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RESEARCH ARTICLE

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Studies on the full vibrational energy spectra for some electronic states of diatomic molecular ions XY⁺

Abstract The first accurate studies on the vibrational spectroscopic constants and the corresponding full vibrational energy spectra of some electronic states of diatomic molecular ions XY^+ were performed using algebraic method(AM). The AM is applied on the $X^1\Sigma^+$ state of BeH^+, the $X^2\Sigma^+$ state of CO^+, the $X^2\Pi_g$ state of F_2^+, the $A^2\Pi_u$ state of O_2^+ and the $X^2\Sigma_g^+$ state of Li_2^+. The results show that AM can generate accurate vibrational spectroscopic constants as well as accurate full vibrational energy spectra by using some accurate experimental vibrational energies,and that the AM vibrational energies are better than other theoretical data.

Keywords diatomic molecular ion，vibrational energy，algebraic method，electronic state

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1 Introduction

The electronic states, spectral properties, vibrational energy spectra and potential energy curves of diatomic molecular ions XY^+ have been studied by spectroscopists, theorists and chemists [1–6]. However, data on the full vibrational energy spectra including the maximum vibrational energy are wanting experimentally and theoretically. The accurate spectroscopic constants and the full vibrational energy spectra of BeH^+, CO^+, F_2^+, O_2^+ and Li_2^+ are particularly needed.

The accurate vibrational energies （$\upsilon = 0$–10）of the BeH^+-$X^1\Sigma^+$ state were determined by Coxon and Colin [7] through the latest experimental spectral information. Nevertheless, they admitted that some other subtle spectra between E_υ（$\upsilon = 10$） and the correct dissociation energy $D_e^{\exp}$ [8] could not be given precisely, due to the limits of resolution and computational accuracy. So, it is now necessary to further search for the higher vibrational energies to make a complete understanding of the spectra and vibrational structure of this state. The experimental vibrational energies of the CO^+-$X^2\Sigma^+$ state fitted by Coxon and Foster [9] appeared continuous in high-lying vibrational transition because of the resolution of the device. Therefore, it is important to accurately figure out the high-lying vibrational spectra nearly reaching the dissociation region using an appropriate theoretical method based on reliable experimental spectral data on this state. F_2^+ plays a central role in the rare gas-halogen laser system. The limited vibrational energies of the F_2^+-$X^2\Pi_g$ state were evaluated theoretically by Cartwright and Hay [4], taking advantage of the generalized valence bond-configuration interaction （GVB-CI）approach. However, this set of GVB-CI energies did not coincide with the accurate experimental data of $\left[E_\upsilon^{\exp}\right]$[4]. Furthermore, the accuracy of existing experimental or theoretical vibrational spectroscopic constants of this state were somewhat suspect, and deserved to be focused on continuously. The experimental energies of the O_2^+-$A^2\Pi_u$ state and the theoretical results of the Li_2^+-$X^2\Sigma_g^+$ state were both incomplete, so the accurate

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vibrational spectroscopic constants and the full vibrational energy spectra of these two electronic states need to be pursued as well. The algebraic method （AM） is briefly described in Section 2 of this paper. In Section 3, the vibrational spectroscopic constants and the full vibrational energy spectra of the $\mathrm{BeH^+}$-$\mathrm{X^1\Sigma^+}$, $\mathrm{CO^+}$-$\mathrm{X^2\Sigma^+}$, $\mathrm{F_2^+}$-$\mathrm{X^2\Pi_g}$, $\mathrm{O_2^+}$-$\mathrm{A^2\Pi_u}$ and $\mathrm{Li_2^+}$-$\mathrm{X^2\Sigma_g^+}$ states were studied using AM. Our research works are summarized in Section 4.

2 Algebraic method(AM)

The analytical non-relativistic vibrational energy formula for a stable diatomic molecular system was derived by Sun *et al.* [14,15] using second-order perturbation theory, and was expressed as

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

Both ω_0 and ω_{e0} are small quantities, but they may be important in calculating high-lying rovibrational energies.

