

Method for studying diatomic rovibrational spectra at a given vibrational state

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Received August 13, 2018; accepted October 11, 2018; published online February 14, 2019

An algebraic method for rotational energies at a given vibrational state (AMr(v)) is proposed in this study in order to obtain unknown high-lying rovibrational energies. Applications of this method to the ground electronic state $X^1\Sigma^+$ of CO and the excited state $C^1\Sigma^+$ of $^{39}\text{K}^7\text{Li}$ molecules show the following: (1) the AMr(v) can give the rational upper limit J of a rotational quantum number of a diatomic electronic state; (2) the full AMr(v) rovibrational energies $\{E_{vJ}\}_v$ of given vibrational states not only reproduce all known experimental data excellently but also predict precisely the values of all high-lying rovibrational energies, which may not be available experimentally.

rovibrational energies, diatomic systems, algebraic method

PACS number(s): 33.20.Sn, 33.20.Vq, 33.15.Mt

Citation: Y. Zhang, W. G. Sun, J. Fu, Q. C. Fan, J. Ma, L. T. Xiao, and S. T. Jia, Method for studying diatomic rovibrational spectra at a given vibrational state, *Sci. China-Phys. Mech. Astron.* **62**, 943011 (2019), <https://doi.org/10.1007/s11433-018-9311-3>

1 Introduction

Molecular rovibrational spectra are indispensable for studying molecular spectral structures and the molecular dynamics [1-3]. Molecular rotations may cause molecular anisotropic phenomena, which are very important in investigating molecular collisions and reactions. Accurate information on full rovibrational spectra is crucial for calculating molecular reaction cross-sections and reaction rates [4], as well as assigning molecular spectroscopic bands and identifying astronomic materials. In particular, highly excited rovibrational levels are essential for intramolecular

vibrational redistribution and collision energy transfer [5-7].

However, it is usually difficult to obtain accurate values of high-lying rovibrational levels for many molecular electronic states [8-11] because of the limitations in the experimental measurements. Although some diatomic rovibrational levels can be obtained quantum-mechanically [12-16], accurate high-lying rovibrational energies are still rarely given theoretically because of basic approximations used in the different quantum methods.

Recently, Sun et al. [17] have proposed an algebraic method for rotational energies (AMr) to study theoretically rotational energies $[\varepsilon_J]$ and rovibrational interaction energies $[\varepsilon_{vJ}^{\text{int}}]$ based on some known accurate experimental rovibra-

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tional spectra $[E_{vJ}^{\text{exp}}]$. Although the AMr obtained the correct rotational energies $[\varepsilon_J]$ and rovibrational interaction energies $[\varepsilon_{vJ}^{\text{int}}]$ of some electronic systems, the high-lying rovibrational energies of highly excited rotational states (J') for given vibrational states v 's were still not acquired. One of the main obstacles in obtaining them was that the upper boundary (limit) of the rotational states (J') for a given vibrational state v could not be estimated based on molecular spectroscopic theory. The present study solves this problem, and we propose a novel algebraic method for rotational energies at given vibrational states (AMr(v)) that allows us to obtain the high-lying rotational energies $[E_{vJ}]_v$ of given v , which may not be otherwise obtained experimentally and theoretically. Sect. 2 presents the AMr(v) method. Sect. 3 studies the high-lying rovibrational energies of $\text{CO}-X^1\Sigma^+$ and $^{39}\text{K}^7\text{Li}-C^1\Sigma^+$ systems using the AMr(v). Finally, sect. 4 concludes this study.

