



Studies on the full vibrational energies and dissociation energies of some heteronuclear diatomic molecules

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ARTICLE INFO

Article history:

Received 31 May 2009

Received in revised form 1 August 2009

Accepted 10 August 2009

Keywords:

Algebraic method

Parameter-free formula

Heteronuclear diatomic molecules

Vibrational energy

Molecular dissociation energy

ABSTRACT

A parameter-free analytical formula for dissociation energies of diatomic molecules is proposed by Fan and Sun (2009) [20] based on LeRoy and Bernstein's vibrational energy expression near dissociation limit. Using three highest vibrational energies which may be generated by the algebraic method (AM) presented in our previous study and by some other physical methods, the new formula is applied to study the molecular dissociation energies of 10 electronic states of KH, ⁷LiD, ⁷LiH, ⁶LiH, NaK, NaLi and NaRb heteronuclear diatomic molecules which have regular (Morse-like) potentials in this work. The results show that the AM energies E_v^{AM} and dissociation energies D_e^{AM} have excellent agreement with experimental values.

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1. Introduction

Molecular high-lying vibrational excited data are important for studying molecular scattering [1]. 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 [2].

The dissociation energies D_e of stable diatomic electronic states play a significant role in atomic and molecular physics, molecular structures, reactive scatterings, and chemical physics [3]. However, it is usually difficult to directly measure dissociation energy. Theoretically, many studies on D_e have used *ab initio* methods having different features and using many variationally changed basis function parameters [4–6]. However, 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 *ab initio* studies is usually very complicated, even if for the ground state of simplest molecule H₂, the molecular wave function for calculating dissociation energy contains many constituents and many correction terms. Experimentally, recently extensive efforts have been focused on dissociation energies of a series of

electronic states of diatomic alkali molecules [7–16] using high resolution experimental apparatus such as the Doppler-free polarization spectroscopy, the polarization labeling spectroscopy, and the optical-optical double resonance excitation spectroscopy.

In our previous study, based on LeRoy and Bernstein's work for molecular dissociation energy [17,18], a parameter-free analytical formula was suggested to evaluate molecular dissociation energies for some electronic states of homonuclear diatomic molecules which have regular (Morse-like) potentials has been proposed recently by Sun et al. [19,20]

$$D_e \cong E_{v_{\max}} + \frac{\Delta E_{v_{\max}, v_{\max}-1}^2}{\Delta E_{v_{\max}, v_{\max}-2} - \Delta E_{v_{\max}, v_{\max}-1}} = E_{v_{\max}} + F(\Delta E_{v_{\max}, v_{\max}-1}), \quad (1)$$

where

$$\Delta E_{v_{\max}, v_{\max}-1} = E_{v_{\max}} - E_{v_{\max}-1}, \quad \Delta E_{v_{\max}, v_{\max}-2} = E_{v_{\max}} - E_{v_{\max}-2}.$$

Eq. (1) is only the function of the highest three vibrational energies $E_{v_{\max}}$, $E_{v_{\max}-1}$ and $E_{v_{\max}-2}$, and the calculated results agree excellently with known experimental values for each state. One may calculate the correct molecular dissociation energy D_e of a stable diatomic molecular electronic state by using its three highest vibrational energies $E_{v_{\max}}$, $E_{v_{\max}-1}$ and $E_{v_{\max}-2}$, and must satisfy the condition

$$D_e D_e^{\text{expt}}. \quad (2)$$

If Eq. (2) is violated, the three highest vibrational energies used to calculate D_e^{cal} have errors. Since Eq. (1) should use the three highest

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Table 1
Vibrational spectroscopic constants of some heteronuclear diatomic electronic states (all quantities are in cm^{-1}).

