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Lie-algebraic approach to vibrational spectra of a linear symmetrical tetratomic molecule: C_2H_2

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Using Lie-algebraic techniques and the simpler expressions of the matrix elements of Majorana operators given by us, we obtain an effective Hamiltonian operator which conveniently describes vibrational spectra of linear tetratomic molecules, including both stretching and bending modes. For a linear symmetrical four-atom molecule C_2H_2, the highly excited vibrational levels are obtained by applying the u(4) algebraic approach. We have found that the spectra are made up of a clustering structure. The number of levels in one cluster depends on the total quantum number of stretching and bending vibrations. In addition, some other properties, such as the level assignment and the labeling of calculated theoretical results, are also discussed.

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I. INTRODUCTION

Molecular spectroscopy is an area of active interest from many standpoints. Due to its numerous connections with other scientific areas, this branch of modern physics is playing an essential role in both experimental and theoretical approaches to understanding a huge number of important problems. From the very outset, the interplay between quantum theory and experiments has revealed the importance of molecular spectroscopy. With the development of more powerful experimental techniques, such significance is getting broader-scale attention in the scientific community. In recent years, molecular spectroscopy has been going through an exciting time of renewed interest, which, once again, is being fueled by the rapid development of sophisticated experimental approaches. Recent developments include tunable, stable, and powerful lasers that are available to create complex excitation schemes, which allow for the investigation of highly excited levels with unprecedented resolution. Second, new detection techniques are constantly being developed with sensitivities far exceeding the limits of detectors used just a few years ago. Finally, a variety of molecules can be chosen among a very large number of extremely pure samples with careful initial state preparation. In such work, large-amplitude distortions of a molecule from its equilibrium configuration are frequently encountered. This leads to both a decline in the usefulness of the conventional normal mode techniques, which are based on the idea of small-amplitude motion, and a search for alternative methods. In order to deal with these problems, a local mode method contrasted with the usual normal mode analysis [1] has been developed. The theoretical description of the observed features has so far mostly focused on the study of the stretching modes. In fact, we have to consider in many cases both bending modes and stretching modes. Thus, the theoretical studies of excited vibrational states of molecules provide new challenges.

In the last few years, an algebraic method has been introduced as a computational tool for the analysis and interpretation of experimental rovibrational spectra of small- and medium-size molecules [2,3]. This method has been used extensively in chemical physics and molecular physics. This method is based on the idea of dynamic symmetry, which, in turn, is expressed through the language of Lie algebras. By applying algebraic techniques, one obtains an effective Hamiltonian operator that conveniently describes the rovibrational degrees of freedom of the physical system. Within this framework, any specific mechanism relevant to the correct characterization of the molecular dynamics and spectroscopy can be accounted for. The algebraic methods are formulated in such a way that they contain the same physical information of both *ab initio* theories (based on the solution of the Schrödinger equation) and of semiempirical approaches (making use of phenomenological expansions in powers of appropriate quantum numbers). However, by employing the powerful method of group theory, the results can be obtained in a more rapid and straightforward way. Now this approach and its hybird is used to treat polyatomic vibrations [4–9] and various other problems [10–15]. The method is so simple that one can easily compute all overtone frequencies up to the dissociation.

Detailed and systematic studies of the pattern of vibrational energy levels in gas phase molecules are of critical importance in predicting and understanding the underlying intramoleculer dynamics and of possibly one day controlling some aspects of chemical reactivity. Acetylene is a linear four-atom dihydride with thus seven normal modes of vibration and the literature on the vibrational spectroscopy of it is quite extensive [16–26]. The ν_3 fundamental of C_2H_2 by fully treating the Fermi-type interaction was discussed and its deperturbed spectroscopic parameters concerning $v_3=1$ were provided [16]. Fermi coupling and *l*-type resonance effects in the the hot bands of C_2H_2 in the 2650 cm^{-1} region were investigated [17]. Venuti and co-workers [18] studied the anharmonic quartic resonances of vibration-rotation spectra of ^{13}C containing acetylene. Using clustering models [19–22], the vibrational energy levels of $^{12}C_2H_2$, $^{12}C_2D_2$, and $^{13}C_2H_2$ were reproduced up to 12 000, 16 600, and 23 670 cm^{-1}, respectively. Experimental absorption spectra data from *Q* branch line mixing in C_2H_2, HCN, etc., were inverted to extract their respective relaxation *W* matrices [23]. Applying a two-step pump/probe technique, the Raman

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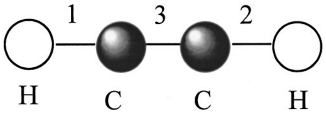

FIG. 1. Bond coordinates of acetylene.

spectra of the Q branches of the $v_1+v_2-v_2$ band of $^{12}C_2H_2$ and of the $v_1+v_2-v_2$ band of $^{13}C_2H_2$ were recorded [24]. Using a Ti:Sa autoscan laser spectrometer, a detailed investigation of individual line profiles in the v_1+3v_3 absorption band of $^{12}C_2H_2$, around 12 676 cm^{-1} were performed [25]. Self-collisional line shifts were determined using a long white-type multiple-pass cell [26].

We consider in this paper the vibrational spectrum of a linear symmetrical tetratomic molecule C_2H_2, using a dynamical algebraic approach. In Sec. II, we briefly review the theory of u(4) algebra applied to linear four-atom molecules and give the algebraic Hamiltonian of the C_2H_2 molecule. In order to improve the running speed of the computer program, we provide the simpler expressions of the matrix element of Majorana operators. In Sec. III, the fitting coefficients and calculated results are presented. Some discussions of highly excited vibrational states of C_2H_2 are given in Sec. IV. Conclusions are presented in Sec. V.