2 Theoretical method

The non-relativistic expression of rovibrational energies for a stable diatomic molecular electronic state can be given as the Dunham formula [18]:

$$\begin{aligned} E_{vJ} &= \sum_{i,k} Y_{ik} \left(v + \frac{1}{2} \right)^i [J(J+1) - A^2]^k \\ &= \sum_k \mathbf{X}_{vJ} [J(J+1) - A^2]^k, \end{aligned} \quad (1)$$

where \mathbf{X}_{vJ} stands for the component of the molecular-constant vector $\mathbf{X}_v = (G_v, B_v, -D_v, H_v, \dots)$ at a given rotational state J , which appears in the Herzberg equation [19]

$$\begin{aligned} E_{vJ} &= G_v + B_v[J(J+1) - A^2] - D_v[J(J+1) - A^2]^2 \\ &\quad + H_v[J(J+1) - A^2]^3 + \dots \end{aligned} \quad (2)$$

The expressions of \mathbf{X}_{vJ} are

$$G_v = \sum_{i=0}^m Y_{i0} \left(v + \frac{1}{2} \right)^i, \quad (3)$$

$$B_v = \sum_{i=0}^m Y_{i1} \left(v + \frac{1}{2} \right)^i, \quad (4)$$

$$D_v = -\sum_{i=0}^m Y_{i2} \left(v + \frac{1}{2} \right)^i \dots \quad (5)$$

The algebraic method for rotational energies at a given vibrational state (AMr(v)) is proposed based on the methodology of the algebraic method for vibrational energies (AMv) [20-22], and it starts by rewriting eq. (2) into a matrix form

$$A\mathbf{X}_v = E_v + \delta E_v = \mathbf{E}'_v, \quad (6)$$

where

$$\begin{aligned} A_{Jk} &= [J(J+1) - A^2]^k, \quad \mathbf{X}_v = \begin{pmatrix} G_v \\ B_v \\ -D_v \\ \vdots \end{pmatrix}_{n \times 1}, \\ \mathbf{E}'_v &= \begin{pmatrix} E_{vJ_0} + \delta E_{vJ_0} \\ E_{vJ_1} + \delta E_{vJ_1} \\ E_{vJ_2} + \delta E_{vJ_2} \\ \vdots \end{pmatrix}_{n \times 1}, \end{aligned} \quad (7)$$

and δE_v is a small variational term to offset any possible experimental error, as mentioned in ref. [22]. Of course, if the experimental data are accurate enough, $\delta E_v \equiv 0$ could be set to increase the computation speed of the $\text{CO}-X^1\Sigma^+$ and $^{39}\text{K}^7\text{Li}-C^1\Sigma^+$ systems below.

Since, for some given vibrational state v , modern laser spectroscopic technologies can almost always obtain an energy subset consisting of m rovibrational energies $[E_{vJ}^{\text{exp}}]_m$ of a diatomic electronic state for m rotational states J 's, $n (< m)$ of the m experimental rovibrational energies could be chosen and used to solve eq. (6) using the standard algebraic method. Then, the C_m^n molecular-constant vectors $\mathbf{X}_v = (G_v, B_v, -D_v, H_v, \dots)$ are obtained using C_m^n groups of energies $(E_{vJ}^{\text{exp}})_n$. One of the C_m^n vectors best satisfies the following physical criteria

$$\overline{\Delta E(e, c)} = \sqrt{\frac{1}{m} \sum_{J=0}^{m-1} |E_{vJ, \text{exp}} - E_{vJ, \text{cal}}|^2} \rightarrow 0, \quad (8)$$

$$E_{v+1, J} > E_{v, J}, \quad (9)$$

$$E_{v, J+1} > E_{v, J}, \quad (10)$$

$$N_J(v+1) \leq N_J(v) < \mathcal{J}, \quad (11)$$

$$\delta E_{vJ_i} \rightarrow \text{sufficiently small}, \quad (12)$$

$$E_{\min}(J) < E_{vJ} < E_{\max}(J), \quad (13)$$

where ‘‘exp’’ stands for ‘‘experimental data’’ and ‘‘cal’’ indicates ‘‘calculated data’’. $N_J(v)$ in eq. (11) denotes the number of possible rovibrational levels at any given vibrational state v , and the symbol \mathcal{J} represents the maximum rotational quantum number of the given electronic state. The physical value of \mathcal{J} may be determined as follows.