The analytical non-relativistic vibrational energy formula for diatomic molecular ion $\mathrm{XY^+}$ may also be expressed as Eq.(1), whose generation was not relevant to the expression of potential function $V(R)$, which is quite unlike for diatomic molecular ion $\mathrm{XY^+}$ and its neutral molecule [6]. Then, the algebraic method (AM) [10] proposed to study the vibrational spectroscopic constants and energies may be stated by rewriting Eq.(1) in a matrix form

$$AX = E \quad (2)$$

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

$$X = \begin{pmatrix} \omega_0 \\ \omega_e^{'} \\ -\omega_e x_e \\ \omega_e y_e \\ \vdots \\ \omega_e r_e \end{pmatrix}, \text{ and } E = \begin{pmatrix} E_\upsilon \\ E_{\upsilon+i} \\ E_{\upsilon+j} \\ \vdots \\ E_{\upsilon+s} \end{pmatrix}, \qquad \upsilon = 0,1,2,\cdots \quad (3)$$

and the matrix element of the $n\times 8$ coefficient matrix A is $A_{\upsilon k} = \left(\upsilon+\frac{1}{2}\right)^k$, $k = 0,1,2,3,\cdots,7.$ In Eq.(3) $\omega_e' = \omega_e + \omega_{e0}$.

For a given diatomic molecular electronic system, it is better to choose 8 energies of the known accurate vibrational energy subset of $[E_\upsilon]$ to form the energy matrix E to generate the vibrational spectroscopic constants matrix X through solving Eq.（2）using the standard algebraic method. Subsequently, a set of full vibrational energy spectra $\{E_\upsilon\}$ of system can be obtained by putting the vibrational spectroscopic constants $\{\omega_0,\ \omega_e+\omega_{e0},\ -\omega_e x_e,\ \omega_e y_e,\ \omega_e z_e,\ \omega_e t_e,\ \omega_e s_e,\ \omega_e r_e\}$, namely matrix X solved above into Eq.(1). The best solution for the vibrational spectroscopic constants which truly reflects the full vibrational information for a given electronic state should best satisfy the requirements

$$E_{\upsilon_{\max}} \leqslant D_e \quad (4)$$

$$D_e - E_{\upsilon_{\max}} \to \text{ small enough} \quad (5)$$

$$\Delta E\left(\upsilon_{\max},\upsilon_{\max}-1\right) = E_{\upsilon_{\max}} - E_{\upsilon_{\max}-1} \to \text{small enough} \quad (6)$$

$$\left.\frac{\mathrm{d}E_\upsilon}{\mathrm{d}\upsilon}\right|_{\upsilon=\upsilon_{\max}} = 0 \quad (7)$$

$$\overline{\Delta E(c,e)} = \left(\frac{1}{m+1}\sum_{\upsilon=0}^{m}\left[E_{\upsilon,\exp} - E_{\upsilon,\mathrm{cal}}\right]\right)^{1/2} \to 0 \quad (8)$$

The five relations are the principal requirements and criteria of choosing the correct full vibrational energy spectra $\{E_\upsilon\}$ of a system, where Eq.(4)shows the convergency limit of the maximum vibrational energy, and D_e corresponds to the equilibrium dissociation energy of the molecular system when inter-nuclear distance incline to infinity for a long-range molecular potential without potential rampart. In this way, the best subset satisfying the requirements i.e., Eqs.(4)–(8) can be found out of the known reliable vibrational spectra $[E_\upsilon]$, thus obtaining the vibrational spectroscopic constants $\{\omega_0,\ \omega_e+\omega_{e0}, -\omega_e x_e,\ \omega_e y_e, \omega_e z_e,\ \omega_e t_e,\ \omega_e s_e,\ \omega_e r_e\}$ which is the true representation of a given electronic state, thereby generating the full vibrational energy spectra $\{E_\upsilon\}$. This is the algebraic method (AM) used to obtain the vibrational spectroscopic constants and the full vibrational energy spectra of diatomic molecules and its ions.

3 Application of AM to some diatomic molecular ions $\mathrm{XY^+}$

The AM vibrational energy spectra of the $\mathrm{BeH^+}$-$\mathrm{X^1\Sigma^+}$ state listed in Table 1 is calculated using experimental energies $\left[E_\upsilon^{\exp}\right]$ [7] given by Coxon and Colin in 1997. It is shown that the absolute errors between the AM values and the input data is no more than 0.037 $\mathrm{cm^{-1}}$, and the percentage error between the maximum energy of AM and the dissociation energy $D_e^{\exp}$=26 426.637 $\mathrm{cm^{-1}}$ [8] is 3.909 5 × 10^{-2} %. All the properties satisfy the requirements Eqs.(4)–(8). Our research shows that the AM spectra of the $\mathrm{BeH^+}$-$\mathrm{X^1\Sigma^+}$ state, which compensates for the lack of report on high-lying vibrational energies in the results of Coxon and Colin, is the correct full vibrational energy spectra of this system.

