7851.195	7854.137		4856.879	4855.521	4855.546	4855.544
66		7927.453	7927.293	7927.293	7931.003		4911.147	4909.723	4909.754	4909.771
67		8001.711	8001.538	8001.539	8006.151		4964.713	4963.222	4963.260	4963.305
68		8074.078	8073.893	8073.893	8079.557		5017.569	5016.007	5016.053	5016.138
69		8144.513	8144.315	8144.315	8151.198		5069.703	5068.069	5068.124	5068.263
70		8212.974	8212.762	8212.762	8221.052		5121.105	5119.395	5119.462	5119.673
71		8279.418	8279.192	8279.192	8289.097		5171.763	5169.976	5170.056	5170.361
72		8343.800	8343.560	8343.559	8355.312		5221.667	5219.799	5219.894	5220.320
73		8406.076	8405.820	8405.819	8419.678		5270.804	5268.853	5268.966	5269.544
74		8466.197	8465.926	8465.924	8482.173		5319.163	5317.126	5317.259	5318.026
75		8524.116	8523.828	8523.826	8542.781		5366.731	5364.606	5364.762	5365.760
76		8579.782	8579.478	8579.475	8601.482		5413.496	5411.279	5411.461	5412.742
77		8633.147	8632.825	8632.820	8658.261		5459.445	5457.133	5457.345	5458.967
78		8684.156	8683.816	8683.810	8713.103		5504.563	5502.154	5502.400	5504.431
79		8732.758	8732.399	8732.392	8765.993		5548.839	5546.329	5546.613	5549.131
80		8778.896	8778.518	8778.509	8816.919		5592.257	5589.643	5589.970	5593.063
81		8822.515	8822.117	8822.106	8865.870		5634.804	5632.083	5632.458	5636.226
82		8863.557	8863.139	8863.125	8912.838		5676.464	5673.634	5674.063	5678.620
83		8901.964	8901.525	8901.508	8957.815		5717.224	5714.280	5714.769	5720.244
84		8937.675	8937.214	8937.194	9000.796		5757.067	5754.007	5754.563	5761.100
85		8970.628	8970.145	8970.120	9041.778		5795.979	5792.798	5793.429	5801.190
86		9000.759	9000.254	9000.224	9080.761		5833.943	5830.638	5831.353	5840.519
87		9028.005	9027.477	9027.441	9117.746		5870.942	5867.511	5868.318	5879.090
88		9052.298	9051.747	9051.705	9152.738		5906.962	5903.400	5904.309	5916.912
89		9073.572	9072.996	9072.947	9185.745		5941.984	5938.288	5939.309	5953.991
90		9091.756	9091.156	9091.099	9216.777		5975.992	5972.158	5973.304	5990.339
91		9106.781	9106.155	9106.089	9245.847		6008.968	6004.992	6006.274	6025.966
92		9118.573	9117.922	9117.844	9272.973		6040.894	6036.773	6038.205	6060.887
93		9127.059	9126.382	9126.292	9298.175		6071.753	6067.482	6069.079	6095.118
94		9132.163	9131.459	9131.356	9321.477		6101.525	6097.101	6098.879	6128.676
95		9133.808	9133.077	9132.959	9342.907		6130.192	6125.610	6127.586	6161.582
96					9362.499		6157.735	6152.992	6155.183	6193.858
97					9380.288		6184.135	6179.225	6181.652	6225.531
98					9396.317		6209.371	6204.291	6206.975	6256.628
99					9410.631		6233.424	6228.170	6231.132	6287.180
100					9423.282		6256.273	6250.840	6254.106	6317.222
101					9434.326		6277.898	6272.282	6275.877	6346.792
102					9443.826		6298.277	6292.473	6296.426	6375.929
103					9451.850		6317.389	6311.393	6315.733	
104					9458.472		6335.213	6329.020	6333.778	
105					9463.772		6351.727	6345.332	6350.542	
106					9467.837		6366.908	6360.306	6366.004	
107					9470.762		6380.733	6373.920	6380.145	
108					9472.647		6393.181	6386.151	6392.942	
109					9473.600		6404.226	6396.975	6404.377	
110					9473.739		6413.847	6406.369	6414.427	
111							6422.018	6414.309	6423.072	
112							6428.716	6420.770	6430.290	
113							6433.916	6425.728	6436.059	
114							6437.593	6429.157	6440.358	
115							6439.722	6431.033	6443.166	
116							6440.278	6431.330	6444.459	
$\Delta E_{\upsilon_{max},\upsilon_{max}-1}$	91.161	1.645	1.618	1.603	0.139	63.166	0.556	0.297	1.293	29.137
D_e^{cal}		9134.3377	9133.593	9133.466	<u>9473.759</u>		6440.423	6431.377	6445.055	<u>6404.641</u>
D_e^{expt}	9475.3[12]					6406.2[21]				
E_{rror}		270.272	211.191	213.246	11.086		–61.552	–84.771	–30.050	0.0535

