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Boson-realization model for the vibrational spectra of tetrahedral molecules

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An algebraic model of boson realization is proposed to study the vibrational spectra of a tetrahedral molecule, where ten sets of boson creation and annihilation operators are used to construct the Hamiltonian with T_d symmetry. There are two schemes in our model. The first scheme provides an eight-parameter fit to the published experimental vibrational eigenvalues of methane with a root-mean-square deviation 11.61 cm^{-1}. The second scheme, where the bending oscillators are assumed to be harmonic and the interactions between the bending vibrations are neglected, provides a five-parameter fit with a root-mean-square deviation 12.42 cm^{-1}.

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I. INTRODUCTION

The characterization of highly excited vibrational states has become one of the central goals in chemical physics. There were two general methods used to describe molecular vibrations. In the traditional approach the molecular Hamiltonian was parametrized in terms of internal coordinates [1]. The potential was modeled by the force field constants with many parameters due to poor knowledge of the large number of force constants. Those parameters have to be determined by fitting the spectroscopic data phenomenologically.

As an alternative, an algebraic approach has been proposed for the study of polyatomic molecular spectra. The first step toward the establishment of an algebraic approach was given by Iachello, Levine, and their co-workers [2] with the vibron model, where the rotation-vibration spectra of diatomic molecules are described in terms of a u(4) algebra. Although this model was extended [3] to polyatomic molecules by introducing a u(4) algebra for each bond, it is rather difficult to apply when the number of atoms in the molecule becomes larger than four [4].

Recently, an alternative technique [5] for the automatic computation of symmetrized local mode basis functions was used to provide a four-parameter potential model for the stretching modes of octahedron XY_6 that gave an excellent fit to the published experimental vibrational eigenvalues of SF_6, WF_6, and UF_6. An improved algebraic method [6], where the one-dimensional Morse oscillator was described by the Lie algebra u(2), was proposed to provide another better fit to those experimental data with four parameters plus one fixed parameter N that describes the anharmonic property of the Morse potential. This algebraic approach was extended to study the vibrational spectra, both stretching and bending, of tetrahedral molecules [4], where the interactions between stretching and bending vibrations were neglected and seven adjustable parameters plus two fixed parameters N_i were used to fit the experimental data. This algebraic method was also used to study the vibrational spectroscopy and intramolecular relaxation of benzene [7].

In this paper we proposed another algebraic model, the boson-realization model, to study the vibrational spectra of tetrahedral molecules, where ten coupled one-dimensional anharmonic oscillators are described by ten sets of bosonic creation and annihilation operators. The interbond interactions and the interactions between stretching and bending vibrations are expressed by the T_d invariant combinations of the products of one creation operator and one annihilation operator such that the total number of vibrational quanta is conservative. The symmetrized bases are used to simplify the calculation. There are two schemes in our model. The first scheme provides an eight-parameter fit to the published experimental vibrational eigenvalues of methane better than the previous results. The results show that the bending oscillators are near harmonic ones, the interbond interactions between bending vibrations are quite weak, and the interactions between stretching and bending vibrations are strong. Those conclusions reflect the properties of the molecular structure of methane. From the properties we propose our second scheme where the bending oscillators are harmonic and there is no interaction between the bending vibrations. The second scheme provides a five-parameter fit to the experimental data of methane with the root-mean-square deviation 12.42 cm^{-1}. It may be a model with the least parameters that well

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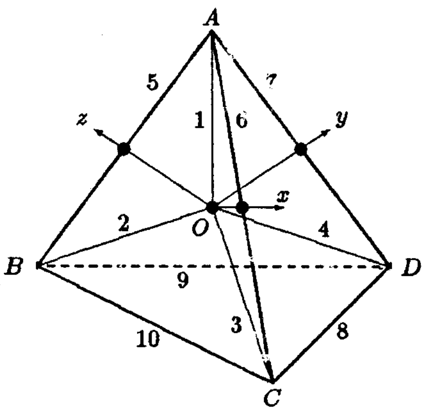

FIG. 1. Schematic representation of an XY_4 tetrahedral molecule.

fits the published experimental vibrational data of methane. To some extent, our method is a generalization of that used in Ref. [5].

This paper is organized as follows. In Sec. II the vibrational Hamiltonian of a tetrahedral molecule is introduced in terms of ten sets of boson operators. In Sec. III the vibrational functions are combined into the symmetrized bases belonging to given rows of given irreducible representations of T_d. In these symmetrized bases the Hamiltonian becomes a block matrix with eight parameters. The spurious states are ruled out in the calculation. In Sec. IV, fitting the published 19 experimental data [4,8] for methane with the total number of quanta $v \leqslant 3$, in our first scheme with eight parameters we obtain the root-mean-square deviation of energy to be 11.61 cm^{-1}. Our second scheme provides a good five-parameter fit. For comparison, the experimental data, the previous calculated energies by the algebraic model [4] and the present calculated results for methane of $v \leqslant 3$ in two schemes are listed in Table II. The remaining calculated energies for methane up to $v=3$ by this boson-realization model in the first scheme are also presented. The higher energy levels can be calculated straightforwardly. In Sec. V we give some conclusions.

