Vol 16 No 6, June 2007
1009-1963/2007/16(06)/1641-09

Chinese Physics

© 2007 Chin. Phys. Soc.
and IOP Publishing Ltd

Studies on heteronuclear diatomic molecular dissociation energies using algebraic energy method*

Fan Kai-Min(范开敏), Ren Wei-Yi(任维义)†,
Liu-Yan(刘 艳), Wang A-Shu(王阿暑), and Liu Song-Hong(刘松红)

Institute of Theoretical Physics, China West Normal University, Nanchong 637002*, China*

(Received 6 July 2006; revised manuscript received 18 December 2006)

The algebraic energy method (AEM) is applied to the study of molecular dissociation energy D_e for 11 heteronuclear diatomic electronic states: $a^3\Sigma^+$ state of NaK, $X^2\Sigma^+$ state of XeBr, $X^2\Sigma^+$ state of HgI, $X^1\Sigma^+$ state of LiH, $A^3\Pi(1)$ state of ICl, $X^1\Sigma^+$ state of CsH, $A(^3\Pi_1)$ and $B0^+(^3\Pi)$ states of ClF, $2^1\Pi$ state of KRb, $X^1\Sigma^+$ state of CO, and $c^3\Sigma^+$ state of NaK molecule. The results show that the values of D_e computed by using the AEM are satisfactorily accurate compared with experimental ones. The AEM can serve as an economic and useful tool to generate a reliable D_e within an allowed experimental error for the electronic states whose molecular dissociation energies are unavailable from the existing literature.

Keywords: algebraic energy method, dissociation energy, vibrational energy, electronic excited states

PACC: 3190, 3420

1. Introduction

We have recently reported our preliminary results on some homonuclear diatomic electronic states.[1,2] In this paper we present our analysis of the heteronuclear diatomic molecules.

Heteronuclear diatomic molecular dissociation energy D_e of a stable diatomic electronic state has become an object studied extensively both in theory and in experiment for many years. Theoretical investigations include *ab initio* calculations by using different methods, such as the complete-active-space self-consistent field (CAS SCF) approach[3] and multireference singles and doubles configuration–interaction approach (MRD CI).[4] Generally, these theoretical methods require quite a number of experiential parameters of basis functions, therefore if the heteronuclear diatomic molecular dissociation energy D_e wants to be accurately determined, then the diverse and complicated calculations have to the carried out. Besides the calculation, the experimental study of the D_e has also become an important topic in last two decades because of the fast development of laser spectroscopic technique.[5−8] In addition, the reliable results about heteronuclear diatomic molecular dissociation energy can also be derived by combining the thermochemical equilibrium measurement method with the spectroscopic technique.[9,10] However, in most cases, the results are influenced due to the lack of reliable theoretical spectroscopic data and the difficulty in experimentally measuring the high-lying vibrational levels in a highly excited state, particularly, close to the dissociation limit for most molecular states. Therefore, we have to seek for a new research method to acquire more accurate results of diatomic molecular dissociation energy,[11] which is our purpose here in this paper.

The present study is carried out based on a limited experimental energy difference by using the AEM to easily determine the reliable value of the heteronuclear diatomic molecular dissociation energy without theoretically performing the diverse and complicated calculations and/or experimentally making costly measurements.

2. Method

When neglecting the nuclear rotation, the vibrational energy of a diatomic molecular system can be expressed using the second-order perturbation theory as[12]

*Project supported by the Science Foundation of China West Normal University (Grant No 05B016) and the Science Foundation of Sichuan province Educational Bureau of China (Grant No 2006A080).

†E-mail: renweiyi118@163.com

$$E_\upsilon = \omega_0 + (\omega_e + \omega_{e0})\left(\upsilon+\frac{1}{2}\right) - \omega_e x_e\left(\upsilon+\frac{1}{2}\right)^2 + \omega_e y_e\left(\upsilon+\frac{1}{2}\right)^3 + \omega_e z_e\left(\upsilon+\frac{1}{2}\right)^4 + \omega_e t_e\left(\upsilon+\frac{1}{2}\right)^5 + \omega_e s_e\left(\upsilon+\frac{1}{2}\right)^6 + \omega_e r_e\left(\upsilon+\frac{1}{2}\right)^7 + \cdots, \quad (1)$$

which is similar to Herzberg's expression.[13] In Eq.(1), ω_0 is the vibrational constant with the zeroth-order $\left(\upsilon+\frac{1}{2}\right)$ and corresponds to the Y_{00} term of Dunham's energy expression.[14] ω_{e0} is the correction term to the harmonic vibrational constant ω_e with the first-order $\left(\upsilon+\frac{1}{2}\right)$. The analytical expressions of both ω_0 and ω_{e0} are given as[12]

$$\omega_0 = -\frac{7}{16\omega_e}b_3^2f_3^2 + \frac{1}{2}b_4f_4 - \frac{1107}{256\omega_e}b_5^2f_5^2 - \frac{945}{128\omega_e}b_4b_6f_4f_6 - \frac{1155}{128\omega_e}b_3b_7f_3f_7 - \frac{180675}{2048\omega_e}b_7^2f_7^2 - \frac{89775}{512\omega_e}b_6b_8f_6f_8 + \frac{315}{128}b_8f_8, \quad (2)$$