II. REVIEW OF THEORY

It is necessary to begin with a brief review of the theory. In tetratomic molecules, there are three independent vector coordinates, $\mathbf{r}_1$, $\mathbf{r}_2$, and $\mathbf{r}_3$, which can be thought of as three bonds. The general algebraic theory tells us that a quantization of these coordinates (and associated momenta) leads to the following algebra:

$$G=\mathrm{u}_1(4)\otimes\mathrm{u}_2(4)\otimes\mathrm{u}_3(4). \tag{1}$$

Here, u_i stands for a bond of tetratomic molecule, its meaning has been discussed in [15]. In order to conveniently present the general scheme, we label the bonds of acetylene as in Fig. 1. When three or more bonds are coupled with each other, a new problem arises. The problem is that one has to choose the order of coupling of the bonds. If one carries out a full calculation, the order of coupling is not important. However, in many cases, the bond-bond interactions are not all of similar strength. In the case of C_2H_2 or C_2D_2, it is convenient to couple first the two C-H (or C-D) bonds and subsequently the C-C bond. In this way, one can easily impose the symmetry condition under the interchange of the two C-H bonds (g and u labels). The algebraic basis for this coupling scheme is characterized by the quantum numbers

$$|[N_1],[N_2],[N_3]p_1p_2(p_{12},q_{12})p_3(p,q)\rangle. \tag{2}$$

Its corresponding subgroup chain is

$$\begin{aligned}&U_1(4)\otimes U_2(4)\otimes U_3(4)\\&\quad\supset O_1(4)\otimes O_2(4)\otimes O_3(4)\\&\quad\supset O_{12}(4)\otimes O_3(4)\supset O_{123}(4)\supset O_{123}(3)\supset O_{123}(2).\end{aligned} \tag{3}$$

Here, $[N_i]$ denotes the totally symmetric representation of $U_i(4)$, $(p_i,0)$ denotes the symmetrical representation of $O_i(4)$ $(i=1,2,3)$, and (p_{12},q_{12}) denotes the irreducible representation of $O_{12}(4)$. Here, N_1, N_2, and N_3 are fixed and the remaining quantum number p_1, p_2, p_3, p_{12}, q_{12}, p, q, J, and M are precisely used to characterize the states of tetratomic molecules and their degeneracies. This is a general statement which applies to any molecule. The relations between the group quantum numbers and the conventional quantum numbers of linear tetratomic molecules v_a, v_b, v_c, $v_d^{l_d}$, and $v_e^{l_e}$ are

$$p_1=N_1-2v_a,\quad p_2=N_2-2v_c,\quad p_3=N_3-2v_b, \tag{4}$$

$$p_{12}=N_1+N_2-(2v_a+2v_c+v_e),\quad q_{12}=l_e, \tag{5}$$

$$\begin{aligned}p&=N_1+N_2+N_3-(2v_a+2v_c+2v_c+v_d+v_e),\\q&=l_d+l_e.\end{aligned} \tag{6}$$

The quantum numbers v_a, v_b, and v_c denote the three local stretching modes, while $v_d^{l_d}$ and $v_e^{l_e}$ denote the two local bending modes. For linear tetratomic molecules, how the bonds are coupled becomes important. Here, we consider the coupling scheme (12)3, which emphasizes the coupling (12).

The Hamiltonian operator is constructed from the algebraic bond variables and interactions. There are three types of interactions that play a dominant role in the algebraic approach to molecular structure [15,27]:

(1) Casimir operators $C(\mathrm{o}(4))$ and their combinations, which provide the local basis.

(2) Majorana operators $M(\mathrm{u}(4))$ and their combinations, which lead from local to normal behavior.

(3) Fermi operators, F, which play a role when accidental degeneracies of Fermi type occur.

Our Hamiltonian operator is thus built only from the operators shown in (1) and (2).

The local mode Hamiltonian in the coupling scheme (12)3 is

$$\begin{aligned}H^{\mathrm{local}}=&E_0+A_1C(\mathrm{o}_1(4))+A_2C(\mathrm{o}_2(4))+A_3C(\mathrm{o}_3(4))\\&+A_{12}C(\mathrm{o}_{12}(4))+A_{13}C(\mathrm{o}_{13}(4))+A_{23}C(\mathrm{o}_{23}(4))\\&+A_{123}C(\mathrm{o}_{123}(4)),\end{aligned} \tag{7}$$

with $C(\mathrm{o}_{ij}(4))$ being the Casimir operator of $\mathrm{o}_i(4)\oplus\mathrm{o}_j(4)$ $(i,j=1,2,3)$ and $C(\mathrm{o}_{123}(4))$ being the Casimir operator of $\mathrm{o}_1(4)\oplus\mathrm{o}_2(4)\oplus\mathrm{o}_3(4)$. Here, we have deleted all terms contributing to rotational energies. It is easy to prove that the four terms and the last term in Eq. (7) are diagonal in the basis shown in Eq. (2) with eigenvalues

$$\langle C(\mathrm{o}_i(4))\rangle = p_i(p_i+2), \quad (i=1,2,3), \tag{8}$$

$$\langle C(\mathrm{o}_{12}(4))\rangle = p_{12}(p_{12}+2)+q_{12}^2, \tag{9}$$

$$\langle C(\mathrm{o}_{123}(4))\rangle = p(p+2)+q^2. \tag{10}$$

But the fifth and the sixth terms are not. However, it is straightforward to compute their matrix elements, since the operators $C(\mathrm{o}_{13}(4))$ and $C(\mathrm{o}_{23}(4))$ are diagonal in coupling schemes $(13)2$ and $(23)1$, respectively. The corresponding matrix elements are given by [27]

$$\begin{aligned}&\langle p_1'p_2'(p_{12}',q_{12}')p_3'(p',q')L'M'|C(\mathrm{o}_{13}(4))|p_1p_2(p_{12},q_{12})p_3(p,q)LM\rangle\\&\quad=\delta_{(p_1',p_1)}\delta_{(p_2',p_2)}\delta_{(p_3',p_3)}\delta_{(p',q')(p,q)}\delta_{(L',M')(L,M)}\sum_{p_{13},q_{13}}\langle p_1p_2(p_{12},q_{12})p_3(p,q)|p_1p_3(p_{13},q_{13})p_2(p,q)\rangle\\&\qquad\times\langle p_1p_2(p_{12}',q_{12}')p_3(p,q)|p_1p_3(p_{13},q_{13})p_2(p,q)\rangle(p_{13}(p_{13}+2)+q_{13}^2)\end{aligned}\tag{11}$$