Any bound rovibrational energy E_{vJ} must satisfy the radial Schrodinger equation of a diatomic system

$$\left\{ -\frac{\hbar^2}{2\mu} \frac{d^2}{dr^2} + U(r) + \frac{[J(J+1) - A^2]\hbar^2}{2\mu r^2} \right\} \varphi(r) = E_{vJ} \varphi(r), \quad (14)$$

with the effective potential

$$V_J(r) = U(r) + \frac{[J(J+1) - A^2]\hbar^2}{2\mu r^2}, \quad (15)$$

where $U(r)$ is the total electron (potential) energy, μ is the reduced mass of the two nuclei, r is the internuclear distance, J denotes the total angular momentum or the rotational quantum number, and A represents the projection of orbital angular momentum. \mathcal{J} is the rotational quantum number that makes the effective potential $V_{\mathcal{J}}(r)$ a monotonously decreasing function with r increasing to r_{\max} (as shown in Figure 1, curve $V_{J=294}$). r_{\max} is the dissociation internuclear distance of a diatomic system. Such a monotonously decreasing potential $V_{\mathcal{J}}(r)$ has no potential well and cannot hold any bound rovibrational state. Therefore, eq. (14) has no bound physical solution. In other words, any meaningful rotational quantum number J that corresponds to a bound rovibrational (rotational) energy cannot be greater than \mathcal{J} .

Since, for most stable diatomic systems, the derivative of the potential $U(r)$ is zero when r is equal to the equilibrium internuclear distance r_e or r_{\max} , $U'(r_e)=0$ and $U'(r \rightarrow r_{\max}) \approx 0$. Therefore, there must be a maximum derivative $u_{\max} = \max\{U'(r_e < r < r_{\max})\}$ between the equilibrium position r_e and the dissociation distance r_{\max} , and it has

$$\begin{aligned} V'_{\mathcal{J}}(r) &= U'(r) - \frac{[J(J+1) - A^2]\hbar^2}{\mu r^3} \\ &\leq u_{\max} - \frac{[J(J+1) - A^2]\hbar^2}{\mu r^3} \\ &\leq u_{\max} - \frac{[J(J+1) - A^2]\hbar^2}{\mu r_{\max}^3}. \end{aligned} \quad (16)$$

If the rotational quantum number J is large enough, with the derivative of the effective potential $V_{\mathcal{J}}(r)$ will always be less than zero. That is, there is no bound molecular rovibrational state at all, and this is where the definition and the value of \mathcal{J} originate from Figure 1 shows an example of this process.

$E_{\min}(J)$ and $E_{\max}(J)$ in eq. (13) are defined, respectively, as:

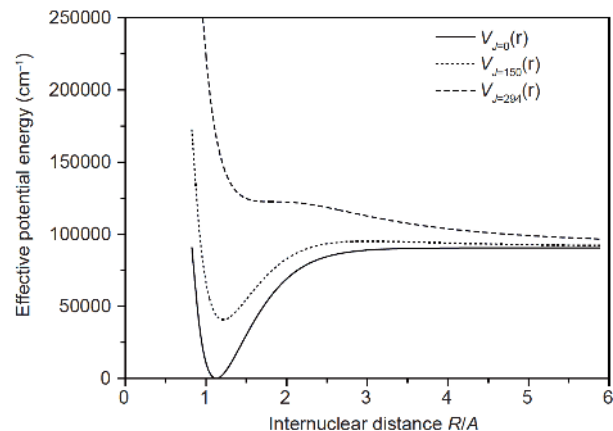


Figure 1 Effective potentials $V_{\mathcal{J}}(r)$ for a different rotational state J of the $\text{CO-X}^1\Sigma^+$ system. It is shown that the upper limit \mathcal{J} of the rotational quantum number for this system is 294.