$\Delta E_{\upsilon_{max},\upsilon_{max}-1} = E_{\upsilon_{max}} - E_{\upsilon_{max}-1}$. D_e^{expt}: experimental dissociation energy. D_e^{cal}: theoretical dissociation energy calculated using Eq.(9). $E_{rror} = \frac{D_e^{expt} - D_e^{cal}}{\Delta E_{\upsilon_{max},\upsilon_{max}-1}}$.

Table 2. (*Continued*).

	NaK$-d^3\Pi$				
v	$E_v^{expt[15]}$	$E_v^{ref[15]}$	$E_v^{LS(1)}$	$E_v^{LS(2)}$	E_v^{AM}
0	33.515	33.515	33.515	33.515	33.515
1	99.372	99.372	99.372	99.372	99.372
2	163.809	163.809	163.809	163.809	163.809
3	226.930	226.930	226.930	226.930	226.930
4	288.830	288.830	288.830	288.830	288.830
5	349.599	349.599	349.599	349.599	349.599
6	409.317	409.317	409.317	409.317	409.317
7	468.058	468.058	468.058	468.058	468.059
8	525.889	525.889	525.889	525.889	525.890
9	582.868	582.868	582.868	582.868	582.870
10	639.049	639.049	639.049	639.049	639.051
11	694.474	694.474	694.474	694.474	694.477
12	749.182	749.182	749.182	749.182	749.185
13	803.202	803.202	803.202	803.202	803.205
14	856.557	856.557	856.557	856.556	856.559
15	909.260	909.260	909.260	909.260	909.262
16	961.321	961.321	961.321	961.321	961.323
17	1012.740	1012.740	1012.740	1012.740	1012.741
18	1063.509	1063.509	1063.509	1063.509	1063.509
19	1113.614	1113.614	1113.614	1113.614	1113.614
20	1163.033	1163.033	1163.033	1163.033	1163.033
21	1211.738	1211.738	1211.738	1211.738	1211.738
22	1259.692	1259.692	1259.692	1259.692	1259.692
23	1306.850	1306.850	1306.850	1306.850	1306.850
24	1353.163	1353.163	1353.163	1353.163	1353.163
25	1398.571	1398.571	1398.571	1398.571	1398.571
26	1443.009	1443.009	1443.009	1443.009	1443.009
27	1486.403	1486.403	1486.403	1486.403	1486.403
28	1528.673	1528.674	1528.673	1528.673	1528.673
29	1569.732	1569.732	1569.732	1569.732	1569.731
30		1609.483	1609.482	1609.484	1609.483
31		1647.824	1647.823	1647.826	1647.826
32		1684.645	1684.645	1684.649	1684.651
33		1719.829	1719.829	1719.836	1719.842
34		1753.251	1753.251	1753.263	1753.277
35		1784.780	1784.779	1784.797	1784.825
36		1814.275	1814.275	1814.300	1814.351
37		1841.590	1841.590	1841.625	1841.711
38		1866.572	1866.571	1866.619	1866.756
39		1889.058	1889.057	1889.120	1889.331
40		1908.879	1908.878	1908.962	1909.275
41		1925.860	1925.859	1925.967	1926.420
42		1939.818	1939.817	1939.953	1940.593
43		1950.561	1950.559	1950.731	1951.616
44		1957.891	1957.889	1958.102	1959.306
45		1961.602	1961.600	1961.863	1963.474
46					1963.929
$\Delta E_{v_{max},v_{max}-1}$	41.059	3.711	3.711	3.760	0.455
D_e^{cal}		1963.4810	1963.4791	1963.7807	1963.9785
D_e^{expt}	1964[24]				
E_{rror}		0.139	0.140	0.0583	0.0473

Table 2. (*Continued*).