and

$$\begin{aligned}&\langle p_1'p_2'(p_{12}',q_{12}')p_3'(p',q')L'M'|C(\mathrm{o}_{23}(4))|p_1p_2(p_{12},q_{12})p_3(p,q)LM\rangle\\&\quad=\delta_{(p_1',p_1)}\delta_{(p_2',p_2)}\delta_{(p_3',p_3)}\delta_{(p',q')(p,q)}\delta_{(L',M')(L,M)}\sum_{p_{23},q_{23}}\langle p_1p_2(p_{12},q_{12})p_3(p,q)|p_2p_3(p_{23},q_{23})p_1(p,q)\rangle\\&\qquad\times\langle p_1p_2(p_{12}',q_{12}')p_3(p,q)|p_2p_3(p_{23},q_{23})p_1(p,q)\rangle(p_{23}(p_{23}+2)+q_{23}^2).\end{aligned}\tag{12}$$

Here, $\langle p_1,p_2(p_{12},q_{12})p_3(p,q)|p_1,p_3(p_{13},q_{13})p_2(p,q)\rangle$ and the similar terms in Eqs. (11) and (12) are the recoupling coefficient of $\mathrm{so}(4)$. In order to consider the splitting of the degenerate C-H stretching modes into g and u species and of all combination modes and overtones, Majorana operators must be added. The corresponding Hamiltonian is then given by

$$H=H^{\mathrm{local}}+\lambda_{12}M_{12}+\lambda_{13}M_{13}+\lambda_{23}M_{23}. \tag{13}$$

Here, M_{12}, M_{13}, and M_{23} are Majorana operators. Their matrix element expressions can be found in Ref. [27]; however, we have obtained their new matrix element expressions [29]. They are so much simpler that the calculating speed can be improved. The expression of M_{12} is

$$\begin{aligned}&\langle[N_1],[N_2],[N_3]p_1p_2(p_{12},q_{12})p_3(p,q)LM|M_{12}|[N_1],[N_2],[N_3]p_1'p_2'(p_{12}',q_{12}')p_3'(p',q')L'M'\rangle\\&\quad=\delta_{(p_3',p_3)}\delta_{(p_{12}',q_{12}')(p_{12},q_{12})}\delta_{(p',q')(p,q)}(-1)^{p_1'+p_2+p_{12}}\begin{Bmatrix}\frac{1}{2}p_1 & \frac{1}{2}p_2 & \frac{1}{2}(p_{12}+q_{12})\\ \frac{1}{2}p_2' & \frac{1}{2}p_1' & 1\end{Bmatrix}\begin{Bmatrix}\frac{1}{2}p_1 & \frac{1}{2}p_2 & \frac{1}{2}(p_{12}-q_{12})\\ \frac{1}{2}p_2' & \frac{1}{2}p_1' & 1\end{Bmatrix}\\&\qquad\times\langle[N_1](p_1,0)||T^{[211]}_{1(2,0)}||[N_1](p_1',0)\rangle\langle[N_2](p_2,0)||T^{[211]}_{2(2,0)}||[N_2](p_2',0)\rangle.\end{aligned}\tag{14}$$

The expressions of M_{13} and M_{23} can be found in Ref. [29]. For C_2H_2, the calculation shows that M_{12} plays an important role. However, M_{13} and M_{23} do not. So we only consider M_{12} in our Hamiltonian operator.

For linear tetratomic molecules, an important problem is that of vibrational l-doubling. This case appears in the combination modes of the bending modes $v_4^{l_4}$ and $v_5^{l_5}$. In the algebraic approach, there is a class of operators leading naturally to l-splitting, which are denoted by $\overline{C}$. Hence, the l-splitting algebraic Hamiltonian is

$$H^{l\text{-split}}=d_{12}\overline{C}_{12}^2+d_{13}\overline{C}_{13}^2+d_{23}\overline{C}_{23}^2+d_{123}\overline{C}_{123}^2. \tag{15}$$

The first and the fourth terms in this Hamiltonian shown in Eq. (14) are diagonal in the local basis and have the corresponding eigenvalues

$$\langle\overline{C}_{12}^2\rangle=|q_{12}(p_{12}+1)|^2, \tag{16}$$

$$\langle\overline{C}_{123}^2\rangle=|q(p+1)|^2, \tag{17}$$

but the second and the third terms are not. The matrix elements can be obtained by using the method similar to the operator $C(\mathrm{o}_{13}(4))$ shown in Eq. (11). So the Hamiltonian for tetratomic molecules can be written as

$$H=H^{\mathrm{local}}+H^{l\text{-split}}+\lambda_{12}M_{12}+\lambda_{13}M_{13}+\lambda_{23}M_{23}. \tag{18}$$

To improve the accuracy of the calculation of vibrational levels of linear tetratomic molecules, higher-order operators should be added. Finally, we can write the Hamiltonian, which includes the local part, the l-splitting part, Majorana interactions, and part of higher-order terms, as

TABLE I. The fitting parameters of C_2H_2.[a]

X_2Y_2	C_2H_2	
$N_1=N_2$	43	43
N_3	137	137
A_1	$-0.190\,151\,05(+2)$	$-0.189\,678\,25(+2)$
A_3	$-0.358\,854\,62(+1)$	$-0.357\,627\,80(+1)$
A_{12}	$-0.202\,586\,51(0)$	$-0.166\,056\,93(0)$
A_{123}	$-0.136\,850\,30(+1)$	$-0.138\,258\,57(+1)$
λ_{12}	$0.884\,073\,20(0)$	$0.940\,331\,20(0)$
d_{12}	$0.103\,750\,96(-4)$	$0.744\,059\,35(-4)$
d_{13}	$0.103\,635\,72(-3)$	$0.978\,136\,86(-4)$
d_{123}	$0.247\,455\,91(-4)$	$-0.485\,283\,46(-4)$
x_1		$0.112\,540\,171(-4)$
x_3		$0.803\,117\,53(-4)$
x_{12}		$0.679\,368\,41(-4)$
x_{123}		$-0.194\,719\,22(-4)$
$\overline{x}_{13}$		$0.385\,086\,11(-3)$
y_1		$-0.170\,614\,11(-3)$
y_2		$0.119\,392\,48(-3)$
y_3		$0.116\,150\,94(-3)$