$$\omega_{e0} = -\frac{95}{8\omega_e}b_3b_5f_3f_5 - \frac{67}{16\omega_e}b_4^2f_4^2 + \frac{25}{8}b_6f_6 - \frac{19277}{256\omega_e}b_6^2f_6^2 - \frac{22029}{128\omega_e}b_5b_7f_5f_7 - \frac{10521}{64\omega_e}b_4b_8f_4f_8 - \frac{5450499}{2048\omega_e}b_8^2f_8^2, \quad (3)$$

where constants b_n and vibrational force constants f_n can be obtained in the way given in Ref.[12].

An algebraic method (AM)[12] has been suggested to generate accurate vibrational spectrum constants and vibrational energies by using limited experimental vibrational energies. In the AM Eq.(1) is rewritten in an matrix form as

$$AX = E, \quad (4)$$

where the solution matrix X and the energy matrix E are

$$X = \begin{pmatrix} \omega_0 \\ \omega_e' \\ -\omega_e x_e \\ \omega_e y_e \\ \vdots \\ \omega_e r_e \end{pmatrix}, \quad E = \begin{pmatrix} E_\upsilon \\ E_{\upsilon+i} \\ E_{\upsilon+j} \\ \vdots \\ E_{\upsilon+s} \end{pmatrix},$$

$$\upsilon = 0, 1, 2, \cdots, \quad (5)$$

respectively, and the matrix elements of the $n \times 8$ coefficient matrix A are $A_{\upsilon k}(\upsilon) = \left(\upsilon+\frac{1}{2}\right)^k$ with $k = 0, 1, 2, 3, \cdots, 7$. In Eq.(5) $\omega_e' = \omega_e + \omega_{e0}$. There are only 8 terms in Eq.(5) because Eq.(1) for the nuclear vibrational potential of a diatomic molecular electronic state can be derived using Taylor series expansion only to the eighth order nearby an equilibrium internuclear distance. Our computational results show that the spectrum constants above the eighth order can make too a small contribution to the vibrational energy. However, if only four terms in Eq.(5) are used then the computational results have a greater error, which may be seen from Table 1.

Equation (4) can be solved using a standard algebraic method for m limited known experimental energies in a subset $[E_\upsilon]$ of a full energy spectrum $\{E_\upsilon\}$ to obtain the vibrational constants in X, without any mathematical and/or physical approximations made. The solution vector X should satisfy the following requirements:

$$\overline{\Delta E(e,c)} = \left[\frac{1}{m}\sum_{\upsilon=0}^{m-1}|E_{\upsilon,\mathrm{exp}} - E_{\upsilon,\mathrm{cal}}|^2\right]^{1/2} \to 0, \quad (6)$$

$$\Delta E(\upsilon_{\max}, \upsilon_{\max}-1) = E_{\upsilon_{\max}} - E_{\upsilon_{\max}-1} \to \text{small enough}, \quad (7)$$

where $\{E_{\upsilon,\mathrm{cal}} \equiv E_\upsilon\}$ are generated by using vibrational constants in the solution vector X obtained by solving Eq.(4). Here 'small enough' means that the high-lying vibrational energy difference must be smallest and close to the dissociation limit for a molecular state of excellent physical convergence. Since most important physical and vibrational information about a diatomic system is included in the accurate experimental energies and there are not any ap-

proximations and numerical fittings in the AM process, the AM vibrational constants $X = \{\omega_0, \omega_e + \omega_{e0}, -\omega_e x_e, \omega_e y_e, \omega_e z_e, \omega_e t_e, \omega_e s_e, \omega_e r_e\}$ should reproduce the energy subset $[E_\upsilon]$, and correctly generate all other high-lying vibrational energies of the full spectrum $\{E_\upsilon\}$ which are unavailable for many diatomic electronic states. The vibrational constant in X is directly related to the accuracy of the known experimental data $[E_\upsilon]$.

The algebraic energy method (AEM) is based on the vibrational energies obtained by using the AM and the following theoretical bound[1] for molecular dissociation energy,

$$E_{\upsilon_{\max}} \le D_e \le E_{\upsilon_{\max}} + \sum_{j=J_{\min}}^{J_{\max}-1} (E_{\upsilon_{\max},j+1} - E_{\upsilon_{\max},j}) \tag{8}$$

or

$$E_{\upsilon_{\max}} \le D_e \le E_{\upsilon_{\max}} + \Delta E(\upsilon_{\max}, \upsilon_{\max} - 1). \tag{9}$$

For many diatomic molecular electronic states, the sum of the rotational energy differences of the last vibrational state $\upsilon_{\max}$ in Eq.(8) is zero, therefore

$$D_e = E_{\upsilon_{\max}} \tag{10}$$

or the sum is very small, and the theoretical D_e should be very close to the lower bound $E_{\upsilon_{\max}}$. In this study we use $D_e^{\rm AEM} = E_{\upsilon_{\max}}^{\rm AM}$ to denote the dissociation energy which exactly or approximately satisfies Eq.(10).