	NaK−$c^3\Sigma^+$				NaLi−$A^1\Sigma^+$			
υ	$E_\upsilon^{expt[16]}$	$E_\upsilon^{ref[16]}$	$E_\upsilon^{LS(2)}$	E_υ^{AM}	$E_\upsilon^{expt[17]}$	$E_\upsilon^{ref[17]}$	$E_\upsilon^{LS(2)}$	E_υ^{AM}
0	36.59	36.594	36.588	36.590	93.8174	93.7852	93.8233	93.8174
1	109.02	109.022	109.023	109.020	280.0037	279.9725	279.9974	280.0037
2	180.49	180.490	180.489	180.490	464.3545	464.3255	464.3453	464.3546
3	250.98	250.982	250.981	250.986	646.8806	646.8546	646.8763	646.8806
4	320.49	320.493	320.492	320.499	827.5915	827.5696	827.5972	827.5915
5	389.02	389.017	389.017	389.022	1006.4962	1006.4793	1006.5137	1006.4961
6	456.55	456.546	456.548	456.550	1183.6024	1183.5913	1183.6306	1183.6022
7	523.08	523.082	523.082	523.080	1358.9172	1358.9126	1358.9527	1358.9169
8	588.61	588.610	588.610	588.608	1532.6381	1532.4491	1532.4847	1532.4461
9	653.13	653.128	653.129	653.130	1704.1950	1704.2058	1704.2314	1704.1948
10	716.63	716.630	716.631	716.641	1874.1672	1874.1867	1874.1975	1874.1671
11	779.11	779.109	779.110	779.135	2042.3662	2042.3950	2042.3874	2042.3662
12	840.56	840.560	840.562	840.604	2208.7942	2208.8329	2208.8052	2208.7942
13	900.98	900.977	900.979	901.040	2373.4524	2373.5015	2373.4539	2373.4525
14	960.35	960.354	960.357	960.433	2536.3413	2536.4012	2536.3356	2536.3413
15	1018.69	1018.686	1018.688	1018.772	2697.4602	2697.5315	2697.4507	2697.4601
16	1075.97	1075.966	1075.968	1076.045	2856.8076	2856.8906	2856.7981	2856.8075
17	1132.19	1132.188	1132.190	1132.242	3014.3810	3014.4762	3014.3748	3014.3809
18	1187.35	1187.346	1187.348	1187.350	3170.1771	3170.2848	3170.1761	3170.1771
19	1241.44	1241.435	1241.437	1241.358	3324.1915	3324.3120	3324.1957	3324.1917
20	1294.45	1294.449	1294.451	1294.257	3476.4189	3476.5526	3476.4263	3476.4195
21	1346.38	1346.382	1346.383	1346.036	3626.8532	3627.0002	3626.8598	3626.8541
22	1397.23	1397.227	1397.228	1396.691	3775.4871	3775.6477	3775.4888	3775.4880
23	1446.98	1446.980	1446.980	1446.216	3922.3127	3922.4871	3922.3072	3922.3127
24	1495.63	1495.634	1495.633	1494.610	4067.3208	4067.5091	4067.3125	4067.3182
25	1543.18	1543.183	1543.181	1541.875	4210.5016	4210.7040	4210.5072	4210.4933
26	1589.62	1589.621	1589.619	1588.017		4352.0607	4351.9014	4351.8252
27	1634.94	1634.943	1634.941	1633.044		4491.5674	4491.5157	4491.2995
28	1679.14	1679.142	1679.140	1676.971		4629.2112	4629.3845	4628.9000
29	1722.21	1722.213	1722.211	1719.815		4764.9786	4765.5599	4764.6082
30	1764.15	1764.149	1764.149	1761.596		4898.8547	4900.1160	4898.4038
31	1804.95	1804.946	1804.946	1802.342		5030.8241	5033.1540	5030.2636
32	1844.60	1844.596	1844.597	1842.079		5160.8701	5164.8080	5160.1618
33	1883.09	1883.095	1883.096	1880.840		5288.9753	5295.2508	5288.0694
34	1920.44	1920.436	1920.437	1918.660		5415.1213	5424.7018	5413.9540
35	1956.61	1956.613	1956.613	1955.575		5539.2888	5553.4339	5537.7794
36	1991.62	1991.620	1991.618	1991.620		5661.4574	5681.7825	5659.5050
37		2025.452	2025.445	2026.832		5781.6060	5810.1547	5779.0858
38		2058.103	2058.086	2061.244		5899.7123	5939.0394	5896.4712
39		2089.566	2089.534	2094.887		6015.7534	6069.0186	6011.6053
40		2119.836	2119.782	2127.783		6129.7052	6200.7791	6124.4256
⋮		⋮	⋮	⋮		⋮	⋮	⋮
50		2355.613	2354.102	2411.408		7148.3559	7871.4151	7105.7736
51		2372.369	2370.447	2433.152		7237.4719	8113.1135	7186.5142
52		2387.861	2385.440	2452.853		7324.1374	8378.7757	7263.4295
53		2402.083	2399.059	2470.138		7408.3160	8672.0213	7336.3013
54		2415.029	2411.284	2484.567		7489.9706	8996.8576	7404.8920
55		2426.694	2422.089	2495.622		7569.0633	9357.7102	7468.9430
56		2437.071	2431.447	2502.702		7645.5550	9759.4538	7528.1734
57		2446.154	2439.330	2505.116		7719.4057	10207.4455	7582.2782
58		2453.939	2445.706			7790.5747	10707.5588	7630.9271
59		2460.418	2450.540			7859.0200	11266.2198	7673.7625
60		2465.586	2453.796			7924.6990	11890.4452	7710.3981
61		2469.437	2455.432			7987.5679	12587.8809	7740.4166
62		2471.966				8047.5822	13366.8433	7763.3684
63		2473.165				8104.6963	14236.3621	7778.7693
64						8158.8637	15206.2247	7786.0985
65						8210.0370	16287.0220	
66						8258.1678	17490.1972	
⋮						⋮	⋮	
76						8560.8313	39485.1158	
77						8572.0355	43087.2281	
78						8579.5438	47035.6312	
79						8583.2958	51358.1135	
80							56084.1999	
							Not converged!	
$\Delta E_{\upsilon_{max},\upsilon_{max}-1}$	35.01	1.199	1.636	2.414	143.1808	3.7520		7.32915
D_e^{cal}		2473.734	2456.255	2505.938		8585.171		7789.586
D_e^{expt}	2508[16]				7791[17]			
E_{rror}		28.579	31.629	0.854		–211.666		0.193