Table 1 Literature and AM vibrational energies for electronic states of some diatomic molecular ions XY$^+$ (energies are in cm^{-1}).

υ	Li_2^+ - X $^2\Sigma_g^+$		CO^+ - X $^2\Sigma^+$		υ	Li_2^+ - X $^2\Sigma_g^+$		CO^+ - X $^2\Sigma^+$	
	$E_\upsilon^{\mathrm{Theo}^a}$	E_υ^{AM}	$E_\upsilon^{\mathrm{exp}}$	E_υ^{AM}		$E_\upsilon^{\mathrm{Theo}^a}$	E_υ^{AM}	$E_\upsilon^{\mathrm{exp}}$	E_υ^{AM}
	Ref.[5]		Ref.[9]						
0	132	132.0	1103.34	1 103.340	36	7 555	7 554.8		60 171.098
1	392	392.7	3287.21	3 287.210	37	7 704	7 704.4		61 177.636
2	649	650.0	5440.80	5 440.800	38	7 851	7 850.8		62 137.169
3	903	904.0	7564.08	7 564.080	39	7 994	7 993.9		63 046.698
4	1 154	1 154.6	9657.02	9 657.020	40	8 134	8 133.6		63 902.783
5	1 402	1 402.0	1 1719.59	11 719.593	41	8 270	8 270.0		64 701.497
6	1 646	1 646.1	1 3751.77	13 751.769	42	8 403	8 402.9		65 438.374
7	1 887	1 887.1	1 5753.52	15 753.515	43	8 532	8 532.2		66 108.356
8	2 125	2 124.9	1 7724.80	17 724.800	44	8 658	8 658.0		66 705.735
9	2 360	2 359.7	1 9665.59	19 665.586	45	8 780	8 780.0		67 224.092
10	2 592	2 591.3	2 1575.84	21 575.837	46	8 898	8 898.4		67 656.231
11	2 820	2 820.0	2 3455.51	23 455.514	47	9 013	9 012.9		67 994.113
12	3 046	3 045.5	2 5304.58	25 304.575	48	9 124	9 123.6		68 228.782
13	3 268	3 268.0	2 7122.98	27 122.980	49	9 231	9 230.2		68 350.287
14	3 488	3 487.5	2 8910.69	28 910.686	50	9 333	9 332.7		
15	3 704	3 703.9	3 0667.65	30 667.650	51	9 432	9 431.1		
16	3 918	3 917.4	3 2393.83	32 393.825	52	9 526	9 525.2		
17	4 128	4 127.8	3 4089.16	34 089.160	53	9 615	9 615.0		
18	4 335	4 335.2	3 5753.61	35 753.600	54	9 701	9 700.3		
19	4 540	4 539.7		37 387.080	55	9 782	9 781.2		
20	4 741	4 741.1		38 989.523	56	9 858	9 857.4		
21	4 939	4 939.5		40 560.833	57	9 929	9 929.0		
22	5 135	5 135.0		42 100.894	58		9 995.9		
23	5 327	5 327.5		43 609.556	59		10 057.9		
24	5 517	5 517.0		45 086.635	⋮		⋮		
25	5 703	5 703.5		46 531.894	71		10 433.3		
26	5 887	5 887.0		47 945.040	72		10 436.9		
27	6 067	6 067.4		49 325.705	73		10 437.4		
28	6 245	6 245.0		50 673.433					
29	6 419	6 419.4		51 987.668					
30	6 591	6 590.8		53 267.726					
31	6 759	6 759.2		54 512.784					
32	6 925	6 924.6		55 721.850					
33	7 087	7 086.8		56 893.743					
34	7 246	7 246.0		58 027.062					
35	7 402	7 402.0		59 120.157					
$D_e^{\mathrm{exp*}}$							10464$^{\mathrm{b)}}$		68353.8209