3. Results and discussion

The molecular dissociation energy D_e has been studied using the AEM for 11 heteronuclear diatomic molecular electronic states: $a^3\Sigma^+$ of NaK, $X^2\Sigma^+$ of XeBr, $X^2\Sigma^+$ of HgI, $X^1\Sigma^+$ of LiH, $A^3\Pi(1)$ of ICl, $X^1\Sigma^+$ of CsH, $A(^3\Pi_1)$ and $B0^+(^3\Pi)$ of ClF, $2^1\Pi$ of KRb, $X^1\Sigma^+$ of CO, and $C^3\Sigma^+$ of NaK molecule. In Table 1 are listed the vibrational spectrum constants $(\omega_0, \omega_{e0}, \omega_e, \omega_e x_e, \omega_e y_e, \omega_e z_e, \omega_e t_e, \omega_e s_e, \omega_e r_e)$, the maximum vibrational quantum numbers $\upsilon_{\max}$ generated by the AM, and the dissociation energies $D_e^{\rm AEM}$ produced by the AEM for these states. The data for these states cited from the relevant references are also given in Table 1. The reliable vibrational force constants $(f_3, f_4, f_5, f_6, f_7, f_8)$ used to generate constant ω_{e0} by using Eq.(3) are calculated as described in Ref.[12].

Table 1 shows that the agreement between the harmonic vibrational constant ω_e obtained by using the AM and the ω_e cited from the reference is excellent and their difference appears in the lower-order anharmonic constants $\omega_e x_e, \omega_e y_e, \omega_e z_e$. It can be seen that higher anharmonic vibrational constants $\omega_e t_e, \omega_e s_e$ and $\omega_e r_e$ are unavailable from the existing literature for most electronic states studied here. When the values of vibrational energy E_υ are calculated using the lower-order constants that are available from the existing literature for a diatomic state, a vibrational spectrum $\{E_\upsilon\}$ with wrong high-lying energies and $E_{\upsilon_{\max}}$ are usually obtained. Such a $E_{\upsilon_{\max}}$ is less accurate than the $E_{\upsilon_{\max}}$ (AM) or violates

$$E_{\upsilon_{\max}} \le D_e. \tag{11}$$

It should be noted from Table 1 that each $D_e^{\rm AEM}$ excellently agrees with the experimental D_e within errors less than 1.0%. Each AM $E_{\upsilon_{\max}}$ satisfies Eq.(11).

In Fig.1 plotted are the percent errors of energy differences $\Delta D\%$, $\Delta E^{\rm cal}\%$ and $\Delta E^{\rm inp}\%$. $\Delta D\%$ is the percentage error of energy difference between the experimental molecular dissociation energy D_e and the AEM dissociation energy $D_e^{\rm AEM}$ (marked with symbol '◯' sign), the $\Delta E^{\rm cal}\%$ is that between the experimental D_e and the calculated $E_{\upsilon_{\max}}^{\rm cal}$ in the literature for vibrational spectrum constants (denoted with symbol '■'), and the $\Delta E^{\rm inp}\%$ is that between the experimental D_e and the input literature $E_{\upsilon_{\max}}^{\rm inp}$ (represented with symbol '▲'). It is shown that for most cases the $\Delta D\%$ obtained from $D_e^{\rm AEM}$ is smaller or much smaller than the $\Delta E^{\rm cal}\%$ and the $\Delta E^{\rm inp}\%$. All vibrational energies and the corresponding date available form the literature for each electronic state studied here are listed in Table 2.

Table 1. Dissociation energies $D_e^{\dagger}$, vibrational spectrum constants, and maximum vibrational quantum numbers $\upsilon_{\max}$ for some heteronuclear diatomic states (all quantities but $\upsilon_{\max}$ are in cm^{-1}).