$$E_{\min}(J) = \min\{V_{\mathcal{J}}(r)\}, \quad (17)$$

$$E_{\max}(J) = \max\{V_{\mathcal{J}}(r_e < r < r_{\max})\} + \{D_e - U(r_{\max})\}, \quad (18)$$

where $E_{\min}(J)$ is the minimum of the effective potential, and $E_{\max}(J)$ denotes the maximum of the effective potential when $r > r_e$. The second term in eq. (18) is a compensation term that is used to offset the potential truncation error, since $V_{\mathcal{J}}(\infty)$ is usually unavailable, and it also leads to the self-consistent result $E_{\max}(J=0) \equiv D_e$.

On the basis of the above definitions and discussions, one may analyze the physical criteria in eq. (8) to (13). Eq. (8) indicates that the calculated rovibrational levels should reproduce the experimentally derived levels precisely. Eqs. (9) and (10) require that the rovibrational state with the larger quantum number has the higher energy. Eq. (11) states that the number of rotational energies $N_{\mathcal{J}}(v+1)$ of a higher vibrational state $(v+1)$ should be smaller than $N_{\mathcal{J}}(v)$ of a lower v , and both are smaller than the upper limit \mathcal{J} of a given electronic state. Such a quality is consistent with the statement in ref. [19]. Eq. (12) means that the variational term $\delta E_{v,J}$ (if it is necessary to use it) should be sufficiently small so that energy $E_{v,J}$ change will be significantly smaller than the experimental error. Finally, eq. (13) represents the physical restriction that any physical bound state energy $E_{v,J}$ must stay in-between the minimum and maximum energies $E_{\min}(J)$ and $E_{\max}(J)$, respectively, of the given effective potential $V_{\mathcal{J}}(r)$ obtained by our AMv [20-22] or other methods such as accurate *ab initio* calculations. Actually, if there is no accurate potential curve $V_{\mathcal{J}}(r)$ available, the AMr(v) can still work well, just without criterion eq. (13).

The number $N_{\mathcal{J}}(v)$ of rotational energies for a given vibrational state v is determined using the physical criteria eqs. (9)-(11), and (13) together. For example, if the rovibrational energy $E_{v,J}$ predicted by eq. (6) falls outside the limits $E_{\min}(J)$ and $E_{\max}(J)$ in eq. (13), it cannot exist, which implies that $J-1$ is the last rotational level and may determine $N_{\mathcal{J}}(v)$ simultaneously. The same applies for the other physical criteria eqs. (9)-(11). If one of these criteria cannot be satisfied, the prediction stops, and $N_{\mathcal{J}}(v)$ is determined.

Figure 2 gives the calculation process of the AMr(v). For each vibrational state v , n rovibrational energies from m experimental energies are selected to calculate the molecular-constant vector $\mathbf{X}_v = (G_v, B_v, -D_v, H_v, \dots)$ and generate the rovibrational energies. If these results meet the physical criteria in eq. (8) to (13) better, they are saved, and the previous results are replaced. This process continues for all C_m^n possible selections, and the best solution X_v^{best} is found out of the C_m^n results. Then, the AMr(v) turns to the next vibrational state.

In order to show the influence of different selections and how the physical criteria work, Table 1 lists 10 different calculated rovibrational energies for the $(v=28, J=50)$ state of