State	ω_0	ω_{e0}	ω_e	$\omega_e x_e$	$10^2 \omega_e y_e$	$10^3 \omega_e z_e$	$10^4 \omega_e t_e$	$10^5 \omega_e s_e$	$10^{10} \omega_e r_e$
NaRb – $X^1\Sigma^+$	–0.02016	–0.00013	106.8559	0.3805	–0.0669	–0.00093	–0.00137	0.00013	–0.1262
Ref. [23]	–0.0183		106.8560	0.3805	–0.06283	–0.0135			
KH – $X^1\Sigma^+$	0.7947	–0.45159	986.1990	15.3068	8.07539	4.9823	–6.64172	3.35753	–8651.5100
Ref. [24]	0.670859		986.6595	15.844615					
$^6\text{LiH} - X^1\Sigma^+$	1.02881	0.06876	1419.75354	23.34232	7.26434	15.3305	–16.5157	7.42114	–16388.37175
Ref. [25]			1419.68479	23.15436					
$^7\text{LiH} - X^1\Sigma^+$	0.97014	–0.37830	1405.2706	22.94698	8.29105	15.3382	–18.30155	8.81461	–19152.8897
Ref. [26]	1.061		1405.07781	22.68035					
NaK – $c^3\Sigma^+$	0.01553	–0.01244	73.38756	0.47657	–0.13945	0.02190	–0.00556	0.00059	–0.11784
Ref. [27]			73.4	0.480173	–0.0982485				
NaK – $d^3\Pi$	0.01954	0.00105	67.3833	0.79453	1.98123	–0.37087	0.0070	–0.00164	1.50585
Ref. [28]			67.38222	0.7938763	1.966478	–0.306383			
NaK – $B^1\Pi$	–0.04199	–0.00322	71.45970	1.14786	–1.17148	1.19447	–0.376	0.08566	–160.68422
Ref. [29]			71.4630	1.15092	–1.0613	0.99950	–0.19426		
$^7\text{LiD} - X^1\Sigma^+$	0.552062	–0.27895	1054.72789	12.9237	3.72176	4.23328	–3.67030	1.26444	–2088.9394
Ref. [26]			1055.00696	13.18954	0.16183				
NaLi – $X^1\Sigma^+$	0.0929	–0.1875	256.8050	1.5715	–2.0771	1.1306	–0.3680	0.04231	–20.7977
Ref. [30]			256.9926	1.657189	–0.6379382	0.1607073	–0.0669253		
NaLi – $A^1\Sigma^+$	0.03243	–0.000075	188.0326	0.9264	0.2027	–0.02992	–0.00659	0.00229	–3.0797
Ref. [31]			188.0328	0.926	0.208	–0.039			

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.

The key condition to obtain correct diatomic molecular dissociation energy D_e using Eq. (1) is that one has to use accurate high-lying vibrational energies near molecular dissociation limit. However modern experimental methods and quantum methods usually give a vibrational energy subset $[E_v]$ which may not be very close to the dissociation limit of a given diatomic system. In our previous study [21,22], an algebraic method (AM) is suggested by second order perturbation theory to generate a full set of vibrational energy spectrum $\{E_v\}$ using a known experimental vibrational energy subset $[E_v]$. In this work, with the algebraic method (AM) for full E_v , the new formula is applied to study the molecular dissociation energies of 10 electronic states of KH, ^7LiD , ^7LiH , ^6LiH , NaK, NaLi and NaRb heteronuclear diatomic molecules which have regular potentials, respectively. Section 2 presents the applications of AM method and the new formula for some heteronuclear diatomic molecules. Section 3 summarizes this study.

2. Application and discussion

The improved computational program of the AM method is used to study the vibrational spectroscopic constants and the full vibrational spectra, respectively, for 10 heteronuclear diatomic molecular electronic states: the $X^1\Sigma^+$ state of KH, ^6LiH , ^7LiH , ^7LiD , NaLi and NaRb, the $B^1\Pi$, $d^3\Pi$, $c^3\Sigma^+$ states of NaK, the $A^1\Sigma^+$ state of NaLi. The dissociation energies of the above electronic states are calculated using Eq. (1) and their three highest AM vibrational energies, respectively. The vibrational spectroscopic constants from references and the AM of these states are given 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 anharmonic vibrational constants $\omega_e x_e$ 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 are listed in Table 2, respectively. For each electronic state, the eight 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 eight 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 described in Refs. [21,22] 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. (1), the correct molecular dissociation energies can be calculated.

Table 2 also gives the maximum vibrational quantum number v_{\max} , the energy difference $\Delta E_{v_{\max}, v_{\max}-1} [= E_{v_{\max}} - E_{v_{\max}-1}]$ of the highest two AM vibrational energies, the approximate molecular dissociation energy $D_e^{\text{app}} = E_{v_{\max}} + \Delta E_{v_{\max}, v_{\max}-1}$, the molecular dissociation energy D_e^{cal} obtained using the new analytical formula in Eq. (1), the experimental molecular dissociation energy D_e^{expt} , and

Table 2Vibrational energies of some electronic states (energies in cm^{-1}).