State		ω_0	ω_{e0}	ω_e	$\omega_e\chi_e$	$10^2\omega_e y_e$	$10^3\omega_e z_e$	$10^4\omega_e t_e$	$10^5\omega_e s_e$	$10^{10}\omega_e r_e$	$\upsilon_{\max}$	$E_{\upsilon_{\max}}$	D_e
NaK $-a^3\Sigma^+$	AM	−0.05470	−0.01578	22.8160	0.5772	−0.9509	1.1679	−1.2029	0.5534	−797.4777	19	203.070	203.070(AEM)
	Ref.[17]			22.816	0.5916	−0.346	0.047				17‡	203.967‡	
	Ref.[17]										19▲	203.070▲	203.1±0.5*
XeBr$-X^2\Sigma^+$	AM	−0.01515	0.1999	25.670	0.7302	1.4575	−1.4755	0.5837	−0.05884	−23.9478	23	254.2870	254.2870(AEM)
	Ref.[18]			25.67	0.622	−0.55	0.18				20‡	249.8611‡.	
	Ref.[18]										23▲	254.287▲	254±2*
HgI$-X^2\Sigma^+$	AM	0.02023	−0.05390	126.0710	1.2391	0.8366	−0.6926	−0.2582	0.1576	−178.2625	43	2750.266	2750.266(AEM)
	Ref.[19]			126.071	1.2704	1.5899	−1.5785	0.27681			34‡	2606.9093‡	
	Ref.[19]										30▲	2478.64▲	2750±80*
LiH$-X^1\Sigma^+$	AM	0.8841	−0.0905	1406.240	23.45471	19.7103	3.6250	−12.8697	7.9429	−19320.186	23	20263.331	20263.331(AEM)
	Ref.[20]			1406.24	23.5505	24.174	−6.8				28‡	22058.7154‡	
	Ref.[20]										12▲	14204.55▲	20286.8±0.5*[a],
ICl$-A^3\Pi(1)$	AM	−0.04499	−0.2648	211.0	1.9342	−7.5330	6.1588	−3.7141	0.9717	−868.8323	39	3814.730	3814.730(AEM)
	Ref .[21]			211.0	2.12	−2.4	0.2				36‡	4065.0570‡	
	Ref .[21]										35▲	3789.63▲	3814.7±0.6*
CsH$-X^1\Sigma^+$	AM	0.06946	3.3732	883.73501	12.4065	0.1869	12.9646	−12.8317	5.9708	−1107.886	26	14800.99	14800.99(AEM)
	Ref.[22]			883.77350	12.6324	7.7717	−0.9632				39‡	17642.9220‡	
	Ref.[23]										14▲	10352.4▲	14805±30*
KRb$-2^1\Pi$	AM	−0.0456	0.00016	51.70040	0.420703	−0.37545	0.01555	−0.03817	0.02953	−76.6980	31	1043.1154	1043.1154(AEM)
	Ref.[5]	−0.046		51.7004	0.420405	−0.37896					39‡	1152.6303‡	
	Ref.[5]										13▲	611.967▲	1050.0±0.8*
ClF$-A(^3\Pi_1)$	AM	−0.1874	0.4484	361.230	8.0907	−22.4646	−17.4485	29.3063	−15.5032	31866.28	16	2979.06	2979.06(AEM)
	Ref.[24]			361.23	7.74	−36	10				11‡	2757.9156‡	
	Ref.[24]										11▲	2757.9▲	2988.4+
ClF$-B0^+\Sigma^+$	AM	−0.00914	0.02645	362.5780	8.2648	−21.8050	5.5828	9.8727	−14.1204	46296.296	16	3066.653	3066.653(AEM)
	Ref.[24]			362.578	8.227	−24.5	15	−6.7			14‡	3014.3649‡	
	Ref.[24]										9▲	2562.28▲	3078.7+
CO$-X^1\Sigma^+$	AM	0.1890	0.003681	2169.80	13.2845	0.9952	0.09764	−0.005523	−0.000164	−2.3533	77	90672.88230	90672.88230(AEM)
	Ref.[25]			2169.8	13.3						81‡	88496.775‡	
	Ref.[6]										41+	68042.48990+	90674+
NaK$-c^3\Sigma^+$	AM	0.01183	−0.00366	73.40	0.479482	−0.1016571	−0.0012918	0.0016205	−0.000487	0.4825506	69	2505.973	2505.973(AEM)
	Ref.[7]			73.4	0.480173	−0.0982485					63‡	2473.1592‡	
	Ref.[7]										36▲	1991.62▲	2508+

†The upper bound for D_e is $D_e^{\upsilon} = E_{\upsilon_{\max}} + \Delta E(\upsilon_{\max}, \upsilon_{\max} - 1)$. ‡Calculated using vibrational spectroscopic constants from references. *Experimental value. ▲Recent experimental energy and state available. [a] $D_e = D_0 + E_0$ Both experimental value $D_0 = 19588.7 \pm 0.5\,\mathrm{cm}^{-1}$ and zero point energy $E_0 = 698.12\,\mathrm{cm}^{-1}$ are calculated using the spectroscopic data from Ref.[20]. +From other theoretical studies in references.

Table 2. The vibrational energies for some heteronuclear diatomic electronic states (energies are in cm^{-1}) cited from literature and calculated by using the AM.