II. HAMILTONIAN

We begin with enumerating ten oscillators for an XY_4 tetrahedral molecule such as that in Fig. 1. The atom X is located at the center O of the tetrahedron, and four atoms Y at its vertices A, B, C, and D. The coordinate axes x, y, and z point from O to the centers of edges AC, AD, and AB, respectively. The first four equivalent oscillators describe the fundamental stretching modes ($A_1 \oplus F_2$), and the other six equivalent ones describe the fundamental bending modes. As is well known [9], there are only five degrees of freedom for the bending vibrations ($E \oplus F_2$), so that the six bending oscillators must contain a spurious one. The spurious states related to the spurious degree of freedom should be ruled out in the later calculation.

Now, for the 10 oscillators we introduce 10 sets of bosonic operators $a_\alpha^\dagger$ and a_α, $1 \leqslant \alpha \leqslant 10$, that satisfy the well known relations

$$[a_\alpha, a_\beta^\dagger] = \delta_{\alpha\beta}, \quad [a_\alpha, a_\beta] = [a_\alpha^\dagger, a_\beta^\dagger] = 0,$$

$$|n\rangle \equiv |n_1, n_2, \ldots, n_{10}\rangle,$$

$$a_\alpha^\dagger |n\rangle = \sqrt{n_\alpha + 1}\,|\ldots, n_{\alpha-1}, (n_\alpha + 1), n_{\alpha+1}, \ldots\rangle$$

$$a_\alpha |n\rangle = \sqrt{n_\alpha}\,|\ldots, n_{\alpha-1}, (n_\alpha - 1), n_{\alpha+1}, \ldots\rangle, \quad (2.1)$$

where $|n\rangle$ denotes the common eigenstate of the phonon number operators N_α with the eigenvalues n_α, respectively.

$$N_\alpha = a_\alpha^\dagger a_\alpha, \quad N_\alpha |n\rangle = n_\alpha |n\rangle. \quad (2.2)$$

The first four bosonic operators $a_j^\dagger$ (or a_j), $1 \leqslant j \leqslant 4$, describing the stretching vibrations, are the irreducible tensor operators belonging to the representations $A_1 \oplus F_2$ of T_d. The other six $a_\mu^\dagger$ (or a_μ), $5 \leqslant \mu \leqslant 10$, describing the bending vibrations, are those belonging to the representations $A_1 \oplus E \oplus F_2$.

The energy of each oscillator depends upon the phonon number. For simplicity we assume that all oscillators are the Morse ones with two parameters ω and x, so that the energy of the αth oscillator can be expressed in the operator form:

$$E_s(N_j) = N_j\{\omega_s - x_s(N_j + 1)\}, \quad 1 \leqslant j \leqslant 4$$

$$E_b(N_\mu) = N_\mu\{\omega_b - x_b(N_\mu + 1)\}, \quad 5 \leqslant \mu \leqslant 10 \quad (2.3)$$

where the subscript s denotes the stretching vibration and b the bending one. The null energy has been removed. Although the Morse potential is known [10] to be not very suitable for all anharmonic oscillators, the deviation can be described by some more parameters that become important for higher energy levels. It was pointed out by Iachello and Oss [7] that the Pöschl-Teller potential is much more appropriate than the Morse one to describe the bending vibrations. However, the expression for the eigenvalues of the bound states is identical for two potentials [7].

As usual, neglecting the mixture of the states with different total number of phonons, and assuming to take the interactions up to the second order, we can express the interactive potentials as the combinations of the products of one creation operator and one annihilation operator. The character table, the representation matrices of the generators, and the Clebsch-Gordan coefficients of the T_d group were explicitly given in Ref. [4]. From that knowledge, there are obviously only five T_d invariant combinations in addition to the sum of phonon number operators. The Hamiltonian now can be expressed in terms of the bosonic operators as follows:

$$\begin{aligned} H=&\sum_{j=1}^{4} E_s(a_j^\dagger a_j)+\sum_{\mu=5}^{10} E_b(a_\mu^\dagger a_\mu)+\lambda_1\sum_{i\neq j=1}^{4} a_i^\dagger a_j+\lambda_2\sum_{\mu\neq\nu=5}^{10} a_\mu^\dagger a_\nu \\ &+\lambda_3\sum_{\mu=5}^{7}(a_\mu^\dagger a_{\mu+3}+a_{\mu+3}^\dagger a_\mu)+\lambda_4\Bigg\{a_1^\dagger\sum_{\mu=5}^{7}(a_\mu-a_{\mu+3}) \\ &+a_2^\dagger\left(a_5-\sum_{\mu=6}^{8}a_\mu+a_9+a_{10}\right)+a_3^\dagger\sum_{\mu=3}^{5}(a_{2\mu}-a_{2\mu-1}) \\ &+a_4^\dagger\left(-a_5-a_6+\sum_{\mu=7}^{9}a_\mu-a_{10}\right)+\text{H.c.}\Bigg\}+\lambda_5\left\{\left(\sum_{j=1}^{4}a_j^\dagger\right)\left(\sum_{\mu=5}^{10}a_\mu\right)+\text{H.c.}\right\}\ . \end{aligned} \tag{2.4}$$