ν	$\text{NaRb} - X^1\Sigma^+$		$\text{KH} - X^1\Sigma^+$		ν	$^6\text{LiH} - X^1\Sigma^+$		ν	$^7\text{LiH} - X^1\Sigma^+$	
	E_{ν}^{expt} [23]	E_{ν}^{AM}	E_{ν}^{expt} [24]	E_{ν}^{AM}		E_{ν}^{expt} [25]	E_{ν}^{AM}		E_{ν}^{expt} [26]	E_{ν}^{AM}
0	53.3126	53.3126	490.0779	490.0779	0	705.08	705.08	0	697.88	697.88
1	159.4054	159.4054	1445.9460	1445.9460	1	2078.45	2078.45	1	2057.59	2057.59
2	264.7310	264.7310	2372.0117	2372.0239	2	3406.08	3406.11	2	3372.48	3372.46
3	369.2849	369.2849	3268.9001	3268.9001	3	4688.81	4688.89	3	4643.37	4643.36
4	473.0624	473.0624	4137.1550	4137.1499	4	5927.55	5927.65	4	5871.14	5871.14
5	576.0584	576.0584	4977.3077	4977.3077	5	7123.12	7123.18	5	7056.58	7056.58
6	678.2676	678.2676	5789.8479	5789.8479	6	8276.16	8276.16	6	8200.35	8200.34
7	779.6845	779.6845	6575.1859	6575.1710	7	9387.21	9387.16	7	9302.95	9302.94
8	880.3030	880.3031	7333.6301	7333.5896	8	10456.61	10456.54	8	10364.73	10364.74
9	980.1170	980.1171	8065.3740	8065.3096	9	11484.55	11484.51	9	11385.90	11385.90
10	1079.1199	1079.1200	8770.4781	8770.4042	10	12470.99	12470.99	10	12366.42	12366.42
11	1177.3047	1177.3048	9448.8363	9448.7739	11	13415.62	13415.66	11	13306.04	13306.04
12	1274.6642	1274.6642	10100.1221	10100.0895	12	14317.74	14317.80	12	14204.13	14204.20
13	1371.1907	1371.1907	10723.7138	10723.7138	13	15176.19	15176.23	13	15059.61	15059.91
14	1466.8761	1466.8762	11318.5972	11318.5972	14	15989.12	15989.14	14	15870.80	15871.63
15	1561.7121	1561.7122	11883.2384	11883.1427	15	16753.86	16753.86	15	16635.24	16637.03
16	1655.6899	1655.6899	12415.4080	12415.0364	16	17466.64	17466.65	16	17349.46	17352.70
17	1748.8002	1748.8002	12911.9331	12911.0393	17	18122.33	18122.34	17	18008.73	18013.85
18	1841.0333	1841.0334	13368.3517	13366.7349	18	18713.93	18713.93	18	18606.62	18613.79
19	1932.3793	1932.3793	13778.4686	13776.2299	19	19232.10	19232.10	19	19134.53	19143.45
20	2022.8276	2022.8276	14133.8621	14131.8020	20	19664.54	19664.65	20	19581.14	19590.74
21	2112.3673	2112.3672	14423.4918	14423.4918	21	19995.83	19995.83	21	19932.13	19939.73
22	2200.9869	2200.9868	14633.7253	14638.6334	22		20205.52	22	20169.84	20169.84
23	2288.6745	2288.6744	14749.3488	14761.3203	23		20268.36	23		20254.79
24	2375.4178	2375.4177		14771.8011	24			24		
25	2461.2038	2461.2038								
26	2546.0193	2546.0193								
27	2629.8504	2629.8504								
28	2712.6825	2712.6825								
29	2794.5008	2794.5007								
30	2875.5899	2875.2895								
31		2955.0326								
32		3033.7133								
33		3111.3142								
34		3187.8174								
..		...								
..		...								
74		5026.8677								
75		5030.1913								
76		5030.5579								
$\Delta E_{\nu_{\text{max}}, \nu_{\text{max}}-1}$		0.3666		10.4808			62.84			84.95
D_e^{app}		5030.925		14782.2819			20331.20			20339.74
D_e^{expt}	5030.75 ^a									
	5030.502(50) ^b		14772.7 ^c			20287.7 ^d			20287.7 ^e	
D_e^{AM}		5030.598[#]		14772.69[#]		20287.2[#]			20286.14[#]	
E_{errors}		0.414		0.001		0.008			0.018	
ν	$\text{NaK} - c^3\Sigma^+$		ν	$\text{NaK} - d^3\Pi$		ν	$\text{NaK} - B^1\Pi$			
	E_{ν}^{expt} [27]	E_{ν}^{AM}		E_{ν}^{expt} [28]	E_{ν}^{AM}		E_{ν}^{expt} [29]	E_{ν}^{AM}		
0	36.59	36.59	41	2149.10	2149.10	0	35.3995	35.3995		
1	109.02	109.02	42	2177.05	2177.05	1	104.5311	104.5311		
2	180.49	180.48	43	2203.83	2203.83	2	171.2926	171.2933		
3	250.98	250.98	44	2229.42	2229.42	3	235.6635	235.6643		
4	320.49	320.49	45	2253.82	2253.82	4	297.6413	297.6419		
5	389.02	389.02	46	2277.05	2277.05	5	357.2394	357.2395		
6	456.55	456.55	47	2299.10	2299.10	6	414.4844	414.4844		
7	523.08	523.08	48	2319.97	2319.97	7	469.4145	469.4145		
8	588.61	588.61	49	2339.67	2339.67	8	522.0765	522.0766		
9	653.13	653.13	50	2358.21	2358.21	9	572.5238	572.5238		
10	716.63	716.63	51	2375.60	2375.60	10	620.8137	620.8137		
11	779.11	779.11	52	2391.83	2391.83	11	667.0058	667.0058		
12	840.56	840.56	53	2406.92	2406.92	12	711.1588	711.1593		
13	900.98	900.97	54	2420.88	2420.88	13	753.3288	753.3302		
14	960.35	960.35	55	2433.73	2433.73	14	793.5667	793.5689		
15	1018.69	1018.68	56	2445.48	2445.48	15	831.9160	831.9160		
16	1075.97	1075.96	57	2456.13	2456.13	16	868.4101	868.3993		
17	1132.19	1132.18	58	2465.72	2465.72	17		903.0290		
18	1187.35	1187.34	59	2474.26	2474.26	18		935.7924		
19	1241.44	1241.43	60	2481.77	2481.77	19		966.6490		
20	1294.45	1294.44	61	2488.27	2488.27	20		995.5230		