Table 1 （continued）

υ	O_2^+ - A $^2\Pi_u$		F_2^+ - X $^2\Pi_g$			BeH^+ - X $^1\Sigma^+$	
	$E_\upsilon^{\mathrm{exp}}$	E_υ^{AM}	$E_\upsilon^{\mathrm{exp}}$	E_υ^{AM}	$E_\upsilon^{\mathrm{GVBCI}^d}$	$E_\upsilon^{\mathrm{exp}}$	E_υ^{AM}
	Ref.[13]		Ref.[4]		Ref.[4]	Ref.[7]	
0	446.15	446.150	542.00	542.000	462.00	1 100.84	1 100.838
1	1 317.65	1 317.650	1 613.00	1 613.000	1 433.00	3 240.93	3 240.935
2	2 161.87	2 161.893	2 666.00	2 666.000	2 449.00	5 300.13	5 300.127
3	2 978.86	2 978.842	3 702.00	3 700.986	3 461.00	7 277.24	7 277.240
4	3 768.51	3 768.510	4 718.00	4 718.000	4 458.00	9 171.00	9 171.002
5	4 530.98	4 530.945	5 717.00	5 717.101	5 435.00	10 979.99	10 979.986
6	5 266.22	5 266.220	6 699.00	6 698.345	6 395.00	12 702.56	12 702.561
7	5 974.34	5 974.421	7 662.00	7 661.765	7 334.00	14 336.85	14 336.846
8	6 655.30	6 655.642	8 608.00	8 607.368	8 225.00	15 880.68	15 880.679
9	7 309.91	7 309.980	9 535.00	9 535.136	9 160.00	17 331.60	17 331.599
10	7 937.52	7 937.520	10 445.00	10 445.030	10 050.00	18 686.81	18 686.847
11	8 538.63	8 538.335	11 337.00	11 337.000	10 926.00		19 943.390
12	9 112.47	9 112.470	12 211.00	12 211.000	11 788.00		21 097.964
13	9 659.93	9 659.930	13 067.00	13 067.000	12 632.00		22 147.156
14	10 180.76	10 180.663	13 905.00	13 905.000	13 459.00		23 087.511
15	10 674.54	10 674.540	14 725.00	14 725.042	14 265.00		23 915.672

Table 1 （continued）

υ	O_2^+ - A $^2\Pi_u$		F_2^+ - X $^2\Pi_g$			BeH^+ - X $^1\Sigma^+$	
	E_υ^{exp}	E_υ^{AM}	E_υ^{exp}	E_υ^{AM}	$E_\upsilon^{GVBCI\,d}$	E_υ^{exp}	E_υ^{AM}
	Ref.[13]		Ref.[4]		Ref.[4]	Ref.[7]	
16		11 141.325	15 527.217				24 628.570
17		11 580.645	16 311.671				25 223.643
18		12 374.469	17 078.601				25 699.115
19		12 727.143	17 828.247				26 054.311
20		13 048.575	18 560.867				26 290.033
21		13 336.942	19 276.717				26 408.994
22		13 589.920	19 976.000				26 416.305
23		13 804.576	20 658.817				
24		13 977.265	21 325.095				
25		14 103.501	21 974.500				
26		14 177.823	22 606.333				
27		14 193.638	23 219.409				
28			23 811.909				
⋮		⋮	⋮				⋮
36			27 229.692				
37			27 348.500				
D_e^{exp*}		14 195.352[c]	27 472.841				26 426.637

Note: E_υ^{exp} are experimental data from literature, E_υ^{AM} are AM energies;

* $D_e^{exp} = D_0^{exp} + \varepsilon(0)$, D_0^{exp} is from Ref.[8], $\varepsilon(0)$ is zero point energy;

[a] E_υ^{Theo} is SCF-CPP data, [b] from Ref.[12];

[c] from Ref.[3], [d] from Ref.[4] using GVB-CI.