It will be seen in the next section that the term with λ_5 relates only to the spurious states so that it is not interesting to us. Removing this term, we obtain the Hamiltonian containing eight parameters. The term with λ_4 describes the interaction between stretching and bending vibrations. In the previous algebraic approach [4] ten parameters were introduced to fit the experimental data, where two spectroscopic constants N_1 and N_2, that are equal to ω_s/x_s-1 and ω_b/x_b-1 in our notations, were taken as fixed parameters, one constraint was assumed to reduce one parameter, and the interactions between stretching and bending vibrations were neglected. In this meaning their algebraic approach [4], in comparison with our model, introduced three more parameters (B_{12}, $B_{5,6}$, and $B_{5,10}$), fixed two parameters N_1 and N_2, reduced one parameter by a constraint, and neglected one parameter λ_4 describing the interaction.

III. IRREDUCIBLE BASES

Since the Hamiltonian has T_d symmetry, each eigenfunction can be combined such that it belongs to a given row of an irreducible representation of T_d. The states that belong to the same irreducible space as partners must correspond to the same energy [11]. This degeneracy of the partners is called the normal one. A symmetric perturbation never splits a normal degeneracy. The calculation for energy levels will be greatly simplified if those bases are used.

The vibrational state of a tetrahedral molecule is described by the phonon numbers n_α of the ten oscillators. The first four numbers n_j describe the stretching vibrations, and the next six numbers n_μ describe the bending vibrations. Those states can be combined into the irreducible bases belonging to given rows of given irreducible representations, respectively. For the general vibrations, those states with both stretching and bending vibrations should be further combined.

Now, we discuss the combinations of the states for pure stretching vibrations. Briefly denote $|n_1n_2n_3n_4000000\rangle$ by $|abcd\rangle$, where the vanishing n_μ ($\mu\geqslant 5$) are neglected in this notation. Firstly assume that a, b, c, and d are all different from each other. Under the transformations of T_d there are 24 independent states that span the regular representation space of T_d. Through the standard group theory method [11] they can be combined into orthogonal bases belonging to ten irreducible representations: $\phi(A_1,abcd)$, $\phi(A_2,abcd)$, $\phi_\nu^{(1)}(E,abcd)$, $\phi_\nu^{(2)}(E,abcd)$, $\phi_\nu^{(1)}(F_2,abcd)$, $\phi_\nu^{(2)}(F_2,abcd)$, $\phi_\nu^{(3)}(F_2,abcd)$, $\phi_\nu^{(1)}(F_1,abcd)$, $\phi_\nu^{(2)}(F_1,abcd)$, and $\phi_\nu^{(3)}(F_1,abcd)$.

Similarly, for pure bending vibrations, briefly denote $|0000n_5n_6n_7n_8n_9n_{10}\rangle$ by $|abcdef\rangle$, where the vanishing n_j ($j\leqslant 4$) are neglected in this notation. Two kinds of states should not be confused: one with four numbers describes the stretching vibration, and the other with six numbers describes the bending vibration. When a, b, c, d, e, and f are all different from each other, we also have 24 independent states, spanning the regular representation space of T_d. Combine them into the irreducible orthogonal bases, and denote them by $\psi(A_1,abcdef)$, $\psi(A_2,abcdef)$, $\psi_\nu^{(1)}(E,abcdef)$, $\psi_\nu^{(2)}(E,abcdef)$, $\psi_\nu^{(1)}(F_2,abcdef)$, $\psi_\nu^{(2)}(F_2,abcdef)$, $\psi_\nu^{(3)}(F_2,abcdef)$, $\psi_\nu^{(1)}(F_1,abcdef)$, $\psi_\nu^{(2)}(F_1,abcdef)$, and $\psi_\nu^{(3)}(F_1,abcdef)$. The explicit combinations of $\phi_\nu(\Gamma,abcd)$ and $\psi_\nu(\Gamma,abcdef)$ can be obtained from us upon request.