[a] All parameters are in cm^{-1} except N_1, N_3, which is dimensionless.

$$\begin{aligned}H={}&A_1C_1+A_2C_2+A_3C_3+A_{12}C_{12}+A_{13}C_{13}+A_{23}C_{23}\\&+A_{123}C_{123}\lambda_{12}M_{12}+\lambda_{13}M_{13}+\lambda_{23}M_{23}+d_{12}\overline{C}_{12}{}^2\\&+d_{13}\overline{C}_{13}^2+d_{23}\overline{C}_{23}^2+d_{123}\overline{C}_{123}^2+\overline{x}_{13}(C_1+C_2)C_3+x_1C_1^2\\&+x_2C_2^2+x_3C_3^2+x_{12}C_{12}^2+x_{123}C_{123}^2\\&+y_1(C_1+C_2)M_{12}+y_2C_{12}M_{12}+y_3C_{123}M_{12}.\end{aligned}\tag{19}$$

Here, A_i, x_i, y_i, A_{ij}, x_{ij}, d_{ij} $(i,j=1,2,3)$, A_{123}, $\overline{x}_{12}$, and x_{123} are the expansion coefficients, which can be determined by spectroscopic dates. For linear symmetrical tetratomic molecules, we have $N_1=N_2$, $A_1=A_2$, $A_{13}=A_{23}$, $x_1=x_2$, $d_{13}=d_{23}$, and $\lambda_{13}=\lambda_{23}$. For the C_2H_2 molecule, we do not consider the operators M_{13} and M_{23}. Here, C_i, C_{ij}, and C_{123} $(i,j=1,2,3)$ are so-called reduced Casimir operators, which can be written as

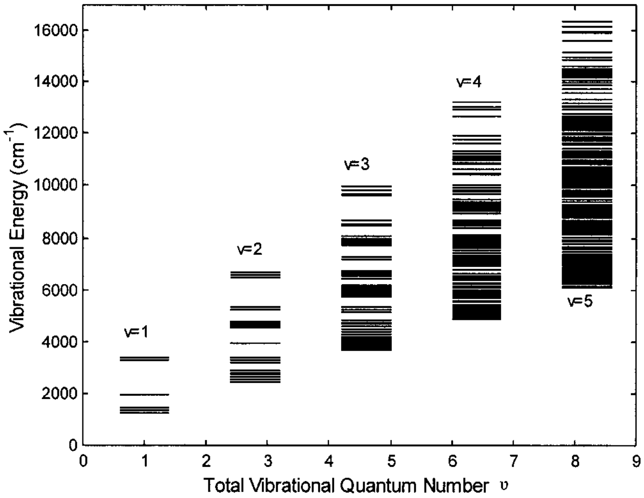

FIG. 2. Σ band vibrational energy levels of C_2H_2 vs total quantum numbers.

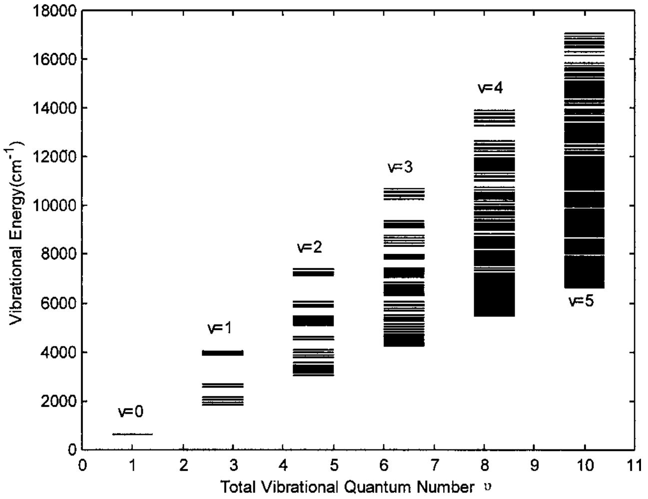

FIG. 3. Π band vibrational energy levels of C_2H_2 vs total quantum numbers.

$$C_i=C(o_i(4))-N_i(N_i+2)\quad(i=1,2,3),\tag{20}$$

$$C_{ij}=C(o_{ij}(4))-(N_i+N_j)(N_i+N_j+2)\quad(i,j=1,2,3),\tag{21}$$

$$\begin{aligned}C_{123}={}&C(o_{123}(4))-(N_1+N_2+N_3)\\&\times(N_1+N_2+N_3+2).\end{aligned}\tag{22}$$

III. CALCULATION DETAILS

Now we use the u(4) algebraic model to study the vibrational spectra, including the stretching and bending vibrations of molecule C_2H_2. The first fitting includes the eight parameters: A_1, A_3, A_{12}, A_{123}, λ_{12}, d_{12}, d_{13}, and d_{123}. The second fitting includes 16 parameters, in which, except for the above parameters, the other eight parameters are x_1, x_3, x_{12}, x_{123}, $\overline{x}_{13}$, y_1, y_2, and y_3.

The vibron numbers N_1, and N_3 are taken to be 43 and 137 for C_2H_2. In the two fittings, we fit 73 observed data, which come from literature [27,28], using the least-squares procedure. Fitting coefficient values are listed in Table I. The fitting rms is 13.74 cm^{-1} for the first fitting and 9.16 cm^{-1} for the second fitting. In the literature [27], one can find a similar calculation which employs the recoupling technique. However, its fitting rms is 16.77 m^{-1} for the first fitting using eight algebraic coefficients and 11.37 cm^{-1} for the second fitting using 16 algebraic coefficients. With regard to the calculation of vibrational spectra of C_2H_2, one can also use the Dunham expansion method. However, one has to take too many coefficients into account in order to obtain the same rms. Partial calculated vibrational results of C_2H_2 are listed in Table II, together with the experimental data. As one can see from Table II, our calculations extend far up in en-