Table 2 (Continued)

NaK – c ³ Σ ⁺					NaK – d ³ Π			NaK – B ¹ Π			
ν	E _ν ^{expt} [27]	E _ν ^{AM}	ν	E _ν ^{expt} [27]	E _ν ^{AM}	ν	E _ν ^{expt} [28]	E _ν ^{AM}	ν	E _ν ^{expt} [29]	E _ν ^{AM}
21	1346.38	1346.37	62		2493.78	21	1211.738	1211.738	21		1022.2966
22	1397.23	1397.22	63		2498.34	22	1259.692	1259.691	22		1046.8010
23	1446.98	1446.97	64		2501.98	23	1306.850	1306.850	23		1068.8075
24	1495.63	1495.63	65		2504.72	24	1353.163	1353.163	24		1088.0168
25	1543.18	1543.18	66		2506.60	25	1398.571	1398.571	25		1104.0469
26	1589.62	1589.62	67		2507.65	26	1443.009	1443.009	26		1116.4205
27	1634.94	1634.94	68		2507.92	27	1486.403	1486.403	27		1124.5503
28	1679.14	1679.14				28	1528.673	1528.673	28		1127.7233
29	1722.21	1722.21				29	1569.732	1569.731			
30	1764.15	1764.15				30		1609.483			
31	1804.95	1804.94				31		1647.826			
32	1844.60	1844.59				32		1684.651			
33	1883.09	1883.09				33		1719.842			
34	1920.44	1920.43						
35	1956.61	1956.61						
36	1991.62	1991.63						
37		2025.47				43		1951.616			
38		2058.15				44		1959.306			
39		2089.64				45		1963.474			
40		2119.96				46		1963.929			
ΔE _{ν_{max}, ν_{max}–1}					0.27			0.455			3.173
D _e ^{app}					2508.19			1964.384			1130.8963
D _e ^{expt}					2508 [*]		1964 ^{*,c}			1129.17 ^{*,d}	
D _e ^{AM}					2507.987[#]			1963.979[#]			1128.962[#]
E _{error}					0.049			0.046			0.007
⁷ LiD – X ¹ Σ ⁺			ν		NaLi – X ¹ Σ ⁺		ν		NaLi – A ¹ Σ ⁺		
ν	E _ν ^{expt} [26]	E _ν ^{AM}	ν	E _ν ^{expt} [30]	E _ν ^{AM}	ν	E _ν ^{expt} [31]	E _ν ^{AM}	ν	E _ν ^{expt} [31]	E _ν ^{AM}
0	524.69	524.69	0	128.10	128.10	0	93.8174	93.8174			
1	1553.71	1553.71	1	381.70	381.70	1	280.0037	280.0037			
2	2557.33	2557.31	2	632.00	632.00	2	464.3545	464.3546			
3	3535.86	3535.84	3	878.90	878.92	3	646.8806	646.8806			
4	4489.67	4489.67	4	1122.40	1122.40	4	827.5915	827.5915			
5	5419.13	5419.15	5	1362.40	1362.39	5	1006.4962	1006.4961			
6	6324.60	6324.63	6	1598.90	1598.85	6	1183.6024	1183.6023			
7	7206.40	7206.41	7	1831.90	1831.75	7	1358.9172	1358.9169			
8	8064.77	8064.77	8	2061.30	2061.06	8	1532.6381	1532.4461			
9	8899.95	8899.93	9	2287.20	2286.77	9	1704.1950	1704.1948			