For example, for the fundamental stretching vibrations ($v=1$) the irreducible bases are listed as follows:

$$\begin{aligned} \phi(A_1,1000)&=2^{-1}\{|1000\rangle+|0100\rangle+|0010\rangle+|0001\rangle\}, \\ \phi_1^{(1)}(F_2,1000)&=2^{-1}\{|1000\rangle-|0100\rangle+|0010\rangle-|0001\rangle\}, \\ \phi_2^{(1)}(F_2,1000)&=2^{-1}\{|1000\rangle-|0100\rangle-|0100\rangle+|0001\rangle\}, \\ \phi_3^{(1)}(F_2,1000)&=2^{-1}\{|1000\rangle+|0100\rangle-|0010\rangle-|0001\rangle\}. \end{aligned} \tag{3.1}$$

Similarly, the irreducible bases of the fundamental bending vibrations ($v=1$) are

$$\begin{aligned} \psi(A_1,100000)=6^{-1/2}\{&|100000\rangle+|010000\rangle+|001000\rangle \\ &+|000100\rangle+|000010\rangle+|000001\rangle\}, \end{aligned} \tag{3.2}$$

$$\begin{aligned} \psi_1^{(1)}(E,100000)=(2\sqrt{3})^{-1}\{&2|100000\rangle-|010000\rangle \\ &-|001000\rangle+2|000100\rangle \\ &-|000010\rangle-|000001\rangle\}, \\ \psi_2^{(1)}(E,100000)=2^{-1}\{&|010000\rangle-|001000\rangle \\ &+|000010\rangle-|000001\rangle\}, \end{aligned}$$

$$\psi_1^{(1)}(F_2,100000)=2^{-1/2}\{|010000\rangle-|000010\rangle\},$$

$$\psi_2^{(1)}(F_2,100000)=2^{-1/2}\{|001000\rangle-|000001\rangle\},$$

$$\psi_3^{(1)}(F_2,100000)=2^{-1/2}\{|100000\rangle-|000100\rangle\}.$$

In those bases the Hamiltonian H given in (2.4) becomes a block matrix with the submatrices $H(\Gamma,v)$, where Γ denotes the irreducible representation, and v is the total phonon number. Obviously, $H(E,1)$ is a 1×1 submatrix, but $H(A_1,1)$ and $H(F_2,1)$ are 2×2 submatrices:

$$H(E,1)=\omega_b-2x_b-\lambda_2+\lambda_3,$$

$$H(A_1,1)=\begin{pmatrix}\omega_s-2x_s+3\lambda_1 & 2\sqrt{6}\lambda_5\\ 2\sqrt{6}\lambda_5 & \omega_b-2x_b+5\lambda_2+\lambda_3\end{pmatrix},$$

$$H(F_2,1)=\begin{pmatrix}\omega_s-2x_s-\lambda_1 & 2\sqrt{2}\lambda_4\\ 2\sqrt{2}\lambda_4 & \omega_b-2x_b-\lambda_2-\lambda_3\end{pmatrix}. \tag{3.3}$$

Note that the state $\psi(A_1,100000)$ represents the fundamental spurious state and should be ruled out.

In the traditional approach, the higher excited states are calculated by symmetrizing the products of the fundamental vibrational states [9]. However, it may be more easy to use the irreducible bases, subtracting the spurious states, for calculating the excited states. In the following, we calculate the excited states for the case with total phonon number $v=2$ in detail. It is straightforward to calculate higher excited states in this way.

Before calculation, we have to study an important problem of how to remove the spurious states. In the recent papers we see two methods of removal. Iachello and Oss [7] placed the spurious states at the energies $\geqslant 10$ times the energies of the physical states by the projection operators. This method of removal is exact for harmonic bending vibrations and acquires a small error for the anharmonic one. Instead, Lemus and Frank [4] directly eliminated the spurious states from both the space and the Hamiltonian. They demanded the matrix elements of the Hamiltonian related with the fundamental spurious state $\psi(A_1,100000)$ vanishing. In our notation, they introduced a constraint in addition to $\lambda_5=0$ that was assumed in Ref. [4] at beginning:

$$\omega_b-2x_b+5\lambda_2+\lambda_3=0 \tag{3.4}$$

so that $H(A_1,1)$ in (3.3) contains only one nonvanishing element.

In the present paper we develop the second method of removal. First of all, it seems to us that the constraint (3.4) is not necessary and reasonable because it restricts only the energy of the fundamental spurious state to be vanishing, but the energies of all other spurious states are nonvanishing. Secondly, we have to answer the problem of how to identify the spurious states. Generally speaking, a state is identified as a spurious state if it contains $\psi(A_1,100000)$ as a factor. In Ref. [4] (p. 8327) the simply additive definition for the product of two functions is used:

$$|n\rangle|m\rangle=|(n+m)\rangle,$$

$$|(n+m)\rangle=|(n_1+m_1),(n_2+m_2),\ldots,(n_{10}+m_{10})\rangle. \tag{3.5}$$

When two states $|n\rangle$ and $|m\rangle$ describe a pure stretching vibration and a bending vibration, respectively, (3.5) is correct. However, in the calculations of removing the spurious states, both states describe bending vibrations where (3.5) may not be suitable.