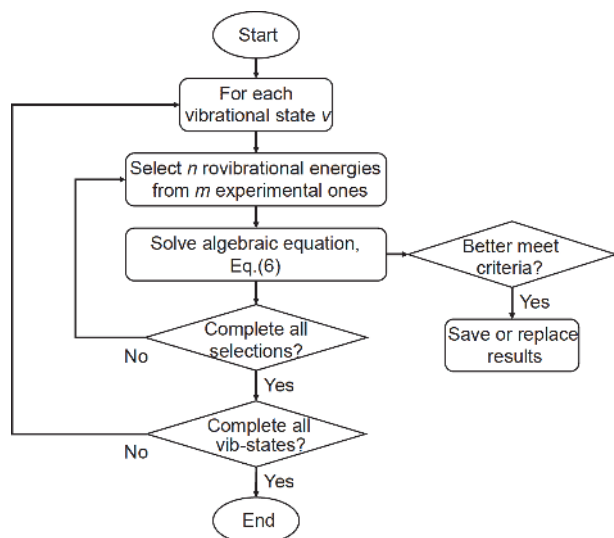


Figure 2 Calculation process diagram of the AMr(v).

Table 1 Different calculated rovibrational energies from different selections

No.	Selections J (cm^{-1})	$E_{v=28, J=50}^{\text{cal}}$	$ E_{v,J}^{\text{cal}} - E_{v,J}^{\text{exp}} $
1	{3, 5, 9, 23, 39, 46, 49}	3183.648	<0.001
2	{1, 2, 4, 6, 8, 9, 10}	3773.802	590.154
3	{8, 9, 10, 11, 13, 14, 15}	3105.730	77.918
4	{5, 8, 9, 10, 12, 13, 15}	3120.974	62.674
5	{5, 7, 8, 11, 12, 15, 17}	3260.563	76.915
6	{5, 6, 7, 12, 13, 14, 17}	3262.907	79.259
7	{20, 21, 22, 23, 24, 25, 30}	3181.888	1.760
8	{1, 2, 4, 9, 10, 23, 47}	3183.033	0.615
9	{1, 3, 5, 6, 11, 29, 49}	3183.863	0.215
10	{42, 44, 45, 46, 47, 48, 49}	3183.648	<0.001

the $^{39}\text{K}^7\text{Li}-\text{C}^1\Sigma^+$ system, which will be discussed in detail in the next section. For comparison, the first line of this table gives the result of the best selection in this study and shows that the error between the AMr(v) and the experiment-based energy is less than 0.001 cm^{-1} . However, Selection 2 (No. 2) gives a completely wrong rovibrational level not only because of its huge error compared to the experimental value but also because the energy is higher than the upper limit $E_{\text{max}}(J=50)=3694.664 \text{ cm}^{-1}$ (listed in Table S8 of the Supporting information online). Selections 3 to 6 also give large differences from the experimental data, and after careful examination in Table S8, it can be found that the energies of these selections do not meet the physical criteria of eq. (9) or (10). Selections 7 to 9 give relatively better results, but not as good as the first one. As illustrated in our previous work [21], these errors usually result from the “butterfly effect” of experimental errors in different selections. It is worth noting that, although the last selection (No. 10) generates the exact

rovibrational energy for the ($v=28, J=50$) state, its rovibrational energies for other rotational states are less accurate than the first selection. For instance, the error of Selection 1 for the ($v=28, J=0$) state is also less than 0.001 cm^{-1} , but that of selection 10 is more than 100 times greater than this. As a matter of fact, for each vibrational state, there are hundreds of concrete requirements from the physical criteria in the AMr(v) to ensure the reliability of its prediction.

Since the AMr(v) does not directly solve the diatomic Schrodinger equation using extensive orbital parameters of base functions to mimic the atomic orbital, it spends much less computational time in theoretical calculations. The mathematical and physical converging requirements in eq. (8) to (13) and the accurate experimental energies used in eq. (6) can ensure a rational and reliable prediction of the rovibrational energies. The smaller the error of the experimental energies $[E_{v,J}^{\text{exp}}]$, the better the accuracy of the predicted rovibrational energies [21,22].