The AM vibrational spectroscopic constants and the full vibrational energy spectra $\{E_\upsilon^{AM}\}$ of the CO^+ - X $^2\Sigma^+$ state are given in Table 1. Obviously, the AM full vibrational energy spectra $\{E_\upsilon^{AM}\}$ generated by Coxon and Foster's experimental data $[E_\upsilon^{exp}]$ [9] not only can reproduce the input energies very well, but the percentage error between the maximum energy $E_{\upsilon_{max}}^{AM} = 68\,350.287$ cm^{-1} ($\upsilon_{max} = 49$) and the dissociation energy D_e^{exp} [8] of this state is just $5.1702 \times 10^{-3}\%$. Moreover, the RKR potential of this state given by Coxon and Foster [9] based on experimental energy subset $[E_\upsilon^{exp}]$ failed to describe the physical performance close to dissociation region. As a result, the complete RKR potential generated by the AM full vibrational energy spectra in our work is presented here, and is shown in Fig.1.

The spectroscopic properties and vibrational structure of F_2^+ - X $^2\Pi_g$ state has been studied for a long time. The GVB-CI energies [4] evaluated by Cartwright et al is given in Table 1. As we can see, the GVB-CI values of which the absolute error with the accurate experimental energies $[E_\upsilon^{exp}]$ [4] was about 80 cm^{-1} at zero point energy, did not accurately represent the vibrational information of this state. The AM full vibrational energy spectra is listed in Table 1. It is shown that the AM energies can reproduce the experimental energies excellently, and that the percentage error between the maximum vibrational energy of AM and the experimental dissociation energy D_e^{exp} [8] of this state is just 0.452 6 %. So, the AM vibrational spectroscopic constants and the full vibrational energy spectra satisfying the requirements Eqs.(4)–(8) are better than GVB-CI results.

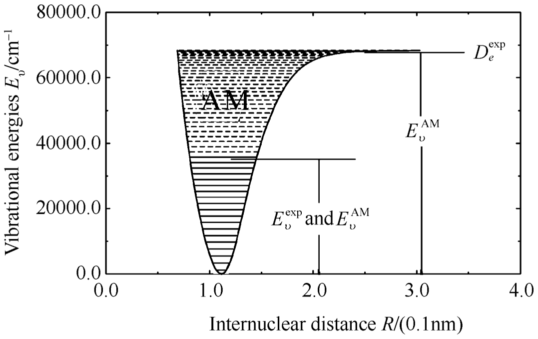

Fig.1 RKR potential, vibrational energies $\{E_\upsilon^{exp}\}$ and $\{E_\upsilon^{AM}\}$ for the X $^2\Sigma^+$ state of CO^+ Experimental vibrational energies $[E_\upsilon^{exp}]$ are from Ref. [12], $\{E_\upsilon^{AM}\}$ is full vibrational energy spectra of AM. D_e^{exp} is experimental dissociation energy.

The AM vibrational spectroscopic constants and the full vibrational energy spectra of the $O_2^+ - A\,^2\Pi_u$ state are also given in Table 1. The absolute error between AM spectra

Table 2 Vibrational spectroscopic constants, maximum vibrational quantum numbers $\upsilon_{\max}$, maximum vibrational energy $E_{\upsilon_{\max}}$ and experimental dissociation energy $D_e^{\exp}$ for electronic states of some diatomic molecular ions XY^+ (all quantities but $\upsilon_{\max}$ are in cm^{-1}).

State		ω_0	ω_{e0}	ω_e	$\omega_e x_e$	$10^2\omega_e y_e$	$10^3\omega_e z_e$	$10^4\omega_e t_e$	$10^5\omega_e s_e$	$10^8\omega_e r_e$	$\upsilon_{\max}$	$E_{\upsilon_{\max}}$	$D_e^{\exp}$
$O_2^+-A^2\Pi_u$	AM	0.207 6	2.662 0	898.662 0	13.539 5	−3.150 1	4.225 3	−2.295 6	0.804 6	−16.202 9	28	14 193.638	
	Ref.[3]			896.00	13.568^a						20^a		14 195.35
	Ref.[8]			898.25	13.573						12$^\diamond$	6 904.205$^\diamond$	
$F_2^+-X^2\Pi_g$	AM	−0.219 0	−0.005 9	1 088.894 1	8.891 4	−4.571 4	8.383 9	−6.530 7	2.280 7	−2 890.63	37	27 348.500	
	Ref.[14]			1 088.90	8.96						15	14 725.00	
	Ref.[8]			1 073.3	9.13						53$^\diamond$	47 047.5$^\diamond$	27 472.84*
$BeH^+-X^1\Sigma^+$	AM	0.804 1	−1.783 0	2 219.917 0	39.604 0	−18.982 1	1.619 1	−4.065 6	−1.081 1	68.893 3	22	26 416.305	
	Ref.[15]			2 221.7	39.79	−2.10							
	Ref.[18]			2 221.7	39.79						41$^\diamond$	74 889.5$^\diamond$	26 426.64*
$CO^+-X^2\Sigma^+$	AM	0.060 7	−0.033 2	2 214.116 8	15.112 8	−0.704 9	0.407 9	−0.363 0	0.140 2	−2.148 8	49	68 350.287	
	Ref.[16]			2 214.15	15.150	0.66^b							
	Ref.[8]			2 214.24	15.164						57$^\diamond$	102 934.8$^\diamond$	68 353.82*
$Li_2^+-X^2\Sigma_g^+$	AM	0.282 4	0.573 5	264.333 5	1.805 5	1.840 9	−0.701 8	0.167 5	−0.021 8	0.106 5	73	10 437.390	
	Ref.[5]			263.76	1.646						57	9 929	10 464.0^c