Borrowing the idea from Ref. [7], we want to find an identification rule for the spurious state such that the spurious species are separated, if possible, from the physical species in the matrix form of the Hamiltonian. As is well known, in the formalism of the boson realization the states $|n\rangle$ contains a factor $(n!)^{-1/2}$:

$$|n\rangle=(n!)^{-1/2}(a^\dagger)^n|0\rangle.$$

Therefore, we embed a factor in the definition (3.5) for the product:

$$|n\rangle|m\rangle=\prod_\mu\left\{\frac{(n_\mu+m_\mu)!}{n_\mu!m_\mu!}\right\}^{1/2}|(n+m)\rangle,$$

$$|(n+m)\rangle=|(n_1+m_1),(n_2+m_2),\ldots,(n_{10}+m_{10})\rangle. \tag{3.6}$$

In terms of this definition we calculate the general spurious states and find that the off-diagonal elements of the Hamiltonian between the spurious species and the physical species linearly depend upon x_b and λ_5, namely, under the conditions that $x_b=0$ and $\lambda_5=0$ the spurious species are totally separated from the physical species in the matrix form of the Hamiltonian.

The condition $\lambda_5=0$ is acceptable because it only appears in those off-diagonal elements. The condition $x_b=0$ means that the bending vibrations are harmonic. Fortunately, to our knowledge, in the known results x_b is quite small (e.g., see Refs. [6,12] and our results below). It is interesting to notice that the first method [7] of removal is exact also only for harmonic bending vibrations.

Now, we turn back to calculate the excited states with $v=2$. When $v=2$, the stretching vibrational states are separated into five sets: $\phi(A_1,2000)$, $\phi_\nu^{(1)}(F_2,2000)$, $\phi(A_1,1100)$, $\phi_\nu^{(1)}(E,1100)$, and $\phi_\nu^{(1)}(F_2,1100)$, and the bending vibrational states are separated into ten sets: $\psi(A_1,200000)$, $\psi_\nu^{(1)}(E,200000)$, $\psi_\nu^{(1)}(F_2,200000)$, $\psi(A_1,100100)$, $\psi_\nu^{(1)}(E,100100)$, $\psi(A_1,110000)$, $\psi_\nu^{(1)}(E,110000)$, $\psi_\nu^{(1)}(F_2,110000)$, $\psi_\nu^{(3)}(F_2,110000)$, and $\psi_\nu^{(1)}(F_1,110000)$. For the mixture states $\Psi_\nu(\Gamma\in\Gamma_1\otimes\Gamma_2,v)$ of stretching and bending vibrations with $v=2$, we have to combine the stretching states $\phi_\nu(\Gamma_1,v=1)$ and the bending states $\psi_\nu(\Gamma_2,v=1)$ by the Clebsch-Gordan coefficients of T_d.

In terms of the definition (3.6), direct calculation shows that there are five sets of spurious states with $v=2$, belonging to the following irreducible representations: two A_1, one E, and two F_2. In the following we list only one spurious state for each irreducible representation space:

$$\begin{gathered}
\phi(A_1,1000)\,\psi(A_1,100000),\\
\{\psi(A_1,200000)+\psi(A_1,100100)+2\,\psi(A_1,110000)\}/\sqrt{3}=\{\psi(A_1,100000)\}^2,\\
\{\psi_2^{(1)}(E,200000)+\psi_2^{(1)}(E,100100)+\psi_2^{(1)}(E,110000)\}/\sqrt{3}=\psi(A_1,100000)\,\psi_2^{(1)}(E,100000),\\
\phi_3^{(1)}(F_2,1000)\,\psi(A_1,100000),\\
\{\psi_3^{(1)}(F_2,200000)+\sqrt{2}\,\psi_3^{(1)}(F_2,110000)\}/\sqrt{3}=\psi(A_1,100000)\,\psi_3^{(1)}(F_2,100000).
\end{gathered}\tag{3.7}$$

Removing the spurious states, we obtain the physical states belonging to given irreducible representations. There are five states belonging to representation A_1, five sets of states belonging to E, seven sets belonging to F_2, and three sets belonging to F_1. Only one state for each irreducible representation space is listed in the following:

$$\begin{gathered}
f_1(A_1,2)=\phi(A_1,2000),\\
f_2(A_1,2)=\phi(A_1,1100),\\
f_3(A_1,2)=\{\psi(A_1,200000)-\psi(A_1,100100)\}/\sqrt{2},\\
f_4(A_1,2)=\{\psi(A_1,200000)+\psi(A_1,100100)-\psi(A_1,110000)\}/\sqrt{3},\\
f_5(A_1,2)=\sum_{\nu=1}^{3}\phi_\nu^{(1)}(F_2,1000)\,\psi_\nu^{(1)}(F_2,100000)/\sqrt{3},\\
f_1(E,2)=\phi_2^{(1)}(E,1100),\\
f_2(E,2)=\{\psi_2^{(1)}(E,200000)-\psi_2^{(1)}(E,100100)\}/\sqrt{2},\\
f_3(E,2)=\{\psi_2^{(1)}(E,200000)+\psi_2^{(1)}(E,100100)-2\,\psi_2^{(1)}(E,110000)\}/\sqrt{6},\\
f_4(E,2)=\phi(A_1,1000)\,\psi_2^{(1)}(E,100000),\\
f_5(E,2)=\{\phi_1^{(1)}(F_2,1000)\,\psi_1^{(1)}(F_2,100000)-\phi_2^{(1)}(F_2,1000)\,\psi_2^{(1)}(F_2,100000)\}/\sqrt{2},\\
f_1(F_2,2)=\phi_3^{(1)}(F_2,2000),\\
f_2(F_2,2)=\phi_3^{(1)}(F_2,1100),\\
f_3(F_2,2)=\{\sqrt{2}\,\psi_3^{(1)}(F_2,200000)-\psi_3^{(1)}(F_2,110000)\}/\sqrt{3},\\
f_4(F_2,2)=\psi_3^{(3)}(F_2,110000),\\
f_5(F_2,2)=\phi_3^{(1)}(F_2,1000)\,\psi_1^{(1)}(E,100000),\\
f_6(F_2,2)=\phi(A_1,1000)\,\psi_3^{(1)}(F_2,100000),\\
f_7(F_2,2)=\{\phi_1^{(1)}(F_2,1000)\,\psi_2^{(1)}(F_2,100000)+\phi_2^{(1)}(F_2,1000)\,\psi_1^{(1)}(F_2,100000)\}/\sqrt{2},\\
f_1(F_1,2)=\phi_3^{(1)}(F_1,110000),\\
f_2(F_1,2)=\phi_3^{(1)}(F_1,1000)\,\psi_2^{(1)}(E,100000),\\
f_3(F_1,2)=\{\phi_1^{(1)}(F_2,1000)\,\psi_2^{(1)}(F_2,100000)-\phi_2^{(1)}(F_2,1000)\,\psi_1^{(1)}(F_2,100000)\}/\sqrt{2},
\end{gathered}$$

where the number 2 in the argument denotes $\upsilon=2$. Those states belonging to the same irreducible representation will be mixed by the Hamiltonian.

Directly calculating the Hamiltonian matrix H in those bases, we obtain a block matrix with 5×5 submatrix for A_1, 5×5 submatrix for E, 7×7 submatrix for F_2, and 3×3 submatrix for F_1:

$$H(A_1,2)=\begin{pmatrix} 2\omega_s-6x_s & 2\sqrt{3}\lambda_1 & 0 & 0 & 2\sqrt{3}\lambda_4 \\ 2\sqrt{3}\lambda_1 & 2\omega_s-4x_s+4\lambda_1 & 0 & 0 & -2\lambda_4 \\ 0 & 0 & C_1 & -\sqrt{2/3}x_b & 4\lambda_4 \\ 0 & 0 & -\sqrt{2/3}x_b & C_2 & 0 \\ 2\sqrt{3}\lambda_4 & -2\lambda_4 & 4\lambda_4 & 0 & C_3 \end{pmatrix},$$

$$H(E,2)=\begin{pmatrix} 2\omega_s-4x_s-2\lambda_1 & 0 & 0 & 0 & 4\lambda_4 \\ 0 & C_1 & -x_b/\sqrt{3} & 0 & 4\lambda_4 \\ 0 & -x_b/\sqrt{3} & C_4 & 0 & 0 \\ 0 & 0 & 0 & C_5+2\lambda_3 & 0 \\ 4\lambda_4 & 4\lambda_4 & 0 & 0 & C_3 \end{pmatrix},$$

$$H(F_2,2)=\begin{pmatrix} 2\omega_s-6x_s & 2\lambda_1 & 0 & 0 & 0 & 2\lambda_4 & 2\sqrt{2}\lambda_4 \\ 2\lambda_1 & 2\omega_s-4x_s & 0 & 0 & 0 & 2\lambda_4 & -2\sqrt{2}\lambda_4 \\ 0 & 0 & C_6 & 0 & 2\sqrt{2}\lambda_4 & 0 & 0 \\ 0 & 0 & 0 & C_7 & 0 & 0 & 4\lambda_4 \\ 0 & 0 & 2\sqrt{2}\lambda_4 & 0 & C_3+2\lambda_3 & 0 & 0 \\ 2\lambda_4 & 2\lambda_4 & 0 & 0 & 0 & C_5 & 0 \\ 2\sqrt{2}\lambda_4 & -2\sqrt{2}\lambda_4 & 0 & 4\lambda_4 & 0 & 0 & C_3 \end{pmatrix},$$

$$H(F_1,2)=\begin{pmatrix} 2\omega_b-4x_b-2\lambda_2 & -2\sqrt{2}\lambda_4 & 0 \\ -2\sqrt{2}\lambda_4 & C_3+2\lambda_3 & 0 \\ 0 & 0 & C_3 \end{pmatrix},$$

where $C_1=2\omega_b-5x_b-2\lambda_2-2\lambda_3$, $C_2=2\omega_b-(14/3)x_b-2\lambda_2+2\lambda_3$, $C_3=\omega_s-2x_s+\omega_b-2x_b-\lambda_1-\lambda_2-\lambda_3$, $C_4=2\omega_b-(13/3)x_b-2\lambda_2+2\lambda_3$, $C_5=\omega_s-2x_s+\omega_b-2x_b+3\lambda_1-\lambda_2-\lambda_3$, $C_6=2\omega_b-(16/3)x_b-2\lambda_2$, and $C_7=2\omega_b-4x_b-2\lambda_2-2\lambda_3$.