It should be mentioned that the present AMr(v) has a certain application scope. First, as we stated before, eqs. (1) and (2) are non-relativistic formulae, so the current AMr(v) method may not be used to study systems with an obvious relativistic effect. Second, all of the above physical analyses are based on the Born-Oppenheimer approximation. Therefore, for the hydrogen molecule or some special degeneracies as described in ref. [23], our results may contain notable errors. Third, mathematically speaking, eqs. (1) and (2) are both expansion series, and the truncation error always exists when only finite terms are taken into account. However, with the flexible order skill [21,22], this truncation error could be suppressed well.

3 Application and discussion

The AMr(v) is applied to study the unknown high-lying rovibrational energies of the $\text{CO}-X^1\Sigma^+$ and $^{39}\text{K}^7\text{Li}-\text{C}^1\Sigma^+$ electronic systems in this section. The experiment-based rovibrational levels $E_{v,J}$ used as the input choices in the AMr(v) calculations are obtained using the Herzberg equation (eq. (2)) and the molecular constants in Table 3 of ref. [24] and in Table 2 of ref. [25] for the $\text{CO}-X^1\Sigma^+$ and $^{39}\text{K}^7\text{Li}-\text{C}^1\Sigma^+$ systems, respectively. The experiment-based energies as the input choices for the $\text{CO}-X^1\Sigma^+$ and $^{39}\text{K}^7\text{Li}-\text{C}^1\Sigma^+$ systems are listed in Tables S1 and S2, respectively. The number of known rotational states for each vibrational state v given in each table of the two systems is specified in Table 1 of ref. [24] and in Figure 2 of ref. [25], respectively. The experiment-based rovibrational energies chosen in the final converged AMr(v) studies are listed in italic bold in each table.

In order to obtain the effective potential $V_e(r)$ used to specify the two boundary limits $E_{\text{min}}(J)$ and $E_{\text{max}}(J)$ in eqs. (17) and (18) for the physical criterion in eq. (13) of the

AMr(v) study, the variational algebraic method (VAM) [22] is used to generate the full vibrational spectrum $\{E_v\}$. The calculated VAM spectra for the $\text{CO}-X^1\Sigma^+$ and $^{39}\text{K}^7\text{Li}-C^1\Sigma^+$ systems are listed in Tables S3 and S4, respectively [24-26]. The VAM Rydberg-Klein-Rees (RKR) potential curves $U(r)$ can be obtained using the full VAM vibrational spectra and the RKR procedure. The effective potentials $V_J(r)$ for a different rotational quantum number J can be obtained using eq. (15), and the value of the upper bound \mathcal{J} of the rotational quantum number of each electronic state can be found using eq. (16) as $\mathcal{J}=294$ for $\text{CO}-X^1\Sigma^+$ and as $\mathcal{J}=226$ for $^{39}\text{K}^7\text{Li}-C^1\Sigma^+$. The respective effective potentials $V_J(r)$ are shown in Figures 1 and 3.

So far, all necessary data required by the physical criteria described in eq. (8) to (13) have been prepared, and one could use the AMr(v) to study the full rovibrational levels $\{E_{vJ}\}$, including the high-lying ones that are not available experimentally for each vibrational state v . The best converged molecular constants, $\mathbf{X}_v=(G_v, B_v, -D_v, H_v, \dots)$, for the converged rovibrational levels $[E_{vJ}]$ and the number of predicted rovibrational levels $V_J(v)$ at each given vibrational state can be generated by solving eq. (6) and using the converging criteria in eq. (8) to (13) and are listed in Tables S5 and S5 for $\text{CO}-X^1\Sigma^+$ and $^{39}\text{K}^7\text{Li}-C^1\Sigma^+$, respectively. The values in parentheses of the last column of both tables are the numbers of rotational states given by refs. [24,25]. All variational terms δE_v in eq. (6) are taken as $\delta E_v \equiv 0$ for each electronic system.

