Boson-Realization Model for the Vibrational Spectra of Tetrahedral Molecules

Zhong-Qi Ma *
CCAST (World Laboratory), PO Box 8730, Beijing 100080, and Institute of High Energy Physics, P.O.Box 918(4), Beijing 100039, P. R. of China

Xi-Wen Hou
Institute of High Energy Physics, P.O.Box 918(4), Beijing 100039, and Department of Physics, University of Three Gorges, Yichang 443000, P. R. of China

Mi Xie
Graduate School, Chinese Academy of Sciences, Beijing 100039, P. R. of China

Abstract

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 $11.61\text{ cm}^{-1}$. 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 $12.42\text{ cm}^{-1}$.

*email address: MAZQ@BEPC3.IHEP.AC.CN
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 polymolecular 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 propose another algebraic model, the boson realization model, to study the vibrational spectra of tetrahedral molecules, where 10 coupled one-dimensional anharmonic oscillators are described by 10 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 $12.42 \text{ cm}^{-1}$. It may be a model with the least parameters that well 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 bosonic 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 $v \leq 3$, 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 $v \leq 3$ in two schemes are listed in Table 2. 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 10 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.

Fig. 1 Schematic representation of a $XY_4$ tetrahedral molecule.

Now, for the ten oscillators we introduce 10 sets of bosonic operators $a^\dagger_\alpha$ and $a_\alpha$, $1 \leq \alpha \leq 10$. 
\( \alpha \leq 10 \), that satisfy the well known relations

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

where \( |n\rangle \) denotes the common eigenstate of the phonon number operators \( N_\alpha \) with the eigenvalues \( n_\alpha \), respectively.

\[
N_\alpha = a_\alpha^\dagger a_\alpha, \quad N_\alpha |n\rangle = n_\alpha |n\rangle. \tag{2.2}
\]

The first four bosonic operators \( a_j^\dagger \) (or \( a_j \)), \( 1 \leq j \leq 4 \), 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 \( a_\mu \)), \( 5 \leq \mu \leq 10 \), 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 \( \omega \) and \( x \), so that the energy of the \( \alpha \)th oscillator can be expressed in the operator form:

\[
E_s(N_j) = N_j \{ \omega_s - x_s (N_j + 1) \}, \quad 1 \leq j \leq 4
\]

\[
E_b(N_\mu) = N_\mu \{ \omega_b - x_b (N_\mu + 1) \}, \quad 5 \leq \mu \leq 10 \tag{2.3}
\]

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:

\[
H = \sum_{j=1}^{4} E_s(a_j^\dagger a_j) + \sum_{\mu=5}^{10} E_b(a_\mu^\dagger a_\mu) + \lambda_1 \sum_{i \neq j=1}^{4} a_i^\dagger a_j + \lambda_2 \sum_{\mu \neq \nu=5}^{10} a_\mu^\dagger a_\nu
\]

\[
+ \lambda_3 \sum_{\mu=5}^{7} \left( a_\mu^\dagger a_{\mu+3} + a_{\mu+3}^\dagger a_\mu \right) + \lambda_4 \left\{ a_1^\dagger \sum_{\mu=5}^{7} (a_\mu - a_{\mu+3}) \right\}
\]

\[
+ a_2^\dagger \left( a_5 - \sum_{\mu=6}^{8} a_\mu + a_9 + a_{10} \right) + a_3^\dagger \sum_{\mu=3}^{5} (a_{2\mu} - a_{2\mu-1})
\]