Table 2. (*Continued*).

	NaLi$-X^1\Sigma^+$				$^7Li_2-3^3\Sigma_g^+$			
υ	$E_\upsilon^{expt[18]}$	$E_\upsilon^{ref[18]}$	$E_\upsilon^{LS(2)}$	E_υ^{AM}	$E_\upsilon^{expt[19]}$	$E_\upsilon^{ref[19]}$	$E_\upsilon^{LS(2)}$	E_υ^{AM}
0	128.1	128.08	128.09	128.10	135.531	135.496	135.616	135.531
1	381.7	381.74	381.72	381.70	403.889	403.853	403.501	403.889
2	632.0	632.03	632.01	632.00	668.019	668.983	668.613	669.019
3	878.9	878.92	878.91	878.92	930.886	930.850	930.626	930.886
4	1122.4	1122.38	1122.38	1122.40	1189.454	1189.417	1189.351	1189.453
5	1362.4	1362.38	1362.38	1362.39	1444.686	1444.650	1444.689	1444.685
6	1598.9	1598.89	1598.90	1598.85	1696.548	1696.512	1696.593	1696.547
7	1831.9	1831.89	1831.90	1831.75	1945.003	1944.968	1945.045	1945.002
8	2061.3	2061.33	2061.34	2061.06	2190.015	2189.981	2190.032	2190.015
9	2287.2	2287.19	2287.19	2286.77	2431.549	2431.517	2431.541	2431.549
10	2509.4	2509.43	2509.42	2508.83	2669.569	2669.538	2669.548	2669.569
11	2728.0	2728.01	2728.00	2727.23	2904.038	2904.010	2904.020	2904.039
12	2942.9	2942.89	2942.87	2941.94	3134.922	3134.896	3134.915	3134.922
13	3154.0	3154.02	3153.98	3152.90	3362.183	3362.161	3362.190	3362.183
14	3361.3	3361.33	3361.29	3360.09	3585.787	3585.769	3585.800	3585.787
15	3564.7	3564.78	3564.73	3563.44	3805.698	3805.684	3805.707	3805.697
16	3764.2	3764.28	3764.23	3762.89	4021.879	4021.870	4021.877	4021.878
17	3959.7	3959.75	3959.71	3958.36	4234.294	4234.291	4234.285	4234.294
18	4151.1	4151.12	4151.08	4149.76	4442.909	4442.912	4442.904	4442.909
19	4338.2	4338.27	4338.24	4336.99	4647.687	4647.696	4647.695	4647.686
20	4521.1	4521.11	4521.08	4519.94	4848.591	4848.609	4848.589	4848.586
21	4699.5	4699.50	4699.47	4698.48		5045.613	5045.462	5045.568
22	4873.3	4873.31	4873.29	4872.47		5238.674	5238.091	5238.590
23	5042.4	5042.40	5042.39	5041.74		5427.756	5426.116	5427.605
24	5206.6	5206.60	5206.59	5206.12		5612.822	5608.973	5612.561
25	5365.7	5365.74	5365.73	5365.43		5793.836	5785.822	5793.399
26	5519.6	5519.62	5519.61	5519.46		5970.764	5955.461	5970.055
27	5668.0	5668.03	5668.02	5668.00		6143.569	6116.219	6142.454
28	5810.7	5810.75	5810.73	5810.81		6312.215	6265.837	6310.510
29	5947.5	5947.53	5947.51	5947.63		6476.667	6401.323	6474.121
30	6078.1	6078.10	6078.08	6078.21		6636.889	6518.797	6633.174
31	6202.2	6202.19	6202.17	6202.27		6792.844	6613.303	6787.533
32	6319.5	6319.49	6319.46	6319.50		6944.497	6678.612	6937.040
33	6429.6	6429.67	6429.65	6429.60		7091.813	6706.987	7081.516
34	6532.4	6532.38	6532.36	6532.24		7234.755		7220.747
35	6627.2	6627.26	6627.25	6627.08		7373.288		7354.491
36	6713.9	6713.90	6713.90	6713.76		7507.376		7482.465
37	6791.9	6791.89	6791.89	6791.90		7636.982		7604.347
38		6860.78	6860.78	6861.12		7762.072		7719.765
39		6920.10	6920.07	6921.01		7882.609		7828.296
40		6969.35	6969.27	6971.15		7998.557		7929.457
41		7008.01	7007.83	7011.09		8109.882		8022.701
42		7035.51	7035.18	7040.38		8216.546		8107.408
43		7051.28	7050.69	7058.54		8318.514		8182.879
44		7054.70	7053.73	7065.08		8415.750		8248.328
45						8508.219		8302.875
46						8595.884		8345.535
47						8678.710		8375.209
48						8756.661		8390.679
49						8829.702		
50						8897.795		
51						8960.906		
52						9018.999		
53						9072.037		
54						9119.986		
55						9162.809		
56						9200.470		
57						9232.933		
58						9260.164		
59						9282.125		
60						9298.782		
61						9310.098		
62						9316.037		
63						9316.564		
$\Delta E_{\upsilon_{max},\upsilon_{max}-1}$	78.0	3.42	3.034	6.54	200.904	0.527	28.375	15.470
D_e^{cal}		7055.4424	7054.3227	<u>7067.4340</u>		9316.611	6719.315	<u>8398.743</u>
D_e^{expt}	7068[18]				8401[25]			
E_{rror}		3.672	4.508	0.0865		–1737.402	59.319	0.146