IV. PURE VIBRATIONAL SPECTRA

Now, we are going to fit the experimental data by our boson-realization model. Methane is a typical molecule with T_d symmetry. To our knowledge, there are 4 data for $v=1$, 7 data for $v=2$ and 8 data for $v=3$. In our first scheme we fit those 19 data to determine the eight parameters (Table I, the first scheme) with the root-mean-square energy deviation 11.61 cm^{-1}, where the standard deviation is calculated unweightedly:

$$\sigma^2=\frac{1}{19-8}\sum_{i}^{19}\left(\nu_i^{(\mathrm{calc})}-\nu_i^{(\mathrm{expt})}\right)^2 \tag{4.1}$$

From the results we come to three conclusions.

(i) Since x_b is relatively small, the bending oscillators are near harmonic ones.

(ii) The interbond interactions between bending vibrations are quite weak.

(iii) The interactions between stretching and bending vibrations are strong.

TABLE I. Parameters in the Hamiltonian obtained by the least square fitting (cm^{-1}).

Scheme	Stretching			Bending				Interac.	
	ω_s	x_s	λ_1	ω_b	x_b	λ_2	λ_3	λ_4	rms
First	2986.74	77.96	34.55	1508.37	−6.635	−5.96	−0.90	−203.73	11.61
Second	2986.24	76.55	33.60	1525.85				−201.65	12.42

TABLE II. Experimental data [8], algebraic calculation [4], and our calculation results for the vibration spectra ($v \leqslant 3$) of methane (cm^{-1}).

$v=1$

Γ	F_2	E	A_1	F_2
Expt. [8]	1310.0	1533.0	2916.5	3019.4
Calc. [4]	1303.7	1520.4	2918.4	3027.2
Scheme 1	1305.7	1526.7	2934.5	3019.0
Scheme 2	1307.8	1525.9	2933.9	3017.6

$v=2$ and F_2

Expt. [8]	2614.0	2830.4	4223.0	4319.0	4549.0	5861.0	6004.7
Calc. [4]	2610.5	2841.5	4222.0	4330.9	4547.7	5856.7	6014.5
Scheme 1	2610.1	2840.1	4226.7	4308.4	4546.9	5855.8	6011.2
Scheme 2	2614.3	2833.6	4228.8	4309.5	4543.5	5855.3	6008.6

$v=3$ and F_2

Expt. [8]	4123.0	5775.0	5861.0	7514.0	8604.0	8807.0	8900.0	9045.0
Calc. [4]	4123.9	5759.9	5868.7	7534.9	8603.0	8794.1	8910.0	9034.5
Scheme 1	4136.9	5759.3	5858.4	7513.8	8601.9	8805.3	8915.9	9035.7
Scheme 2	4140.1	5754.6	5851.2	7534.4	8603.3	8804.1	8913.0	9031.4

From these conclusions, we propose our second scheme where the bending oscillators are harmonic ($x_b=0$) and there is no interaction between the bending vibrations ($\lambda_2=\lambda_3=0$). The second scheme provides a five-parameter fit to the experimental data of methane with the root-mean-square deviation 12.42 cm^{-1} (see Table I, the second scheme). Recall that Ref. [4] presented a seven-parameter fit with the root-mean-square deviation 12.16 cm^{-1}.

For comparison, we list in Table II the 19 experimental data, the calculation results from the algebraic model [4], and our results in two schemes for the vibrational spectra ($v \leqslant 3$) of methane.

In terms of the eight parameters in the first scheme or the five parameters in the second scheme, it is straightforward to calculate the rest of the vibrational spectra for methane. After removing the spurious states, for $v=2$, there are 5 states with A_1, 5 sets of states with E, 7 sets of states with F_2, and 3 sets of states with F_1. For $v=3$, there are 13 states with A_1, 4 states with A_2, 14 sets of states with E, 25 sets of states with F_2, and 15 sets of states with F_1. Except for the states with F_2 and $v=2$ that were listed in Table II, the rest of the calculation results in the first scheme are listed as follows.