\[
+ a_4^\dagger \left( -a_5 - a_6 + \sum_{\mu=7}^{9} a_\mu - a_{10} \right) + H.C. \right\} + \lambda_5 \left\{ \left( \sum_{j=1}^{4} a_j^\dagger \right) \left( \sum_{\mu=5}^{10} a_\mu \right) + H.C. \right\} \tag{2.4}
\]
It will be seen in the next section that the term with \( \lambda_5 \) 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 \( \lambda_4 \) describes the interactions 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 \( \omega_s/x_s - 1 \) and \( \omega_b/x_b - 1 \) 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 \( (B_{12}, B_{5,6}, \text{ and } B_{5,10}) \), fixed two parameters \( N_1 \) and \( N_2 \), reduced one parameter by a constraint, and neglected one parameter \( \lambda_4 \) 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 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 \( n_a \) of the ten oscillators. The first four numbers \( n_j \) describe the stretching vibrations, and the next six numbers \( n_{\mu} \) 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 \( |n_1 n_2 n_3 n_4 00000000 \rangle \) by \( |abcd\rangle \), where the vanishing \( n_{\mu} (\mu \geq 5) \) 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 \( |0000n_5 n_6 n_7 n_8 n_9 n_{10} \rangle \) by \( |abcdef\rangle \), where the vanishing \( n_j (j \leq 4) \) 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.
Similarly, the irreducible bases of the fundamental bending vibration \( s \) demanded the matrix elements of the Hamiltonian related with the fundamental spurious directly eliminated the spurious states from both the space and the Hamiltonian. They vibrations and acquires a small error for anharmonic one. Instead, Lemus and Frank [4] states by the projection operators. This method of removal is exact for harmonic bending states \( \psi \) placed the spurious states at the energies \[7\] in the recent papers we see two methods of removal. Iachello and Oss \[9\] listed the spurious states at the energies.

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

\[
\begin{align*}
\phi_{1}(A_{1}, 1000) &= 2^{-1} \{ |1000\rangle + |0100\rangle + |0010\rangle + |0001\rangle \} \\
\phi_{1}^{(1)}(F_{2}, 1000) &= 2^{-1} \{ |1000\rangle - |0100\rangle + |0010\rangle - |0001\rangle \} \\
\phi_{2}^{(1)}(F_{2}, 1000) &= 2^{-1} \{ |1000\rangle - |0100\rangle - |0100\rangle + |0001\rangle \} \\
\phi_{3}^{(1)}(F_{2}, 1000) &= 2^{-1} \{ |1000\rangle + |0100\rangle - |0010\rangle - |0001\rangle \}
\end{align*}
\] (3.1)

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

\[
\begin{align*}
\psi_{1}(A_{1}, 100000) &= 6^{-1/2} \{ |100000\rangle + |010000\rangle + |001000\rangle + |000100\rangle + |000010\rangle + |000001\rangle \} \\
\psi_{1}^{(1)}(E, 100000) &= (2\sqrt{3})^{-1} \{ 2|100000\rangle - |010000\rangle - |001000\rangle - |000100\rangle \\
&\quad + 2|000100\rangle - |000010\rangle - |000001\rangle \} \\
\psi_{2}(E, 100000) &= 2^{-1} \{ |010000\rangle - |001000\rangle + |000100\rangle - |000010\rangle - |000001\rangle \} \\
\psi_{1}^{(1)}(F_{2}, 100000) &= 2^{-1/2} \{ |010000\rangle - |000100\rangle \} \\
\psi_{2}^{(1)}(F_{2}, 100000) &= 2^{-1/2} \{ |001000\rangle - |000010\rangle \} \\
\psi_{3}^{(1)}(F_{2}, 100000) &= 2^{-1/2} \{ |100000\rangle - |000100\rangle \}
\end{align*}
\] (3.2)

In those bases the Hamiltonian \( H \) given in (2.4) becomes a block matrix with the submatrices \( H(\Gamma, v) \), where \( \Gamma \) denotes the irreducible representation, and \( v \) is the total phonon number. Obviously, \( H(E, 1) \) is a \( 1 \times 1 \) submatrix, but \( H(A_{1}, 1) \) and \( H(F_{2}, 1) \) are \( 2 \times 2 \) submatrices:

\[
\begin{align*}
H(E, 1) &= \omega_{b} - 2x_{b} - \lambda_{2} + \lambda_{3} \\
H(A_{1}, 1) &= \begin{pmatrix}
\omega_{b} - 2x_{b} + 3\lambda_{1} & 2\sqrt{6}\lambda_{5} \\
2\sqrt{6}\lambda_{5} & \omega_{b} - 2x_{b} + 5\lambda_{2} + \lambda_{3}
\end{pmatrix} \\
H(F_{2}, 1) &= \begin{pmatrix}
\omega_{b} - 2x_{b} - \lambda_{1} & 2\sqrt{2}\lambda_{4} \\
2\sqrt{2}\lambda_{4} & \omega_{b} - 2x_{b} - \lambda_{2} - \lambda_{3}
\end{pmatrix}
\end{align*}
\] (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 \( \geq 10 \) 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 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:

\[
\omega_{b} - 2x_{b} + 5\lambda_{2} + \lambda_{3} = 0
\] (3.4)
it contains \( \psi \) identify the spurious states. Generally speaking, a state is identified as a spurious state if the energy of the fundamental spurious state to be vanishing, but the energies of all other spurious states are non-vanishing. Secondly, we have to answer the problem 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:

\[
\begin{align*}
|n\rangle |m\rangle &= |(n + m)\rangle \\
|(n + m)\rangle &= |(n_1 + m_1), (n_2 + m_2), \cdots, (n_{10} + m_{10})\rangle
\end{align*}
\] (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 product:

\[
\begin{align*}
|n\rangle |m\rangle &= \prod_{\mu} \left\{ \frac{(n_{\mu} + m_{\mu})!}{n_{\mu}! m_{\mu}!} \right\}^{1/2} |(n + m)\rangle \\
|(n + m)\rangle &= |(n_1 + m_1), (n_2 + m_2), \cdots, (n_{10} + m_{10})\rangle
\end{align*}
\] (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 \( \lambda_5 \), 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 Ref. [6], [12] and our results below). It is interesting to notice that the first method [7] of removal is exact also 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 5 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 10 sets: \( \psi(A_1, 200000), \psi_{\nu}^{(1)}(E, 200000), \psi_{\nu}^{(1)}(F_2, 200000), \psi(A_1, 100100), \psi_{\nu}^{(1)}(E, 100100), \\
\psi_{\nu}^{(1)}(A_1, 110000), \psi_{\nu}^{(1)}(E, 110000), \psi_{\nu}^{(1)}(F_2, 110000), \psi_{\nu}^{(3)}(F_2, 100000), \) 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 5 sets of spurious states with \( v = 2 \), belonging to the following irreducible representations: two \( A_1 \), one
ducible representations. There are five states belonging to irreducible representation space:

\[ \phi(A_1, 1000) \psi(A_1, 100000), \]
\[ \{\psi(A_1, 200000) + \psi(A_1, 100100) + 2\psi(A_1, 110000)\} / \sqrt{3} = \{\psi(A_1, 100000)\}^2, \]
\[ \{\psi_2^1(E, 200000) + \psi_2^1(E, 100100) + \psi_2^1(E, 110000)\} / \sqrt{3} = \psi(A_1, 100000)\psi_2^1(E, 100000), \]
\[ \phi_3^1(F_2, 1000)\psi(A_1, 100000), \]
\[ \{\psi_3^1(F_2, 200000) + \sqrt{3}\psi_3^1(F_2, 110000)\} / \sqrt{3} = \psi(A_1, 100000)\psi_3^1(F_2, 100000). \]

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:

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

where the number 2 in the argument denotes \( v = 2 \). 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 \( 5 \times 5 \) submatrix for \( A_1 \), \( 5 \times 5 \) submatrix for \( E \), \( 7 \times 7 \) submatrix for \( F_2 \), and \( 3 \times 3 \)
submatrix for $F_1$:

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

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

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

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

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 1, the first scheme) with the root-mean-square energy deviation $11.61 \text{cm}^{-1}$, where the standard deviation is calculated unweightedly:

$$\sigma^2 = \frac{1}{19 - 8} \sum_{i}^{19} (\nu_i(\text{calc}) - \nu_i(\text{expt}))^2$$

(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.

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 1, 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 2 the 19 experimental data, the calculation results from the algebraic model [4], and our results in two schemes for the vibrational spectra ($v \leq 3$) of methane.