Table 2. (*Continued*).

	$^7Li_2 - 1^1\Pi_g$				NaK$-B^1\Pi$			
v	$E_v^{expt[20]}$	$E_v^{ref[20]}$	$E_v^{LS(2)}$	E_v^{AM}	$E_v^{expt[21]}$	$E_v^{ref[21]}$	$E_v^{LS(2)}$	E_v^{AM}
0	46.212	46.213	46.212	46.212	35.3995	35.4425	35.3995	35.3995
1	135.913	135.924	135.913	135.913	104.5311	104.5740	104.5311	104.5311
2	222.100	222.181	222.100	222.100	171.2926	171.3356	171.2926	171.2933
3	304.877	305.179	304.877	304.877	235.6635	235.7065	235.6635	235.6643
4	384.314	385.112	384.314	384.315	297.6413	297.6843	297.6413	297.6419
5	460.454	462.177	460.454	460.455	357.2394	357.2823	357.2393	357.2395
6	533.319	536.568	533.319	533.319	414.4844	414.5273	414.4844	414.4844
7	602.914	608.482	602.914	602.914	469.4145	469.4574	469.4145	469.4145
8	669.237	678.114	669.237	669.237	522.0765	522.1193	522.0765	522.0766
9	732.279	745.658	732.279	732.278	572.5238	572.5665	572.5238	572.5238
10	792.031	811.311	792.031	792.031	620.8137	620.8564	620.8137	620.8137
11	848.488	875.269	848.488	848.489	667.0058	667.0483	667.0058	667.0058
12	901.652	937.725	901.651	901.653	711.1588	711.2012	711.1588	711.1593
13	951.532	998.876	951.532	951.534	753.3288	753.3711	753.3288	753.3302
14	998.154	1058.918	998.154	998.154	793.5667	793.6089	793.5667	793.5689
15	1041.552	1118.045	1041.553	1041.548	831.9160	831.9580	831.9160	831.9160
16	1081.781	1176.453	1081.781	1081.768	868.4101	868.4520	868.4101	868.3993
17	1118.908	1234.337	1118.908	1118.879		903.1123	903.0706	903.0290
18	1153.018	1291.894	1153.018	1152.965		935.9460	935.9045	935.7924
19	1184.211	1349.318	1184.211	1184.124		966.9431	966.9019	966.6490
20	1212.605	1406.804	1212.605	1212.471		996.0749	996.0338	995.5230
21	1238.329	1464.549	1238.329	1238.138		1023.2907	1023.2501	1022.2966
22	1261.528	1522.747	1261.528	1261.269		1048.5164	1048.4764	1046.8010
23	1282.355	1581.595	1282.355	1282.021		1071.6516	1071.6127	1068.8075
24	1300.971	1641.287	1300.971	1300.560		1092.5674	1092.5303	1088.0168
25	1317.542	1702.018	1317.543	1317.062		1111.1044	1111.0700	1104.0469
26	1332.236	1763.985	1332.236	1331.708		1127.0697	1127.0395	1116.4205
27	1345.214	1827.383	1345.214	1344.679		1140.2351	1140.2114	1124.5503
28	1356.631	1892.407	1356.631	1356.158		1150.3346	1150.3205	1127.7233
29	1366.629	1959.252	1366.629	1366.319		1157.0621	1157.0618	
30	1375.329	2028.114	1375.329	1375.329		1160.0691	1160.0882	
31	1382.826	2099.189	1382.826	1383.340				
32		2172.672	1389.185	1390.484				
33		2248.758	1394.428	1396.871				
34		2327.642	1398.532	1402.580				
35		2409.521	1401.417	1407.655				
36		2494.589	1402.937	1412.097				
37		2583.042		1415.862				
38		2675.076		1418.849				
39		2770.885		1420.896				
40		2870.666		1421.772				
41		2974.613						
42		3082.922						
43		3195.789						
44		3313.409						
45		3435.977						
46		3563.688						
47		3696.739						
48		3835.325						
49		3979.641						
50		4129.882						
51		4286.244						
52		4448.922						
53		4618.112						
54		4794.009						
55		4976.809						
56		5166.706						
57		5363.897						
58		5568.577						
59		5780.942						
60		6001.186						
		Not converged!						
$\Delta E_{v_{max},v_{max}-1}$	7.497		1.520	0.876	36.494	3.007	3.026	3.173
D_e^{cal}			1403.7379	<u>1422.1475</u>		1161.4131	1161.4469	<u>1128.9617</u>
D_e^{expt}	1422.5[20]				1129.17[21]			
E_{rror}			12.343	0.402		–10.723	–10.667	0.0656

Table 2. (*Continued*).