$v=2,$	A_1	2614.3	3057.9	4297.7	5807.6	5974.4		
$v=2,$	E	2616.5	3055.6	4326.3	4461.2	6038.2		
$v=2,$	F_1	2832.4	4324.8	4545.7				
$v=3,$	A_1	3913.0	4158.5	4586.8	5514.9	5601.8	5861.8	5992.3
		7100.9	7295.4	7567.2	8587.8	8749.0	8994.0	
$v=3,$	A_2	4141.8	4588.6	5852.6	7564.8			
$v=3,$	E	4142.0	4157.5	4591.3	5526.7	5621.8	5828.1	5858.1
		5990.1	7160.1	7299.4	7334.5	7502.1	7566.1	8838.7
$v=3,$	F_2	3917.6	3930.3	4136.9	4365.5	4378.3	5514.3	5589.1
		5619.9	5633.9	5759.3	5831.1	5858.4	6075.8	6078.6
		7074.8	7134.5	7255.9	7300.1	7331.0	7379.4	7513.8
		8601.9	8805.3	8915.9	9035.7			
$v=3,$	F_1	3919.4	4148.3	4369.1	5605.1	5632.4	5753.6	5840.8
		5854.3	6075.8	7158.7	7291.3	7334.8	7383.0	7539.3
		8941.9						

V. CONCLUSIONS

In this paper we describe ten coupled one-dimensional anharmonic oscillators of a tetrahedral molecule by ten sets of bosonic creation and annihilation operators. The ten oscillators are divided into two classes: stretching and bending oscillators. The energy levels of those oscillators are described by four parameters under the assumption of the Morse potential for stretching vibration and the Pöschl-Teller potential for the bending vibrations: ω_s, x_s, ω_b, and x_b. The interbond interactions and the interactions between stretching and bending vibrations are supposed to be T_d invariant and to preserve the total number v of vibrational quanta so that four parameters λ_i, $1 \leqslant i \leqslant 4$, have to be introduced.

In the first scheme of the boson-realization model with eight parameters we fit the 19 experimental vibrational data for methane, and obtain the root-mean-square energy deviation to be 11.61 cm^{-1}. From the obtained parameters, we see that the interactions between the bending vibrations are weak, the interactions between the stretching and bending vibrations are strong, and the bending oscillators are quite near harmonic ones. These conclusions are different from the previous model [4]. From these conclusions we proposed another five-parameter fit in the second scheme with the root-mean-square energy deviation 12.42 cm^{-1}. To our knowledge, it may be the model with the least parameters that well fits the experimental vibration spectra ($v \leqslant 3$) of methane.

The interaction between vibrational and rotational motions plays an important role in describing the abundant experimental data of vibrorotational energy spectra of a tetrahedral molecule. We will study it by the boson-realization model elsewhere.

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[1] J. L. Dunham, Phys. Rev. **41**, 721 (1932).

[2] F. Iachello and R. D. Levine, J. Chem. Phys. **77**, 3046 (1982); O. S. van Roosmalen, F. Iachello, R. D. Levine, and A. E. L. Dieperink, *ibid.* **79**, 2515 (1983); F. Iachello, A. Leviatan and A. Mengoni, *ibid.* **95**, 1449 (1991).

[3] O. S. van Roosmalen, I. Benjamin, and R. D. Levine, J. Chem. Phys. **81**, 5986 (1984); F. Iachello, S. Oss, and L. Viola, *ibid.* **101**, 3531 (1994).

[4] R. Lemus and A. Frank, J. Chem. Phys. **101**, 8321 (1994).

[5] L. Halonen and M. S. Child, J. Chem. Phys. **79**, 559 (1983).

[6] F. Iachello and S. Oss, Phys. Rev. Lett. **66**, 2976 (1991); A. Frank and R. Lemus, *ibid.* **68**, 413 (1992).

[7] F. Iachello and S. Oss, J. Mol. Spectrosc. **153**, 225 (1992); Chem. Phys. Lett. **205**, 285 (1993); J. Chem. Phys. **99**, 7337 (1993).

[8] D. L. Gray and A. G. Robiette, Mol. Phys. **37**, 1901 (1979); G. Herzberg, *Molecular Spectra and Molecular Structure II* (Van Nostrand Reinhold, New York 1945); J. C. Hilico, J. Phys. (Paris) **31**, 289 (1970); B. Bobin and G. Guelachvili, J. Phys. (Paris) **39**, 33 (1978).

[9] P. R. Bunker, *Molecular Symmetry and Spectroscopy* (Academic Press, New York, 1979).

[10] I. M. Mills and A. G. Robiette, Mol. Phys. **56**, 743 (1985).

[11] E. P. Wigner, *Group Theory and Its Application to the Quantum Mechanics of Atomic Spectra*, English version, translated by J. J. Griffin (Academic Press, New York, 1959); M. Hamermesh, *Group Theory and Its Application to Physical Problems* (Addison-Wesley, Reading, MA, 1962).

[12] T. Lukka, E. Kauppi, and L. Halonen, J. Chem. Phys. **102**, 5200 (1995).