10	9712.08	9712.06	10	2509.40	2508.83	10	1874.1672	1874.1671			
11	10501.29	10501.28	11	2728.00	2727.23	11	2042.3662	2042.3662			
12	11267.63	11267.63	12	2942.90	2941.94	12	2208.7942	2208.7942			
13	12011.09	12011.11	13	3154.00	3152.90	13	2373.4524	2373.4525			
14	12731.57	12731.60	14	3361.30	3360.09	14	2536.3413	2536.3413			
15	13428.90	13428.93	15	3564.70	3563.44	15	2697.4602	2697.4601			
16	14102.75	14102.77	16	3764.20	3762.89	16	2856.8076	2856.8075			
17	14752.68	14752.68	17	3959.70	3958.36	17	3014.3810	3014.3809			
18	15378.05	15378.02	18	4151.10	4149.76	18	3170.1771	3170.1771			
19	15978.00	15977.96	19	4338.20	4336.99	19	3324.1915	3324.1917			
20	16551.42	16551.37	20	4521.10	4519.94	20	3476.4189	3476.4195			
21	17096.85	17096.81	21	4699.50	4698.48	21	3626.8532	3626.8541			
22	17612.46	17612.45	22	4873.30	4872.47	22	3775.4871	3775.4880			
23	18095.94	18095.94	23	5042.40	5041.74	23	3922.3127	3922.3127			
24	18544.37	18544.37	24	5206.60	5206.12	24	4067.3208	4067.3182			
25	18954.15	18954.13	25	5365.70	5365.43	25	4210.5016	4210.4933			
26	19320.78	19320.76	26	5519.60	5519.46	26		4351.8252			
27	19638.84	19638.84	27	5668.00	5668.00	27		4491.2995			
28		19901.82	28	5810.70	5810.81	28		4628.8999			
29		20101.83	29	5947.50	5947.63	29		4764.6082			
30		20229.45	30	6078.10	6078.21	30		4898.4038			
31		20273.55	31	6202.20	6202.27	31		5030.2636			
			32	6319.50	6319.50	32		5160.1618			
			33	6429.60	6429.60	33		5288.0694			
			34	6532.40	6532.24	34		5413.9540			
			35	6627.20	6627.08	35		5537.7794			
			36	6713.90	6713.76			
			37	6791.90	6791.90			
			61		7740.4166			
			42	7040.38	7040.38	62		7763.3684			
			43	7058.54	7058.54	63		7778.7693			
			44	7065.08	7065.08	64		7786.0985			

Table 2 (Continued)

ν	$^7\text{LiD} - X^1\Sigma^+$		ν	$\text{NaLi} - X^1\Sigma^+$		ν	$\text{NaLi} - A^1\Sigma^+$	
	E_{ν}^{expt} [26]	E_{ν}^{AM}		E_{ν}^{expt} [30]	E_{ν}^{AM}		E_{ν}^{expt} [31]	E_{ν}^{AM}
$\Delta E_{\nu_{\text{max}}, \nu_{\text{max}}-1}$		44.10			6.54			7.3292
D_e^{app}		20317.65			7071.62			7793.4277
D_e^{expt}	20293.5 ^a		7067.8 ^a			7791 ^a		
D_e^{AM}		20288.79[#]			7067.434[#]			7789.586[#]
E_{error}		0.107			0.056			0.193

^a Experimental value.