	$^7Li_2-2^3\Pi_g$					$^7Li_2-2^3\Pi_g$			
υ	$E_\upsilon^{expt[22]}$	$E_\upsilon^{ref[22]}$	$E_\upsilon^{LS(2)}$	E_υ^{AM}	υ	$E_\upsilon^{expt[22]}$	$E_\upsilon^{ref[22]}$	$E_\upsilon^{LS(2)}$	E_υ^{AM}
0	94.2493	93.8029	94.2493	94.2493	36	5686.2023	5685.7559	5686.2023	5686.2054
1	280.5636	280.1172	280.5636	280.5635	37	5812.1651	5811.7187	5812.1651	5812.1684
2	464.6401	464.1937	464.6401	464.6401	38	5936.5188	5936.0724	5936.5188	5936.5221
3	646.5657	646.1193	646.5657	646.5656	39	6059.2385	6058.7921	6059.2385	6059.2414
4	826.4178	825.9714	826.4178	826.4178	40	6180.2947	6179.8483	6180.2947	6180.2965
5	1004.2656	1003.8192	1004.2656	1004.2655	41	6299.6522	6299.2058	6299.6522	6299.6522
6	1180.1703	1179.7239	1180.1703	1180.1703	42		6416.8235	6417.2699	6417.2670
7	1354.1864	1353.7400	1354.1864	1354.1864	43		6532.6537	6533.1000	6533.0927
8	1526.3618	1525.9154	1526.3618	1526.3618	44		6646.6411	6647.0874	6647.0739
9	1696.7388	1696.2924	1696.7388	1696.7388	45		6758.7227	6759.1688	6759.1468
10	1865.3544	1864.9080	1865.3544	1865.3544	46		6868.8264	6869.2724	6869.2389
11	2032.2412	2031.7948	2032.2412	2032.2412	47		6976.8706	6977.3165	6977.2679
12	2197.4275	2196.9811	2197.4275	2197.4275	48		7082.7633	7083.2090	7083.1410
13	2360.9381	2360.4917	2360.9381	2360.9381	49		7186.4012	7186.8468	7186.7539
14	2522.7946	2522.3482	2522.7946	2522.7946	50		7287.6689	7288.1142	7287.9902
15	2683.0156	2682.5692	2683.0156	2683.0157	51		7386.4377	7386.8827	7386.7200
16	2841.6177	2841.1713	2841.6177	2841.6178	52		7482.5650	7483.0097	7482.7992
17	2998.6151	2998.1687	2998.6151	2998.6151	53		7575.8930	7576.3373	7576.0686
18	3154.0201	3153.5737	3154.0201	3154.0202	54		7666.2477	7666.6915	7666.3523
19	3307.8437	3307.3973	3307.8437	3307.8438	55		7753.4379	7753.8812	7753.4574
20	3460.0955	3459.6491	3460.0955	3460.0955	56		7837.2542	7837.6969	7837.1719
21	3610.7837	3610.3373	3610.7837	3610.7837	57		7917.4676	7917.9096	7917.2644
22	3759.9157	3759.4693	3759.9157	3759.9157	58		7993.8282	7994.2694	7993.4824
23	3907.4980	3907.0516	3907.4980	3907.4979	59		8066.0643	8066.5047	8065.5511
24	4053.5359	4053.0895	4053.5359	4053.5359	60		8133.8812	8134.3206	8133.1722
25	4198.0344	4197.5880	4198.0344	4198.0343	61		8196.9594	8197.3977	8196.0227
26	4340.9971	4340.5507	4340.9971	4340.9971	62		8254.9535	8255.3907	8253.7530
27	4482.4271	4481.9807	4482.4271	4482.4272	63		8307.4912	8307.9270	8305.9862
28	4622.3264	4621.8800	4622.3264	4622.3266	64		8354.1712	8354.6055	8352.3161
29	4760.6958	4760.2494	4760.6958	4760.6962	65		8394.5621	8394.9949	8392.3060
30	4897.5350	4897.0886	4897.5350	4897.5357	66		8428.2013	8428.6323	8425.4871