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

| Scheme | Stretching | | Bending | | Interac. | | rms |
|---|---|---|---|---|---|---|
| | $\omega_s$ | $x_s$ | $\lambda_1$ | $\omega_b$ | $x_b$ | $\lambda_2$ | $\lambda_3$ | $\lambda_4$ | |
| 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 ($v \leq 3$) of methane (cm$^{-1}$).

| $v = 1$ | | | | | | | | |
|---|---|---|---|---|---|---|
| $F$ | $F_2$ | $E$ | $A_1$ | $F_2$ |
| 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 $F_2$ | | | | | | | |
|---|---|---|---|---|---|---|
| | 2614.0 | 2830.4 | 4223.0 | 4319.0 | 4549.0 | 5861.0 | 6004.7 |
| Expt. [8] | 2610.5 | 2841.5 | 4222.0 | 4330.9 | 4547.7 | 5856.7 | 6014.5 |
| Calc. [4] | 2610.1 | 2840.1 | 4226.7 | 4308.4 | 4546.9 | 5855.8 | 6011.2 |
| Scheme 1 | 2614.3 | 2833.6 | 4228.8 | 4309.5 | 4543.5 | 5855.3 | 6008.6 |
| Scheme 2 | | | | | | | |

| $v = 3$ and $F_2$ | | | | | | | |
|---|---|---|---|---|---|---|
| | 4123.0 | 5775.0 | 5861.0 | 7514.0 | 8604.0 | 8807.0 | 8900.0 | 9045.0 |
| Expt. [8] | 4123.9 | 5759.9 | 5868.7 | 7534.9 | 8603.0 | 8794.1 | 8910.0 | 9034.5 |
| Calc. [4] | 4136.9 | 5759.3 | 5858.4 | 7513.8 | 8601.9 | 8805.3 | 8915.9 | 9035.7 |
| Scheme 1 | 4140.1 | 5754.6 | 5851.2 | 7534.4 | 8603.3 | 8804.1 | 8913.0 | 9031.4 |
| Scheme 2 | | | | | | | |

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 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
\[ v = 3, \ A_1 \]
\[
\begin{array}{cccccccc}
3913.0 & 4158.5 & 4586.8 & 5514.9 & 5601.8 & 5861.8 & 5992.3 \\
7100.9 & 7295.4 & 7567.2 & 8587.8 & 8749.0 & 8994.0 \\
\end{array}
\]
\[ v = 3, \ A_2 \]
\[
\begin{array}{cccccccc}
4141.8 & 4588.6 & 5852.6 & 7564.8 \\
5990.1 & 7160.1 & 7299.4 & 7334.5 & 7502.1 & 7566.1 & 8838.7 \\
\end{array}
\]
\[ v = 3, \ E \]
\[
\begin{array}{cccccccc}
4142.0 & 4157.5 & 4591.3 & 5526.7 & 5621.8 & 5828.1 & 5858.1 \\
5990.1 & 7160.1 & 7299.4 & 7334.5 & 7502.1 & 7566.1 & 8838.7 \\
\end{array}
\]
\[ v = 3, \ F_2 \]
\[
\begin{array}{cccccccc}
3917.6 & 3930.3 & 4136.9 & 4365.5 & 4378.3 & 5514.3 & 5589.1 \\
5619.9 & 5633.9 & 5759.3 & 5831.1 & 5858.4 & 6075.8 & 6078.6 \\
7074.8 & 7134.5 & 7255.9 & 7300.1 & 7331.0 & 7379.4 & 7513.8 \\
8601.9 & 8805.3 & 8915.9 & 9035.7 \\
\end{array}
\]
\[ v = 3, \ F_1 \]
\[
\begin{array}{cccccccc}
3919.4 & 4148.3 & 4369.1 & 5605.1 & 5632.4 & 5753.6 & 5840.8 \\
5854.3 & 6075.8 & 7158.7 & 7291.3 & 7334.8 & 7383.0 & 7539.3 \\
8941.9 \\
\end{array}
\]

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: \( \omega_s, x_s, \omega_b, \) 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 4 parameters \( \lambda_i, 1 \leq i \leq 4 \), 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 \( (v \leq 3) \) 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.

**Acknowledgments.** This work was supported by the National Natural Science Foundation of China and Grant No. LWTZ-1298 of the Chinese Academy of Sciences.
References

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

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

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

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

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

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

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

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

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

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

[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(1995)5200.