	NaK		XeBr		HgI		LiH	
	$a^3\Sigma^+$		$X^2\Sigma^+$		$X^2\Sigma^+$		$X^1\Sigma^+$	
υ	$E_\upsilon^{\text{exp.}}$ Ref.[7]	E_υ^{AM}	$E_\upsilon^{\text{exp.}}$ Ref.[18]	E_υ^{AM}	$E_\upsilon^{\text{exp.}}$ Ref.[19]	E_υ^{AM}	$E_\upsilon^{\text{exp.}}$ Ref.[20]	E_υ^{AM}
0	11.20	11.200	12.754	12.7540	62.72	62.720	698.12	698.120
1	32.82	32.820	37.234	37.2340	186.29	186.282	2058.01	2058.010
2	53.22	53.225	60.347	60.3467	307.42	307.420	3372.78	3372.780
3	72.39	72.390	82.123	82.1230	426.14	426.144	4643.54	4643.540
4	90.29	90.292	102.574	102.5743	542.44	542.448	5871.27	5871.260
5	106.91	106.910	121.699	121.6985	656.30	656.300	7056.74	7056.740
6	122.22	122.218	139.485	139.4850	767.65	767.650	8200.60	8200.606
7	136.19	136.190	155.920	155.9194	876.43	876.430	9303.32	9303.320
8	148.79	148.799	170.988	170.9880	982.56	982.553	10365.19	10365.183
9	160.02	160.023	184.681	184.6812	1085.92	1085.920	11386.35	11386.350
10	169.84	169.847	196.997	196.9970	1186.42	1186.419	12366.78	12366.814
11	178.27	178.270	207.943	207.9435	1283.93	1283.931	13306.30	13306.371
12	185.33	185.309	217.541	217.5413	1378.33	1378.335	14204.55	14204.550
13	191.04	191.005	225.825	225.8250	1469.50	1469.507		15060.494
14	195.47	195.428	232.844	232.8438	1557.33	1557.330		15872.789
15	198.69	198.676	238.662	238.6630	1641.71	1641.691		16639.233
16	200.86	200.883	243.360	243.3628	1722.53	1722.494		17356.517
17	202.19	202.215	247.032	247.0383	1799.72	1799.655		18019.842
18	202.87	202.870	249.786	249.7979	1873.20	1873.112		18622.417
19	203.07	203.070	251.743	251.7615	1942.93	1942.824		19154.884
20			253.032	253.0575	2008.88	2008.775		19604.600
21			253.792	253.8203	2071.05	2070.980		19954.820
22			254.163	254.1857	2129.48	2129.480		20183.724
23			254.287	254.2870	2184.24	2184.345		20263.331
24					2235.41	2235.679		
25					2283.16	2283.613		
26					2327.66	2328.307		
27					2369.14	2369.944		
28					2407.90	2408.730		
29					2444.27	2444.885		
30					2478.64	2478.640		
31						2510.224		
32						2539.862		
33						2567.755		
34						2594.076		
35						2618.948		
36						2642.431		
37						2664.506		
38						2685.048		
39						2703.810		
40						2720.393		
41						2734.225		
42						2744.522		
43						2750.266		
D_e^{exp}		203.1±0.5		254±2		2750±80		20286.8±0.5
		Ref.[7]		Ref.[18]		Ref.[19]		Ref.[20]

Table 2. *continued*

	ICl		CsH		ClF			
	$A^3\Pi(1)$		$X^1\Sigma^+$		$A(^3\Pi_1)$		$B0^+(^3\Pi)$	
υ	$E_\upsilon^{\rm exp.}$	$E_\upsilon^{\rm AM}$	$E_\upsilon^{\rm exp.}$	$E_\upsilon^{\rm AM}$	$E_\upsilon^{\rm exp.}$	$E_\upsilon^{\rm AM}$	$E_\upsilon^{\rm exp.}$	$E_\upsilon^{\rm AM}$
	Ref.[21]		Ref.[23]		Ref.[24]		Ref.[24]	
0	104.83	104.830	438.7	438.70	178.6	178.60	179.20	179.200
1	311.48	311.480	1297.4	1297.40	523.3	523.30	524.60	524.600
2	513.67	513.733	2131.5	2131.55	849.5	849.50	851.72	851.722
3	711.24	711.350	2941.5	2941.50	1155.6	1155.60	1159.64	1159.640
4	904.05	904.148	3727.7	3727.66	1440.1	1440.14	1447.59	1447.590
5	1091.92	1091.977	4490.4	4490.40	1701.9	1701.90	1714.90	1714.900
6	1274.70	1274.700	5230.2	5230.11	1940.0	1939.92	1960.89	1960.890
7	1452.21	1452.175	5947.2	5947.11	2153.6	2153.52	2184.77	2184.779
8	1624.30	1624.250	6641.7	6641.70	2342.4	2342.25	2385.62	2385.620
9	1790.78	1790.750	7314.2	7314.14	2505.9	2505.90	2562.28	2562.280
10	1951.48	1951.480	7964.7	7964.70	2644.4	2644.40		2713.500
11	2106.18	2106.220	8593.6	8593.60	2757.9	2757.90		2838.046
12	2254.66	2254.734	9201.1	9201.07		2846.77		2934.986
13	2396.68	2396.772	9787.3	9787.30		2911.70		3004.100
14	2532.08	2532.080	10352.4	10352.40		2953.91		3046.470
15	2660.59	2660.407		10896.33		2975.33		3065.250
16	2782.01	2781.517		11418.83		2979.06		3066.653
17	2896.12	2895.200		11919.23				
18	3002.66	3001.284		12396.29				
19	3101.47	3099.642		12847.99				
20	3192.39	3190.208		13271.24				
21	3275.32	3272.982		13661.49				
22	3350.20	3348.039		14012.37				
23	3417.22	3415.537		14315.17				
24	3476.62	3475.716		14558.33				
25	3528.90	3528.900		14726.73				
26	3574.69	3575.497		14800.99				
27	3614.93	3615.988						
28	3649.79	3650.921						
29	3680.12	3680.890						
30	3706.52	3706.520						
31	3729.26	3728.436						
32	3748.75	3747.236						
33	3765.16	3763.451						
34	3778.72	3777.498						
35	3789.63	3789.630						
36		3799.875						
37		3807.972						
38		3813.286						
39		3814.730						
$D_e^{\rm exp.}$		3814.7±0.6	14805±30					
$D_e^{\rm lit*}$						2988.4		3078.7
		Ref.[21]	Ref.[23]			Ref.[24]		Ref.[24]

*$D_e^{\rm lit}$ is a fitted value cited from other theoretical studies in references.