Note: [a]from Ref.[17], [b] from Ref.[2], [c] from Ref.[12];

* $D_e^{\exp}=D_0^{\exp}+\varepsilon(0)$ except extra explanation, $D_0^{\exp}$ are from Ref.[8], $\varepsilon(0)$ is zero point energy;

◇ Calculated vibrational quantum numbers $\upsilon_{\max}$ ◇and vibrational energy $E_{\upsilon_{\max}}$ ◇ using vibrational spectroscopic colstants from Ref.[8].

$\left\{E_{\upsilon}^{\mathrm{AM}}\right\}$ and the experimental energies $\left[E_{\upsilon}^{\exp}\right]$ is no more than 0.34 cm^{-1}. The percentage error between the maximum vibrational energy of AM and the dissociation energy $D_e^{\exp}$ [3] is just 1.207 4×10^{-2}%.

The theoretical vibrational energies $\left[E_{\upsilon}^{\mathrm{Theo}}\right]$ of the $\mathrm{Li}_2^+ \text{-} \mathrm{X}^2\Sigma_g^+$ state was evaluated by Schmidt-Mink *et al.* using self consistent field-core polarization potentials method （SCF-CPP）[5] based on the Born-Oppenheimer approximation . At the same time, the difference between the maximum vibrational energy of SCF-CPP $E_{\upsilon_{57}}^{\mathrm{Theo}} = 9\,929\ \mathrm{cm}^{-1}$ and the experimental dissociation energy $D_e^{\exp} = 10\ 464\ \mathrm{cm}^{-1}$ [12] is huge, largely because the Born-Oppenheimer approximation breakdowns at the region of high-lying vibrational and rovibrational energies nearly reaching to dissociation energy, where the nuclear kinetic energy is getting larger, and all kinds of coupling interactions are non-negligible, thus unavoidably producing the notable errors in SCF-CPP.

4 Conclusions

The accurate vibrational spectroscopic constants and the corresponding full vibrational energy spectra of the $\mathrm{BeH}^+ \text{-} \mathrm{X}^1\Sigma^+$， $\mathrm{CO}^+ \text{-} \mathrm{X}^2\Sigma^+$， $\mathrm{F}_2^+ \text{-} \mathrm{X}^2\Pi_g$， $\mathrm{O}_2^+ \text{-} \mathrm{A}^2\Pi_u$ and $\mathrm{Li}_2^+ \text{-} \mathrm{X}^2\Sigma_g^+$ states are first obtained using the algebraic method（AM）. The applied studies of the electronic states of these five diatomic molecular ions XY^+, covering homo-nuclear ions and hetero-nuclear ions in ground states and /or in excited states, show that the AM technique can give the correct full vibrational energy spectra which, in addition to accurately reproducing all the known energies of experiment or quantum theory, include those energies of more excited vibrational states involving the maximum vibrational energy $E_{\upsilon_{\max}}^{\mathrm{AM}}$ immediate to the dissociation energy of the system concerned, which may not be easily determined experimentally or theoretically. In conclusion, our research may provide reliable data for studies requiring accurate vibrational spectroscopic constants and high-lying excited vibrational states of the electronic states for diatomic molecular ions.

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