[#] The values (bold-underlined) calculated using Eq. (1) and the highest three AM vibrational energy. $D_e^{\text{app}} = E_{\nu_{\text{max}}} + \Delta E_{\nu_{\text{max}}, \nu_{\text{max}}-1}$; $E_{\text{error}} = (D_e^{\text{expt}} - D_e^{\text{cal}}) / \Delta E_{\nu_{\text{max}}, \nu_{\text{max}}-1}$.

^a Experimental value from Ref. [32].

^b Experimental value from Ref. [33].

^c Experimental value from Ref. [34].

^d Experimental value from Ref. [35].

the relative error $E_{\text{error}} = (D_e^{\text{expt}} - D_e^{\text{cal}}) / \Delta E_{\nu_{\text{max}}, \nu_{\text{max}}-1}$ of the calculated dissociation energy D_e^{cal} for each electronic state.

It can be seen from Table 2 that the AM dissociation energies D_e^{AM} (those D_e^{cal} with “#”) evaluated using the AM vibrational energies and Eq. (1) have excellent agreement with experimental dissociation energies D_e^{expt} , and all D_e^{AM} satisfy Eq. (2). Table 2 also demonstrates that the AM produces correct maximum vibrational quantum number ν_{max} and correct maximum vibrational energy $E_{\nu_{\text{max}}}$ which is very close to the molecular dissociation limit. A typical example is the electronic excited state $X^1\Sigma^+$ of NaRb. Kasahara and coworkers [23] obtained 31 experimental vibrational energies for this system. However, the AM approach obtains 77 vibrational energies in full energy spectrum $\{E_{\nu}\}$ using the accurate experimental energy subset $\{E_{\nu}^{\text{expt}}\}$ of Kasahara et al., a correct maximum vibrational energy $E_{\nu_{\text{max}}}^{\text{AM}} (= 5030.558 \text{ cm}^{-1})$ which is very close to the $D_e^{\text{expt}} = 5030.75 \text{ cm}^{-1}$ [32] and $D_e^{\text{expt}} = 5030.502(50) \text{ cm}^{-1}$ [33], and an dissociation energy $D_e^{\text{AM}} = 5030.598 \text{ cm}^{-1}$.

A widely recognized experience is that the energy difference $(D_e^{\text{expt}} - D_e^{\text{cal}})$ of an electronic state is usually within a fraction of its last vibrational spacing $\Delta E_{\nu_{\text{max}}, \nu_{\text{max}}-1}$ for a theoretical D_e^{cal} . In other words, the relative error $E_{\text{error}} = (D_e^{\text{expt}} - D_e^{\text{cal}}) / \Delta E_{\nu_{\text{max}}, \nu_{\text{max}}-1}$ of D_e^{cal} is usually smaller than unity. It is clearly seen that all AM E_{errors} in Table 2 are less than unity.

The approximate dissociation energies $D_e^{\text{app}} = E_{\nu_{\text{max}}} + \Delta E_{\nu_{\text{max}}, \nu_{\text{max}}-1}$ listed in Table 2 show that most of these quantities from the AM vibrational constants violate Eq. (2). It can be seen that the second term $\Delta E_{\nu_{\text{max}}, \nu_{\text{max}}-1}$ of D_e^{app} are greater or much greater than the second term $F(\Delta E_{\nu_{\text{max}}, \nu_{\text{max}}-1})$ of D_e^{cal} in Eq. (1) for every state in Table 2. It is this difference that makes the D_e^{app} poorer or much poorer than the D_e^{cal} .

3. Summation

An algebraic method (AM) used to study the full vibrational energy spectra of diatomic systems which have regular (Morse-like) potentials proposed by Sun et al. [21,22], and an analytical formula [19,20] used to calculate molecular dissociation energies are described. At present, 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 homonuclear and heteronuclear diatomic molecules. Studies show that: (a) for many diatomic molecular 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 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. (b) For some diatomic molecular electronic states, it may be difficult to obtain their molecular dissociation energies using modern quantum methods and it is costly to obtain them experimentally. However, the parameter-free analytical expression we proposed recently [19,20] is only the function of the three highest vibrational energies near the dissociation limit. Therefore, if we use the three highest vibrational energies, the analytical formula will generate molecular dissociation energies. In summary, based on accurate experimental vibrational energies, 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 theoretically.

Acknowledgments

This work is supported by the National Natural Science Foundation of China (Grant No. 10774105) and the Science Foundation of the Ministry of Education of China.

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