Table 2. *continued*

	KRb		CO		NaK	
	$2^1\Pi$		$X^1\Sigma^+$		$c^3\Sigma^+$	
υ	$E_\upsilon^{\text{exp.}}$ Ref.[5]	E_υ^{AM}	$E_\upsilon^{\text{exp.}}$ Ref.[6]	E_υ^{AM}	$E_\upsilon^{\text{exp.}}$ Ref.[7]	E_υ^{AM}
0	25.699	25.6990	1081.77097	1081.77097	36.59	36.590
1	76.546	76.5460	3225.04215	3225.03853	109.02	109.024
2	126.518	126.5180	5341.83337	5341.82950	180.49	180.490
3	175.593	175.5925	7432.21043	7432.20813	250.98	250.981
4	223.747	223.7470	9496.24084	9496.24084	320.49	320.492
5	270.959	270.9585	11533.99385	11533.99610	389.02	389.017
6	317.204	317.2041	13545.54043	13545.54460	456.55	456.550
7	362.461	362.4610	15530.95326	15530.95860	523.08	523.083
8	406.706	406.7061	17490.30668	17490.31250	588.61	588.612
9	449.917	449.9170	19423.67665	19423.68240	653.13	653.131
10	492.072	492.0710	21331.14065	21331.14570	716.63	716.632
11	533.147	533.1459	23212.77766	23212.78170	779.11	779.112
12	573.119	573.1190	25068.66794	25068.67080	840.56	840.563
13	611.967	611.9670	26898.89302	26898.89480	900.98	900.980
14		649.6652	28703.53547	28703.53620	960.35	960.356
15		686.1868	30482.67875	30482.67880	1018.69	1018.687
16		721.5010	32236.40702	32236.40650	1075.97	1075.966
17		755.5721	33964.80492	33964.80430	1132.19	1132.187
18		788.3569	35667.95734	35667.95670	1187.35	1187.345
19		819.8026	37345.94912	37345.94880	1241.44	1241.434
20		849.8438	38998.86480	38998.86480	1294.45	1294.447
21		878.3992	40626.78827	40626.78860	1346.38	1346.380
22		905.3675	42229.80246	42229.80300	1397.23	1397.225
23		930.6227	43807.98895	43807.98960	1446.98	1446.978
24		954.0095	45361.42760	45361.42800	1495.63	1495.631
25		975.3371	46890.19610	46890.19610	1543.18	1543.180
26		994.3728	48394.36958	48394.36890	1589.62	1589.619
27		1010.8347	49874.02009	49874.01860	1634.94	1634.940
28		1024.3837	51329.21615	51329.21370	1679.14	1679.140
29		1034.6149	52760.02219	52760.01900	1722.21	1722.210
30		1041.0477	54166.49803	54166.49420	1764.15	1764.146
31		1043.1154	55548.69831	55548.69420	1804.95	1804.942
32			56906.67185	56906.66790	1844.60	1844.592
33			58240.46101	58240.45760	1883.09	1883.090
34			59550.10102	59550.09860	1920.44	1920.430
35			60835.61922	60835.61800	1956.61	1956.609
36			62097.03427	62097.03430	1991.62	1991.620
37			63334.35530	63334.35620		2025.458
38			64547.58089	64547.58210		2058.119
39			65736.69808	65736.69890		2089.600
40			66901.68108	66901.68110		2119.895
41			68042.48990	68042.48990		2149.003
42				69159.07200		2176.920
43				70251.35860		2203.644
...				.....		.....
68				88978.00170		2505.804
69				89329.15160		2505.973
...				.....		
76				90660.75150		
77				90672.88230		
$E_e^{\text{exp.}}$		1050.0±0.8				
E_e^{lit}				90674		2508
		Ref.[5]		Ref.[6]		Ref.[7]