31	5032.8423	5032.3959	5032.8423	5032.8432	67		8454.5924	8455.0216	8451.3569
32	5166.6140	5166.1676	5166.6140	5166.6154	68		8473.2050	8473.6321	8469.3777
33	5298.8449	5298.3985	5298.8449	5298.8467	69		8483.4718	8483.8967	8478.9747
34	5429.5273	5429.0809	5429.5273	5429.5295	70		8484.7879	8485.2104	8479.5348
35	5558.6508	5558.2044	5558.6508	5558.6535					
$\Delta E_{\upsilon_{max},\upsilon_{max}-1}$						119.3575	1.3161	1.3137	0.5601
D_e^{cal}							8484.9556	8485.3785	8479.5675
D_e^{expt}						8479.870[22]			
E_{rror}							–3.864	–4.193	0.540

14 energies more than the $\{E_\upsilon^{AM}\}$. It is noted that, for most electronic states in Table 2, the LS method also reproduces the known experimental energies very well, but the generated high-lying LS vibrational energies have notable even large errors, and converge to a less accurate or a wrong dissociation energy. A typical example is the $3^3\Sigma_g^+$ state of $^7Li_2$ molecule: the Ref.[19] gives 21 experimental vibrational energies, the least-squares LS(2) calculation obtains 34 vibrational energies, and the maxi-

mum vibrational energy $E^{\mathrm{LS(2)}}_{\upsilon_{\max}=33}$ (=6706.987 cm^{-1}) is 1694.013 cm^{-1} smaller than the experimental dissociation energy D_{e}^{expt} (=8401 cm^{-1}). The vibrational energies $\{E_{\upsilon}^{\mathrm{ref}}\}$[19] generated using the reference vibrational constants have 64 energies, and its maximum vibrational energy $E^{\mathrm{ref}}_{\upsilon_{\max}=63}$ (=9316.56 cm^{-1}) is 915 cm^{-1} greater than the D_{e}^{expt}. This comparison is plotted in Fig.1. If these high-lying energies and their incorrect vibrational wave functions are used in accurate quantitative studies, the resulting physical quantities might be poisoned by the errors carried in these vibrational data.

Table 2 also gives the energy difference $\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$ (= $E_{\upsilon_{\max}} - E_{\upsilon_{\max}-1}$) of the last two vibrational energies, the molecular dissociation energy $D_{\mathrm{e}}^{\mathrm{cal}}$ obtained using Eq.(9) and its relative error $E_{\mathrm{rror}} = (D_{\mathrm{e}}^{expt} - D_{\mathrm{e}}^{\mathrm{cal}})/\Delta E_{\upsilon_{\max},\upsilon_{\max}-1}$. It is shown that, for all electronic states in Table 2, the AM spectrum $\{E_{\upsilon}^{\mathrm{AM}}\}$ not only gives all known experimental energies, but also correctly generates all high-lying vibrational energies which may be difficult to obtain experimentally or quantum mechanically, and that the $D_{\mathrm{e}}^{\mathrm{cal}}$(AM) has best agreement with the D_{e}^{expt}.