It can be seen from both Tables S5 and S6 that the lowest order molecular constants (energies) G_v for every vibrational state from the AMr(v) agree perfectly with the energies, with $J=0$ in the first row of Table S1 in ref. [24] and Table S2 in ref. [25]. $V_J(v)$ from the AMr(v) gradually decreases as the vibrational quantum number increases, in agreement with the statement in Chapter 7 of ref. [19], whereas $V_J(v)$ increases with the number of rotational states shown in each parenth-

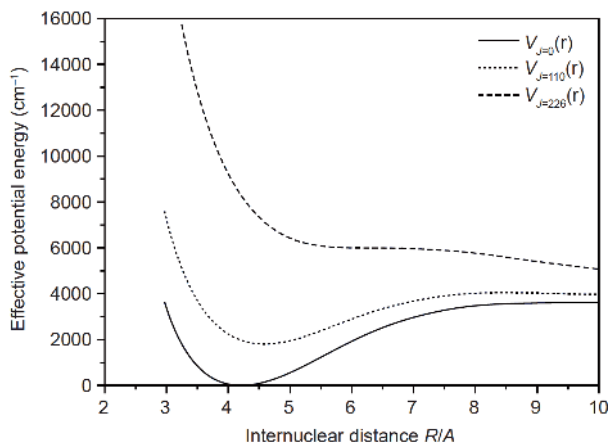


Figure 3 Effective potentials $V_J(r)$ for a different rotational state J of the $^{39}\text{K}^7\text{Li}-C^1\Sigma^+$ system. It is shown that the upper limit \mathcal{J} of the rotational quantum number for this system is 226.

esis of the last column of each table in refs. [24,25].

Tables S7 and S8 present the full AMr(v) rovibrational energies $\{E_{vJ}\}_v$ of each vibrational state for the $\text{CO}-X^1\Sigma^+$ and $^{39}\text{K}^7\text{Li}-C^1\Sigma^+$ systems, respectively. All data in these tables are exact, and they are carefully examined in our calculation.

In Tables S7 and S8, $E_{\min}(J)$ and $E_{\max}(J)$ represent the minimum and maximum of the effective potentials for each rotational state J , as described in sect. 2. It can be seen that all predicted levels are found within these two limits. It can also be observed in Tables S1, S2, S7, and S8 that the greatest difference between the experimental data and the AMr(v) energies exists in the $(v=15, J=32)$ rovibrational state for the $\text{CO}-X^1\Sigma^+$ system and the $(v=36, J=20)$ rovibrational state for the $^{39}\text{K}^7\text{Li}-C^1\Sigma^+$ system, respectively, and they are only 0.0004678 and $0.0043680 \text{ cm}^{-1}$ with 0.00000145% and 0.000126% relative errors, respectively. Therefore, the AMr(v) not only reproduces perfectly all known experimental data but also predicts correctly all high-lying rovibrational energies of given vibrational states. Thus, it is reasonable to believe that all predicted AMr(v) data have the same accuracy as the experimental data in refs. [24,25].

Finally to give an intuitive picture, Figures 4 and 5 show the full rovibrational energies $\{E_{vJ}\}_v$ in each vibrational state v for the $\text{CO}-X^1\Sigma^+$ and $^{39}\text{K}^7\text{Li}-C^1\Sigma^+$ systems, respectively. “Full lines” are the experiment-based rovibrational energies [24,25], and “dashed lines” represent the AMr(v) data. After a careful comparison, some interesting native properties of the levels can be found in these figures. First, for a given vibrational state, the rovibrational energies increase with the rotational quantum number, and they may finally even exceed the dissociation energy D_e for the $V_{J=0}(r)$ potential. Second, for the rovibrational levels with the same rotational quantum number, they also increase with the vibrational quantum number, but by contrast, the relevant increment decreases in most cases.