TABLE II. The comparison of observed and calculated levels of molecule C_2H_2 (cm^{-1}).

v_1	v_2	v_3	$v_4^{l_4}$	$v_5^{l_5}$	Observed	Fit I	Δ(I) [a]	δ(I) [b]	Fit II	Δ(II)	δ(II)
Σ											
0	0	0	2^0	0^0	1230.39	1223.82	−6.57	−0.534	1236.21	5.82	0.473
0	0	0	1^{-1}	1^1	1328.07	1331.17	3.10	0.233	1338.81	10.74	0.808
0	0	0	1^1	1^{-1}	1340.55	1337.50	−3.05	−0.228	1344.78	4.23	0.316
0	0	0	0^0	2^0	1449.11	1441.99	−7.12	−0.491	1448.23	−0.88	−0.061
0	1	0	0^0	0^0	1974.32	1969.93	−4.39	−0.222	1966.99	−7.33	−0.371
1	0	0	0^0	0^0	3294.84	3295.69	0.85	0.026	3287.86	−6.98	−0.212
0	0	1	0^0	0^0	3372.80	3369.81	−2.99	−0.089	3371.25	−1.55	−0.046
0	0	0	4^0	0^0		2436.40			2461.05		
0	0	0	3^{-1}	1^1	2560.60	2543.26	−17.34	−0.677	2551.96	−8.64	−0.337
0	0	0	3^1	1^{-1}	2583.85	2555.26	−28.29	−1.106	2563.29	−20.56	−0.796
0	0	0	2^{-2}	2^2	2648.02	2648.17	0.15	0.006	2641.43	−6.59	−0.249
0	0	0	2^2	2^{-2}	2661.19	2654.27	−6.92	−0.260	2662.16	0.97	0.036
0	0	0	2^0	2^0		2667.10			2665.53		
0	0	0	1^{-1}	3^1	2757.80	2755.21	−2.59	−0.094	2756.34	−1.46	−0.053
0	0	0	1^1	3^{-1}	2783.65[c]	2768.28	−15.37	−0.552	2768.66	−14.99	−0.538
0	0	0	0^0	4^0	2880.22[c]	2861.15	−18.71	−0.650	2871.04	−9.18	−0.319
0	1	0	2^0	0^0	3179.90	3182.74	2.84	0.089	3182.64	2.74	0.086
0	1	0	1^{-1}	1^1	3281.90	3290.16	8.26	0.252	3291.73	9.83	0.299
0	1	0	1^1	1^{-1}		3296.34			3297.56		
0	1	0	0^0	2^0	3420.56	3400.90	−19.75	−0.577	3407.57	−13.08	−0.382
0	2	0	0^0	0^0		3917.98			3919.41		
1	0	0	2^0	0^0	4508.01	4508.54	0.53	0.012	4512.52	4.51	0.100
0	0	1	2^0	0^0		4582.66			4578.72		
1	0	0	1^{-1}	1^1		4616.91			4620.64		
1	0	0	1^1	1^{-1}		4623.18			4626.56		
0	0	1	1^{-1}	1^1	4673.63	4687.45	13.82	0.296	4680.50	6.87	0.147
0	0	1	1^1	1^{-1}		4693.72			4686.42		
1	0	0	0^0	2^0	4727.07	4728.41	1.34	0.028	4734.10	7.03	0.149
0	0	1	0^0	2^0	4800.90	4795.57	−5.33	−0.111	4788.19	−12.71	−0.265
1	1	0	0^0	0^0	5260.02	5254.68	−5.34	−0.102	5251.41	−8.61	−0.164
0	1	1	0^0	0^0		5328.80			5334.91		
2	0	0	0^0	0^0	6502.33	6519.26	16.93	0.260	6505.85	3.52	0.054
1	0	1	0^0	0^0	6556.47	6559.85	3.38	0.052	6557.80	1.33	0.020
0	0	2	0^0	0^0	6709.00	6691.77	−17.23	−0.257	6701.66	−7.34	−0.109
0	1	0	3^{-1}	1^1	4488.81	4491.24	2.34	0.054	4484.52	−4.29	−0.096
0	1	0	3^1	1^{-1}		4502.97			4495.61		
0	1	0	2^{-2}	2^2		4596.23			4580.58		
0	1	0	2^2	2^{-2}		4602.18			4601.02		
0	1	0	2^0	2^0		4614.71			4604.28		
0	1	0	1^{-1}	3^1		4703.18			4701.95		
0	1	0	1^1	3^{-1}		4715.94			4713.96		
0	1	0	0^0	4^0		4809.02			4823.08		
0	2	0	2^0	0^0		5119.77			5114.81		
0	2	0	1^{-1}	1^1	5230.23	5227.26	−2.97	−0.057	5230.23	0.00	0.000
0	2	0	1^1	1^{-1}		5233.30			5235.92		
0	1	1	2^0	0^0	6513.89	6530.63	16.74	0.257	6522.06	8.17	0.125
0	1	1	1^{-1}	1^1	6623.14	6635.50	12.63	0.187	6630.29	7.15	0.108
1	1	0	0^0	2^0	6690.59	6676.37	−14.22	−0.213	6690.12	−0.47	−0.007
1	0	1	2^0	0^0	7732.78	7761.72	28.94	0.374	7753.84	21.06	0.272