The E_{rror} listed in Table 2 are used as one of convergence criteria of vibrational energies according to Eq.(10). It is clearly seen from Table 2 that all E_{rror}(AM) except that of the $\mathrm{Na}_2 - b^3\Pi_{\mathrm{u}}$ state are less than 1. Although the E_{rror} (AM) of the $\mathrm{Na}_2 - b^3\Pi_{\mathrm{u}}$ state is 11.086, it is still much smaller than the E_{rror} (ref)(=270.272), E_{rror} (LS(1))(=211.191) and E_{rror} (LS(2))(=213.246) respectively. For every electronic state in Table 2, the E_{rror} (ref), E_{rror} (LS(1)) and E_{rror} (LS(2)) either violate Eq.(10) (when they are negative values) or are greater even much greater than the corresponding E_{rror} (AM).

The main reason that the AM method produces correct full vibrational spectrum $\{E_{\upsilon}^{\mathrm{AM}}\}$ and the high-lying AM energies $E_{\upsilon}^{\mathrm{AM}}$ converge to correct molecular dissociation energy D_{e}^{expt} is that the AM does not use any mathematical approximation and physical model, but uses a set of physical criteria as given by Eqs.(4)–(10) which must be satisfied by correctly converged vibrational spectrum. These criteria can judge the convergence and the correctness of a vibrational spectrum $\{E_{\upsilon}\}$, and choose the best physical representation that best satisfies these physical requirements out of various possible vibrational representations which are mathematically available. By contrast, the LS method fits all known experimental energies to obtain a set of spectroscopic constants by minimizing the chi-square, and doesn't use any physical criterion to rule out those data having certain errors. Namely, the LS method uses all m experimental energies including those containing some crude or false information which may interfere with accurate physical information during the fitting process. Minimizing the chi-square enforces the generated fitting parameters mimicking all characteristics both correct and false embedded in all m source data. Therefore, although the LS method usually reproduces the m source data, the extracted new data beyond the m original ones by using the fitting parameters may contain some errors. This is the main source why the high-lying vibrational energies generated by the LS method have less accurate or even incorrect values, and so do the LS molecular dissociation energies.

4. Summary

In this study, comparisons and analyses are made on vibrational energy spectra and molecular dissociation energies for 10 electronic states of $^7\mathrm{Li}_2$, Na_2, NaK and NaLi molecules using the AM method and the conventional LS method respectively. Comparisons show that the spectroscopic constants fitted using the LS method can repeat the known experimental energies well, but in many cases the extracted quantitative data of the unknown high-lying vibrational energies usually have notable errors or are incorrect, particularly for those near molecular dissociation limit. The molecular dissociation energies $D_{\mathrm{e}}^{\mathrm{cal}}$ (LS) calculated using three highest LS vibrational energies are usually less accurate than the $D_{\mathrm{e}}^{\mathrm{cal}}$ (AM), or they have greater errors. However, the AM method doesn't use any mathematical approximation and physical model, and instead uses a set of physical criteria as given in Eqs.(4)–(10) which are enforced to be satisfied by correct full vibrational spectrum. It is these physical criteria that pick out those source data with more crude or false physical information and keep those with important physical effects and true vibrational information in the AM mathematical processing. Therefore, the full vibrational spectrum $\{E_{\upsilon}^{\mathrm{AM}}\}$ generated using the AM method not only reproduces the known experimental energies, but also can correctly generate all high-lying vibrational energies. The accuracy of the AM spectrum is uniquely determined by that of the known experimental energies. The molecular dissociation energies $D_{\mathrm{e}}^{\mathrm{cal}}$(AM) obtained using three

highest AM vibrational energies have better or much better agreement with experimental values D_e^{expt} than those D_e^{cal} calculated using the vibrational spectroscopic constants from either literatures or our LS fitting.

The main source of the errors in the data obtained using conventional numerical fitting (e.g. the LS fitting) comes from that the numerical fitting on some kind of physical source data is a pure mathematical process, and that there are usually no physical criteria which should be satisfied by those physical data being used in the numerical procedure. Therefore, this study may suggest that as solving or fitting a physical equation using a group of physical source data, it is important both to apply a good mathematical method and to find and use some correct physical criteria which can physically judge the convergence and the physical nature of the data being studied.

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