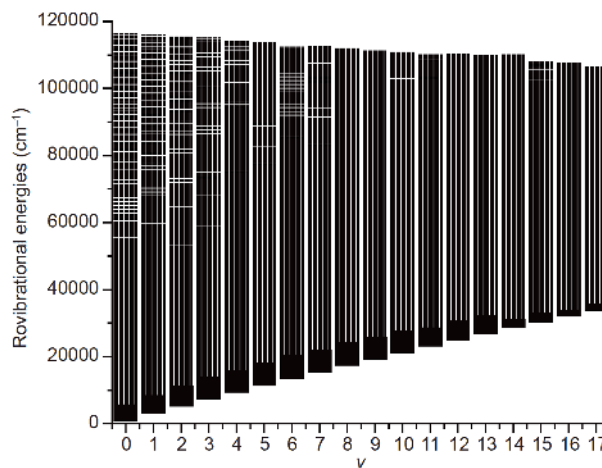


Figure 4 Full rovibrational spectra $\{E_{vJ}\}_v$ for each vibrational state of the $\text{CO}-X^1\Sigma^+$ electronic system. Full lines are the experiment-based data [24]; dashed lines represent the AMr(v) data.

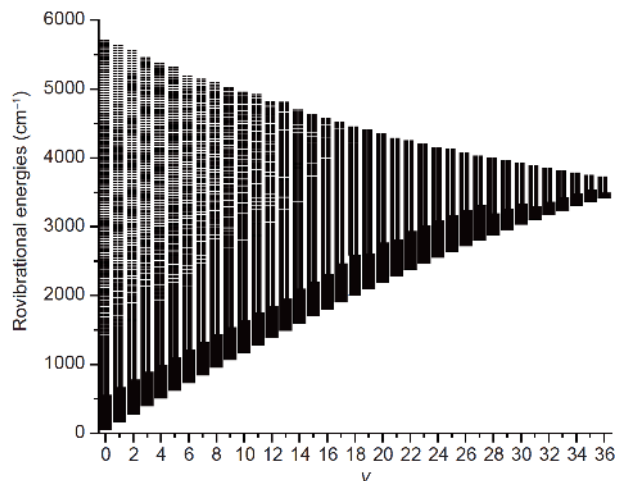


Figure 5 Full rovibrational spectra $\{E_{vJ}\}_v$ for each vibrational state of the $^{39}\text{K}^7\text{Li}-\text{C}^1\Sigma^+$ electronic system. Full lines are the experiment-based data [25]; dashed lines represent the AMr(v) data.

4 Conclusions

In summary, a novel algebraic method AMr(v) for rotational energies at a given vibrational state v is proposed, which allows us to obtain the full rovibrational energies $\{E_{vJ}\}_v$ based on some known accurate experimental energies. The AMr(v) uses a set of physical converging criteria to find the best rovibrational energies, particularly the high ones that may not be found experimentally. The applications of this method to the $\text{CO}-\chi^1\Sigma^+$ and $^{39}\text{K}^7\text{Li}-\text{C}^1\Sigma^+$ systems demonstrate the following: (1) the AMr(v) can find the upper bound \mathcal{J} of the rotational quantum number of a given electronic system and the maximum rotational quantum number J_{\max}^{cal} at the given vibrational state v ; (2) the AMr(v) can give the rotational energy boundaries, namely, the minimum and maximum values $E_{\min}(J)$ and $E_{\max}(J)$, respectively, of the effective potentials $V_J(r)$ for each rotational state J ; (3) the AMr(v) can obtain the well-converged rovibrational constants $\mathbf{X}_v=(G_v, B_v, -D_v, H_v, \dots)$ and the full rovibrational energies $\{E_{vJ}\}_v$ for the given vibrational state; and (4) the full AMr(v) rovibrational energies not only reproduce all known experimental data excellently but also correctly predict all high rovibrational energies, which may not be available experimentally.

This work was supported by the Young Scientists Fund of the National Natural Science Foundation of China (Grant No. 61701515), and the China

Postdoctoral Science Foundation (Grant No. 2017M613367).

Supporting Information

The supporting information is available online at phys.scichina.com and <http://link.springer.com/journal/11433>. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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