It shows that the AM spectrum can reproduce not only the limited known experimental energies in $[E_\upsilon]$ but also all missed high-lying vibrational energies of the full spectrum $\{E_\upsilon\}$ for those electronic states whose known spectra are incomplete. The correct values of these high-lying vibrational energies are difficult to obtain experimentally or quantum mechanically for many electronic systems. Figure 2 shows all known experimental vibrational energies $[E_\upsilon^{\rm expt}]$ and the full vibrational spectrum $\{E_\upsilon^{\rm AM}\}$ obtained by using the AM for the $X^1\Sigma^+$ state of CO molecule. For a further comparison, we analyse the maximum vibrational energies for two typical electronic states. Coxon and Hajigeorgiou[6] have obtained only 42 vibrational energies experimentally with $E(\upsilon_{\max} = 41) = 68042.48990\,{\rm cm}^{-1}$ which is far smaller than the correct $D_e(= 90674)\,{\rm cm}^{-1}$ for the electronic state $X^1\Sigma^+$ of CO molecule, while our AM has 78 vibrational energies of the full energy spectrum $\{E_\upsilon\}$ with correct $E_{\rm AM}(\upsilon_{\max} = 77) = 90672.88230\,{\rm cm}^{-1}$. As the second example, Kasahara *et al*[5] have obtained only 14 vibrational energies experimentally with $E(\upsilon_{\max} = 13) = 611.967\,{\rm cm}^{-1}$ which is far smaller than the correct $D_e(= 1050\,{\rm cm}^{-1})$ for the electronic state $2^1\Pi$ of KRb molecule, while our AM has 32 vibrational energies of the full energy spectrum $\{E_\upsilon\}$ with correct $E_{\rm AM}(\upsilon_{\max} = 31) = 1043.1154\,{\rm cm}^{-1}$. Therefore, the AM makes it possible for one to use correct high-lying vibrational energies and $E_{\upsilon_{\max}}^{\rm AM}$ when necessary, and one may use the AEM to obtain a reliable value for the molecular dissociation energy D_e of an electronic state.

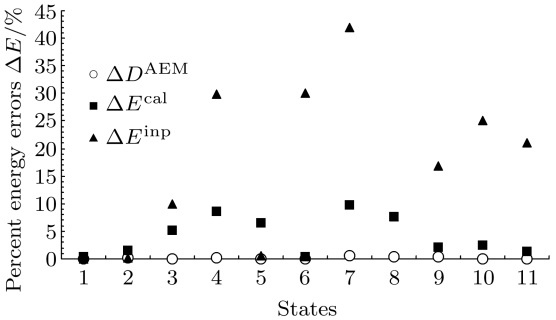


Fig.1. Percentage errors of energy differences $\Delta D\%$, $\Delta E^{\rm cal}\%$ and $\Delta E^{\rm inp}\%$: $\Delta D\% = 100 \times |D_e - D_e^{\rm AEM}|/D_e$, $\Delta E^{\rm cal}\% = 100 \times |D_e - E_{\upsilon_{\max}}^{\rm cal}|/D_e$, $\Delta E^{\rm inp}\% = 100 \times |D_e - E_{\upsilon_{\max}}^{\rm inp}|/D_e$, where D_e is an experimental dissociation energy, $D_e^{\rm AEM} = E_{\upsilon_{\max}}^{\rm AM}$, $E_{\upsilon_{\max}}^{\rm cal}$ is calculated using the vibrational constants cited from literature, and $E_{\upsilon_{\max}}^{\rm inp}$ is an input maximum vibrational energy available in literature. The 11 electronic states are: NaK$-a^3\Sigma^+$; XeBr$-X^2\Sigma^+$; HgI$-X^2\Sigma^+$; LiH$-X^1\Sigma^+$; ICl$-A^3\Pi(1)$; CsH$-X^1\Sigma^+$; KRb$-2^1\Pi$; ClF$-A(^3\Pi_1)$; ClF$-B0^+(^3\Pi)$; CO$-X^1\Sigma^+$; NaK$-c^3\Sigma^+$.

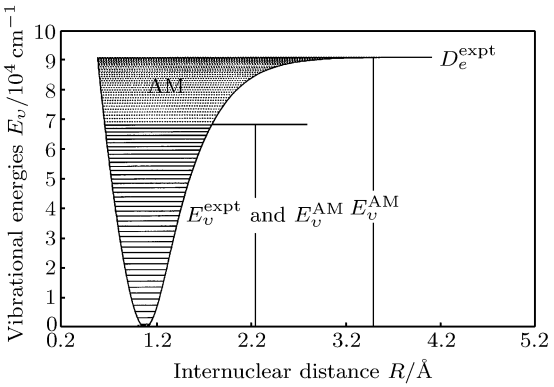


Fig.2. vibrational energies $E_\upsilon^{\rm expt}$ and $E_\upsilon^{\rm AM}$ in the potential well of the $X^1\Sigma^+$ state of CO molecule. The experimental energies $E_\upsilon^{\rm expt}$ are cited from Ref.[6], and the $E_\upsilon^{\rm AM}$ is the full AM vibrational spectrum.

For diatomic molecules, the intermolecular potential energy can be approximated using the Morse potential model, and the accurate potential energy curves of the diatomic molecules are obtained from the calculation of accurate spectroscopic constants, vibrational energy spectrum and the molecular dissociation energy D_e. The so-called accurate vibrational energy spectrum $\{E_\upsilon\}$ may be the measured values, or the 'experimental' energies evaluated using the well-known expansion formula for the term values and the vibrational constants $(\omega_e, \omega_e x_e, \omega_e y_e, \cdots)$, or the exact theoretical energies calculated using a highly accurate quantum mechanical method. As the vibrational spectrum $\{E_\upsilon^{\rm AM}\}$ obtained by using the AM and the dissociation energy $D_e^{\rm AEM}$ obtained by using the AEM can represent the correct physical appearance for diatomic molecules, the potential energy curves can be obtained by using the above AM parameters, which may be superior to the frequently used Morse potential. For discussion of this subject see Ref.[15].