TABLE II. (*Continued*)

v_1	v_2	v_3	$v_4^{l_4}$	$v_5^{l_5}$	Observed	Fit I	Δ(I)[a]	δ(I)[b]	Fit II	Δ(II)	δ(II)
2	0	0	1^{-1}	1^1	7835.01	7836.27	1.26	0.016	7835.06	0.05	0.001
0	0	2	1^1	1^{-1}	7961.84	7976.49	14.65	0.184	7973.08	11.24	0.141
0	0	2	1^{-1}	1^1		7996.42			7985.15		
1	0	1	0^0	2^0		8002.64			7991.01		
0	0	2	0^0	2^0		8102.40			8091.77		
2	1	0	0^0	0^0		8467.30			8465.65		
1	1	1	0^0	0^0	8512.06	8507.89	−4.17	−0.049	8517.87	5.72	0.067
3	0	0	0^0	0^0	9639.86	9653.10	13.24	0.137	9640.79	1.11	0.011
2	0	1	0^0	0^0	9835.19	9819.92	−15.72	−0.155	9820.96	−14.23	−0.145
1	1	1	2^0	0^0	9668.14	9658.15	−9.99	−0.103	9655.92	−12.22	−0.126
3	1	1	0^0	0^0	14968.90	14 914.64	−54.26	−0.363	14 962.23	−6.67	−0.045
0	1	4	0^0	0^0		15 078.29			15 155.16		
5	0	0	0^0	0^0	15 600.16	15 590.32	−9.84	−0.063	15 594.18	−5.98	−0.038
2	0	3	0^0	0^0	15 948.48[c]	15 957.57	9.09	−0.057	15 972.76	24.28	−0.152
1	0	4	0^0	0^0		16 121.77			16 158.10		
0	0	5	0^0	0^0		16 292.56			16 396.87		
1	0	3	0^0	4^0	15 768.60[c]	15 774.76	6.16	0.039	15 772.30	3.70	0.024
0	1	4	0^0	2^0	16 500.08[c]	16 446.16	−53.29	−0.327	16 478.32	−21.76	−0.132
0	0	5	1^1	1^{-1}	17 518.81[c]	17 497.73	−21.08	−0.120	17 505.90	−12.91	−0.074
Π											
5	0	1	0^0	0^0	18 430.07[c]	18 396.36	−33.71	−0.183	18 407.32	−22.75	−0.123
0	0	0	1^1	0^0	611.70	614.51	2.81	0.459	620.56	8.86	1.448
0	0	0	0^0	1^1	729.16	723.68	−5.30	−0.727	729.35	0.19	0.026
0	0	0	3^1	0^0	1854.54	1932.66	−21.88	−1.180	1851.04	−3.50	−0.189
0	0	0	2^0	1^1	1940.00	1940.47	0.47	0.024	1947.09	7.09	0.365
0	0	0	2^2	1^{-1}	1959.70[c]	1949.22	−10.48	−0.535	1955.36	−4.34	−0.221
0	0	0	1^1	2^0	2047.20	2045.97	−2.11	−0.103	2047.31	−0.59	−0.029
0	0	0	1^{-1}	2^2	2065.80[c]	2056.20	−9.60	−0.465	2060.08	−5.72	−0.277
0	0	0	0^0	3^1	2169.16	2153.55	−15.61	−0.720	2169.23	0.07	0.003
0	1	0	1^1	0^0	2573.19	2578.89	5.70	0.222	2577.22	4.03	0.157
0	1	0	0^0	1^1	2701.91	2688.25	−13.66	−0.505	2692.94	−9.51	−0.352
1	0	0	1^1	0^0	3897.16	3904.67	7.51	0.193	3902.60	5.43	0.139
0	0	1	1^1	0^0	3968.22	3978.79	10.57	0.266	3977.40	9.18	0.231
1	0	0	0^0	1^1	4015.14	4015.15	−0.49	−0.012	4017.20	1.66	0.041
0	0	1	0^0	1^1	4091.17	4085.59	−5.58	−0.136	4085.34	−5.93	−0.145
0	0	0	5^1	0^0		3039.57			3037.14		
0	0	0	4^2	1^{-1}		3146.76			3154.47		
0	0	0	4^0	1^1		3161.13			3167.98		
0	0	0	3^{-1}	2^2		3252.03			3235.12		
0	0	0	3^1	2^0		3260.90			3260.76		
0	0	0	3^3	2^{-2}		3275.70			3265.28		
0	0	0	2^2	3^{-1}		3353.14			3343.04		
0	1	0	2^0	1^1	3881.23	3893.89	12.66	0.326	3889.78	8.55	0.220
0	1	0	2^2	1^{-1}		3902.45			3897.87		
0	1	0	1^1	2^0	4001.26	3999.25	−2.01	−0.050	3996.50	−4.76	−0.119
0	1	0	1^{-1}	2^2		4009.82			4009.03		

ergy (to 20 000 cm^{-1}). The Hamiltonian preserves the quantum number $v = v_a + v_b + v_c + (v_d - l_d)/2 + (v_e - l_e)/2$.

IV. RESULTS AND DISCUSSION

We have used the algebraic Hamiltonian to study the highly excited vibrational levels of the molecule C_2H_2. Four bands are studied, which can be labeled the Σ, Π, Δ, and Φ bands, respectively. First, the highly excited vibrational levels, calculated by using the algebraic Hamiltonian Eq. (19), are shown in Figs. 2 and 3. (The detailed calculated vibrational energy levels are listed in Table II.) Figure 2 gives the levels corresponding to the Σ band ($l=0$). Figure 3 gives

TABLE II. (*Continued*)

v_1	v_2	v_3	$v_4^{l_4}$	$v_5^{l_5}$	Obsserved	Fit I	Δ(I)[a]	δ(I)[b]	Fit II	Δ(II)	δ(II)
0	1	0	0^0	3^1	4138.70[c]	4106.92	−31.71	−0.766	4124.78	−13.92	−0.376
0	2	0	1^1	0^0		4521.38			4519.47		
0	2	0	0^0	1^1		4630.76			4640.90		
1	0	0	3^1	0^0	5123.40	5111.84	−11.56	−0.226	5121.54	−1.84	−0.036
0	0	1	3^1	0^0		5185.96			5179.21		
1	0	0	2^2	1^{-1}		5220.68			5222.92		
1	0	0	2^0	1^1		5229.34			5231.10		
0	0	1	2^0	1^1	5268.55	5291.22	22.67	0.430	5274.66	6.11	0.116
0	0	1	2^2	1^{-1}	5289.11	5299.87	10.76	0.023	5282.85	−6.53	−0.124
1	0	0	1^1	2^0		5326.92			5327.18		
1	0	0	1^{-1}	2^2		5337.49			5340.02		
0	0	1	1^{-1}	2^2		5394.00			5373.52		
0	0	1	1^1	2^0	5381.55	5404.63	22.81	0.424	5386.31	4.76	0.088
1	0	0	0^0	3^1		5435.10			5451.74		
0	0	1	0^0	3^1		5498.98			5493.10		
1	1	0	1^1	0^0	5850.64	5858.10	7.46	0.128	5855.87	5.23	0.089
0	1	1	1^1	0^0		5932.22			5930.86		
1	1	0	0^0	1^1		5968.50			5976.83		
0	1	1	0^0	1^1		6039.04			6045.05		
2	0	0	1^1	0^0		7122.71			7113.63		
1	0	1	1^1	0^0	7141.48	7163.30	21.82	0.306	7158.19	16.71	0.234
2	0	0	0^0	1^1	7218.19	7233.64	15.45	0.214	7233.25	15.06	0.209
0	0	2	1^1	0^0	7263.88[c]	7295.22	7.31	0.101	7272.13	8.25	0.114
1	0	1	0^0	1^1	7296.37[c]	7295.22	−1.15	−0.016	7294.87	−1.50	−0.021
0	1	0	4^0	1^1	5101.61	5103.23	2.02	0.040	5090.11	−11.50	−0.225
0	1	0	3^1	2^0		5194.91			5164.17		
1	0	2	1^1	0^0		7122.71			7113.63		
0	1	1	2^0	1^1	7205.93	7233.70	27.77	0.385	7214.36	8.43	0.117
0	1	1	2^2	1^{-1}	7228.27[c]	7242.16	13.89	0.192	7222.36	−5.91	−0.082
1	1	0	1^1	2^0		7269.44			7273.09		
1	1	0	1^{-1}	2^2		7279.76			7285.62		
0	0	1	1^1	2^0		7336.53			7319.74		
0	1	1	1^1	2^0	7329.35	7346.91	−17.56	−0.240	7332.22	2.87	0.039
0	1	1	1^{-1}	2^2		7377.53			7403.89		
1	1	0	0^0	3^1		7441.41			7445.64		
0	1	1	0^0	3^1		7789.65			7794.97		
1	2	0	1^1	0^0		7863.77			7869.86		
0	1	2	0^0	1^1		9342.52			9358.84		
3	0	0	1^1	0^0	10 214.38	10 251.10	36.72	0.360	10 238.97	24.59	0.241
2	0	1	0^0	1^1		10 264.72			10 256.77		
3	0	0	0^0	1^1		10 361.20			10 361.61		
5	0	0	1^1	0^0	16 139.06[c]	16 177.18	38.12	0.236	16 169.62	30.56	0.189
4	0	1	1^1	0^0		16 177.49			16 170.28		
5	0	0	0^0	1^1	16 291.01[c]	16 285.35	−5.66	−0.035	16 295.59	5.58	0.034
3	0	2	1^1	0^0	16 291.48[c]	16 285.58	−5.90	−0.036	16 297.02	6.01	0.037
4	0	1	0^0	1^1		16 504.42			16 487.08		
2	0	3	1^1	0^0		16 544.43			16 545.47		
3	0	2	0^0	1^1		16 615.92			16 618.48		

the levels corresponding to the Π band $(l=1)$. When the quantum number v increases in a fixed band, the number of energy levels increases rapidly. For example, when $v=1$, the number of the levels $n=7$. When $v=2$, $n=27$ and for $v=5$, $n=378$. When we study the higher band, the number of energy levels increases more rapidly with v.

Second, as usual, the degeneracy or quantidegeneracy of energy levels is called clustering. It may be seen from in

TABLE II. (*Continued*)

v_1	v_2	v_3	$v_4^{l_4}$	$v_5^{l_5}$	Observed	Fit I	Δ(I)[a]	δ(I)[b]	Fit II	Δ(II)	δ(II)
Δ											
0	0	0	2^2	0^0	1228.97	1228.49	−0.48	−0.039	1240.26	11.92	0.919
0	0	0	1^1	1^1	1342.80	1339.17	−3.63	−0.270	1343.30	0.50	0.037
0	0	0	0^0	2^2	1458.30[c]	1441.82	−16.48	−1.130	1453.89	−4.32	−0.296
0	0	0	4^2	0^0		2440.88			2464.92		
0	0	0	3^1	1^1	2556.81	2549.34	−7.47	−0.292	2554.67	−2.14	−0.084
0	0	0	3^3	1^{-1}	2584.96[c]	2559.89	−25.07	−0.970	2564.63	−20.33	−0.787
0	0	0	2^2	2^0		2655.32			2646.33		
0	0	0	2^0	2^2	2661.43	2669.24	7.81	0.294	2663.56	2.13	0.080
0	0	0	1^{-1}	3^3	2768.47	2753.81	−14.66	−0.529	2761.09	−7.38	−0.267
0	0	0	1^1	3^1	2790.78[c]	2769.10	−21.68	−0.777	2773.26	−17.52	−0.628
0	0	0	0^0	4^2	2889.35[c]	2859.34	−30.01	−1.039	2886.12	−3.23	−0.112
0	1	0	2^2	0^0		3187.23			3186.55		
0	1	0	1^1	1^1		3297.85			3296.00		
0	1	0	0^0	2^2	3429.45[c]	3400.61	−28.84	−0.841	3413.07	−16.38	−0.478
1	0	0	2^2	0^0		4513.03			4516.39		
0	0	1	2^2	0^0		4587.15			4586.27		
1	0	0	1^1	1^1		4624.76			4625.08		
0	0	1	1^1	1^1		4695.30			4685.02		
1	0	0	0^0	2^2		4728.40			4740.21		
0	0	1	0^0	2^2	4809.55	4795.46	−14.09	−0.293	4794.27	−15.28	−0.318
2	0	0	2^2	0^0	7732.31	7725.45	−6.86	−0.089	7720.20	−12.11	−0.157
2	0	0	1^1	1^1	7847.70	7837.75	−9.95	−0.127	7833.60	−14.10	−0.180
2	0	0	1^1	1^1	7971.55	7976.51	4.96	0.062	7979.90	8.35	0.105
Φ											
0	0	0	3^3	0^0	1851.31	1841.81	−9.50	−0.513	1858.96	7.65	0.413
0	0	0	2^2	1^1	1961.94	1953.57	−8.37	−0.427	1956.11	−5.83	−0.297
0	0	0	1^1	2^2	2074.19[c]	2057.96	−16.23	−0.783	2061.65	−12.54	−0.605
0	0	0	0^0	3^3	2187.48[c]	2153.87	−33.61	−1.536	2173.48	−14.00	−0.640
0	0	0	5^3	0^0		3048.37			3077.72		
0	0	0	4^2	1^1		3157.49			3161.56		
0	0	0	4^4	1^{-1}		3169.57			3172.64		
0	0	0	3^3	2^0		3264.10			3244.52		
0	0	0	3^1	2^2		3280.40			3265.37		
0	0	0	2^2	3^1		3363.95			3353.85		
0	0	0	2^0	3^3		3382.48			3371.04		
0	0	0	1^1	4^2		3455.95			3469.75		
0	0	0	1^{-1}	4^4		3475.92			3482.26		
0	0	0	0^0	5^3		3559.39			3598.44		
0	1	0	3^3	0^0		3794.81			3794.86		
0	1	0	2^2	1^1		3906.47			3898.43		
0	1	0	1^1	2^2		4010.89			4010.34		
0	1	0	0^0	3^3		4107.00			4128.56		
1	0	0	3^3	0^0		5120.64			5129.13		
0	0	1	3^3	0^0		5194.76			5186.95		
1	0	0	2^2	1^1		5233.49			5231.76		
0	0	1	2^2	1^1		5304.10			5283.65		
1	0	0	1^1	2^2		5338.88			5341.59		
0	0	1	1^1	2^2		5405.94			5388.01		
1	0	0	0^0	3^3		5435.74			5456.59		
0	0	1	0^0	3^3		5499.43			5497.98		