4. Summary

In this study we use the AEM to generate reliable values of diatomic molecular dissociation energy $D_e^{\rm AEM}$ for 11 heteronuclear diatomic molecular electronic states based on the algebraic method (AM).[12] Since the accurate experimental energies in the subset $[E_\upsilon]$ contain nearly all important quantum effects and vibrational information, and the AM does not use any mathematical approximations and physical models, the AM vibrational spectrum $\{E_\upsilon^{\rm AM}\}$ reproduces not only those known limited experimental values, but also all high-lying vibrational energies in a dissociation

region by using a set of known energy subsets $[E_v]$. Of course, it is a complicated object to study the molecular high-lying vibrational energies in a dissociation region. An example indicates that the electronic potential energy cross lines maybe arise from the change of electronic energy when molecular vibrational energy is very high. The object appears as a special study topic in ≪Principle and Study of Molecular Vibrational Spectroscopy≫ written by Wu.[16] As our theoretical model is based on the Born–Oppenheimer approximation, the problem about the electronic potential energy lines crossing over high-lying vibrational energy levels has not yet been solved for most diatomic electronic states. Therefore, in all the high vibrational energies obtained by using the AM, the electronic potential energy lines do not occur. The AEM does not rely on a set of high vibrational energies near the molecular dissociation which are hard to obtain experimentally. One may easily generate a correct molecular dissociation energy, and the molecular dissociation energy $D_e^{\rm AEM}$ obtained by using the AEM has a smaller error than $E_{v_{\max}}$ obtained from other methods. The AEM can be taken as a useful alternative to the evaluation of reliable dissociation energies for those electronic states whose D_e may be difficult to obtain experimentally or quantum mechanically. Besides, this method provides a potential and simple way to accurately evaluate molecular dissociation energies for many diatomic molecular electronic excited states, which is unavailable in the existing literature.

References

[1] Sun W G, Ren W Y, Hou S L and Feng H 2005 *Mol. Phys.* **103** 2335

[2] Ren W Y and Sun W G 2005 *Acta Phys. Sin.* **54** 595 (in Chinese)

[3] BauschlicherJr C W and Langhoff S R 1987 *Chem. Phys. Lett.* **135** 67

[4] Omellas F R, Roberto-Neto O, Borin A C and Machado F B C 1991 *J. Chem. Phys.* **95** 9086

[5] Kasahara S, Fujiwara C, Okada N, Katô H and Baba M 1999 *J. Chem. Phys.* **111** 8857

[6] Coxon J A and Hajigeorgiou P G 1992 *CAN J. Phys.* **70** 40

[7] Ferber R, Pazyuk E A, Stolyarov A V, Zaitsevskii A, Kowalczyk P, Chen H, Wang H and Stwalley W C 2000 *J. Chem. Phys.* **112** 5740

[8] Weinstock E M and Preston A 1978 *J. Mol. Spectrosc.* **70** 188

[9] Balducci G, Nunzio P E, Gigli D G and Guido M 1989 *J. Chem. Phys.* **90** 405

[10] Hildenbrand DL and Lau K H 1989 *J. Chem. Phys.* **91** 4909

[11] Hu S D, Sun W G, Ren W Y and Feng H 2006 *Acta Phys. Sin.* **55** 2185 (in Chinese)

[12] Sun W G, Hou S L, Feng H and Ren W Y 2002 *J. Mol. Spectrosc.* **215** 93

[13] Herzberg G 1953 *Molecular Spectra and Molecular Structure* (I), *Spectra of Diatomic Molecules* (Van Nostrand, New York)

[14] Dunham J L 1932 *Phys. Rev.* **41** 721

[15] Li X X, Sun W G and Feng H 2003 *Acta Phys. Sin.* **52** 307 (in Chinese)

[16] Wu G Z 2002 *Principle and Study of Molecular Vibrational Spectroscopy* (Qinghua University Press)

[17] Breford E J and Engelke F 1979 *J. Chem. Phys.* **71** 1994

[18] Clevenger J O and Tellinghuisen J 1995 *J. Chem. Phys.* **103** 9611

[19] Viswanathan K S and TellinghuisenJ 1983 *J. Mol. Spectrosc.* **98** 185

[20] Orth F B and Stwalley W C 1979 *J. Mol. Spectrosc.* **76** 17

[21] Coxon J A and Wickramaaratchi M A 1980 *J. Mol. Spectrosc.* **79** 380

[22] Hsieh Y K, Yang S C, Tam A C and Stwalley W C 1978 *J. Chem. Phys.* **68** 1448

[23] Yang S C 1982 *J. Chem. Phys.* **77** 2884

[24] Alekseev V A, Setser D W and Tellinghuisen J 1999 *J. Mol. Spectrosc.* **195** 162

[25] Huber K P and Herzberg G 1979 *Molecular Spectra and Molecular Structure* (IV), *Constants of Diatomic Molecules* (Van Nostrand, New York)