[a] Δ = fit − obs.

[b] $\delta = (\text{fit} - \text{obs})/\text{obs} \times 100$.

[c] The unfitted observed data.

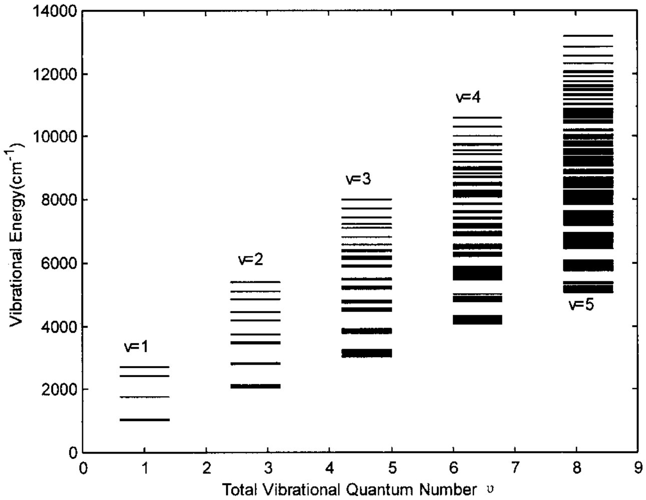

FIG. 4. Σ band vibrational energy levels of C_2D_2 vs total quantum numbers.

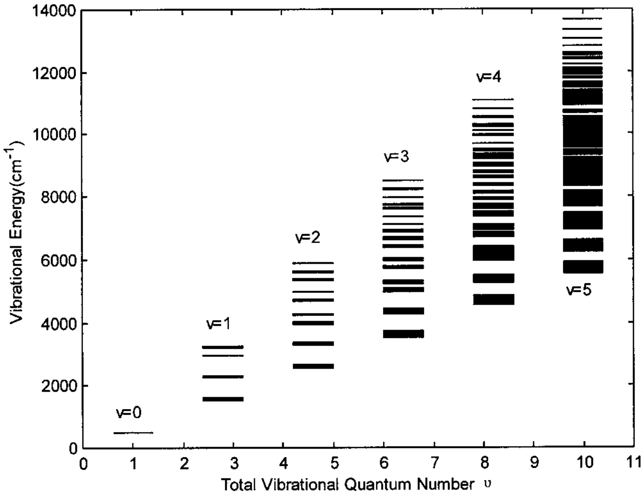

FIG. 5. Π band vibrational energy levels of C_2D_2 vs total quantum numbers.

Figs. 2 and 3 that the vibrational energy levels of C_2H_2 make up clusters. Comparing Fig. 2 with Fig. 3, one can see they have a similar energy level structure. However, Fig. 3 has more levels than Fig. 2 in a fixed cluster if the two figures are studied closely. Figures 2 and 3 also show that linear tetratomic molecules have a more complex energy-level structure than linear triatomic molecules.

Third, comparing Figs. 2 and 3 of molecule C_2H_2 with Figs. 4 and 5 of molecule C_2D_2, which is given in Ref. [29], we find that, according to the same band such as the Σ band, they have a similar structure. However, there are real differences between them. This point can be clearly seen in the top cluster. The cluster in C_2H_2 is denser than that in C_2D_2.

Fourth, when we fit observed data for C_2H_2, 23, observed levels, which are labeled by *c*, are not considered. But using the algebraic Hamiltonian, we obtain perfect results. For the energy level $(1030^0 0^0)$, the observed value is 15 768.60 cm^{-1} and the calculated value is 15 772.30 cm^{-1}. Its relative deviation is 0.024. The other unfitted observed data can be found in Table II.

Fifth, using the algebraic Hamiltonian (19), we calculate the energy of four bands. For calculated theoretical results, we label the levels using a quantum number, which is consistent with those from the conventional method. The partial calculated theoretical results have been listed in Table II.

V. CONCLUSION

In this paper, we calculate the highly vibrational levels including stretching and bending modes using the u(4) algebraic Hamiltonian with fewer parameters. We predicted the highly excited vibrations using this algebraic Hamiltonian. The study shows that the higher levels are clustered.

This algebraic approach can be extended to any tetratomic molecule. We will research their spectra using this method in our future work. In addition, potential-energy surfaces of tetratomic molecules seem to be decipherable by this method, and recently, great progress has been made to decipher potential-energy surfaces for triatomic molecules using this method.

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