Overtone spectra and intensities of tetrahedral molecules
in boson-realization models

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The stretching and bending vibrational spectrum and the intensities of infrared transitions in a tetrahedral molecule are studied in two boson-realization models, where the interactions between stretching and bending vibrations are described by a quadratic cross term and by Fermi resonance terms, called harmonically coupled and Fermi resonance boson-realization model, respectively. The later is a development of our recent model. As an example, the two models are applied to the overtone spectrum and the intensities of silicon tetrafluoride. Those models provide fits to the published experimental vibrational eigenvalues with standard deviations 1.956 cm$^{-1}$ and 0.908 cm$^{-1}$, respectively. The intensities of infrared transitions of its complete vibrations are calculated in the two models, and results show a good agreement with the observed data.
I. INTRODUCTION

In recent years, algebraic methods have been introduced for a description of rotation-vibrational spectra of molecules. A U(4) algebraic model [1] was successfully used to explain the rotation-vibrational states of diatomic molecules. This model was developed for studying small molecules by introducing a U(4) algebra for each bond [2,3]. It was also suggested to use a U(k + 1) model [4] for the \( k = 3m - 3 \) rotational and vibrational degrees of freedom of \( m \)-atomic molecules. Those two models have an advantage that they can treat rotations and vibrations simultaneously, but they are quite complex for larger molecules. A U(n) algebraic approach [5] was also used for a treatment of \( n - 1 \) stretching vibrational degrees of freedom in polyatomic molecules. Iachello and Oss presented a SU(2) algebraic model based on isomorphism between the one-dimensional Morse oscillator and the SU(2) algebra, which was particularly well suited for dealing with the stretching vibrations of polyatomic molecules such as the octahedral and benzene-like systems [6]. The U(4) and SU(2) algebraic models were even modified by the corresponding quantum algebraic ones [7,8] for diatomic molecules.

Incorporating the bending modes in algebraic models for large molecules was not achieved until 1993, when Iachello and Oss proposed a U(2) algebraic model for describing Pöschl-Teller oscillator that was well suitable for bending vibrations [9]. They extended this method to treat coupled bending modes [10]. Frank et al. presented a symmetry-adapted algebraic model [11-13], which described the stretching and bending vibrations in terms of U(2) algebra and made a clear connection between the algebraic approaches and the traditional methods in the configuration space. In a different way, by making use of the bosonic operators for describing vibrations, Ma et al. have recently introduced an algebraic model of boson realization [14] for the complete vibrational modes, and obtained the satisfactory results for some molecules [15,16].

In this paper we will further investigate both the complete vibrations and the intensities of infrared transitions in a tetrahedral molecule in two boson-realization models. The first model is the model that we proposed recently [14], where the interactions between the stretch and the bend are harmonically coupled. Let us refer this model as a harmonically coupled boson-realization model (HCBM). The second model is called Fermi resonance boson-realization model (FRBM), where the interactions between two kinds of vibrations are described by Fermi resonances. As an example of their applications, we study the vibrational spectrum of silicon tetrafluoride SiF\(_4\) in two models. HCBM with seven parameters and FRBM with ten parameters provide fits to the observed values with the standard deviation 1.956 cm\(^{-1}\) and 0.908 cm\(^{-1}\), respectively. Furthermore, we propose another FRBM with only seven parameters, where the standard deviation is still about half of that in HCBM with the same number of parameters. It shows that FRBM is more suitable for highly excited states in this molecule. In addition, intensities of infrared transitions of both the stretching and the bending vibrational spectrum in this molecule are calculated in the two models, and indicate a good agreement with the experimental values.

The organization of this paper is as follows. Sec. II is devoted to construct the symmetrized bases and identify the spurious states. In Sec. III the vibrational Hamiltonian in the two models are
introduced in terms of ten sets of boson operators and applied to the vibrational spectrum of silicon tetrafluoride SiF$_4$. Its intensities of infrared transitions in the two models are presented in Sec. IV. Conclusion is made in Sec. V.

II. SYMMETRIZED BASES AND SPURIOUS STATES

In calculating spectra of polyatomic molecules one needs to construct a basis in which the Hamiltonian matrix is a block matrix. The symmetry adapted bases are widely used for this purpose. Halonen and Child [17] gave symmetrized local mode basis functions for stretching vibrations of symmetry molecules by a combination of promotion operators and Schmidt orthogonalization. Frank et al. [11-13] first constructed the symmetrized bases by projecting the one-phonon local functions, and then obtained the higher-phonon functions from the one-phonon symmetrized states by the Clebsch-Gordan coefficients. This method is quite complex when describing vibrations of large molecules and for high overtones. In this case, the symmetry adapted bases can be achieved by a new technique for constructing representations of the molecular symmetry point groups, that was recently called symmetrized boson representations [18]. This new technique has merits that the basis vectors of those representations have a clear physical picture, and that their combinations are much simpler and general for multiple-phonon states. In this way we constructed the symmetrized bases for a tetrahedral molecule [14]. We hereby outline them for completeness.

For a tetrahedral molecule XY$_4$ there are four stretching oscillators and six bending oscillators. As in our previous paper [14], let the atom X locate at the center O of the tetrahedron, and the 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 four stretching oscillators OA, OB, OC, and OD, which are enumerated one to four, are described by four equivalent bosonic operators $a^\dagger_j (a_j)$, 1 $\leq$ j $\leq$ 4. The six bending oscillators $\angle$ AOB, $\angle$ AOC, $\angle$ AOD, $\angle$ COD, $\angle$ DOB, and $\angle$ BOC, enumerated by five to ten, are described by six equivalent bosonic operators $a^\dagger_\mu (a_\mu)$, 5 $\leq$ $\mu$ $\leq$ 10. Those ten sets of bosonic operators satisfy the well known algebraic relations. Hereafter, the indexes j, $\mu$, and $\alpha$ run from 1 to 4, 5 to 10, and 1 to 10, respectively, and n$\alpha$ denotes the phonon number on the $\alpha$th oscillator, and n$\Sigma$ and n$b$ the total phonon numbers on stretching and bending oscillators, respectively.

From the standard method of group theory, it is easy to reduce the regular representation of the point group $T_d$. Applying those combinations of group elements, that belong to irreducible representations of $T_d$, to the states $|n_1, n_2, n_3, n_4\rangle$ for pure stretching vibrations and the states $|n_5, n_6, n_7, n_8, n_9, n_{10}\rangle$ for pure bending vibrations, respectively, we generally obtain the symmetry adapted bases for the states with any phonon number. Then, the product of two bases can be combined into irreducible bases by the Clebsch-Gordan coefficients of $T_d$, denoted as $|n\rangle \equiv |n_1, n_2, n_3, n_4, n_5, n_6, n_7, n_8, n_9, n_{10}\rangle$.

For the fundamental bending vibrations (n$b$ = 1) there are six states belonging to three irreducible representation: $A_1$, $E$, and $F_2$. As is well known [19], there are only five degrees of freedom for the bending vibrations ($E \oplus F_2$), because there is a constraint between the six angles. The state belonging to the representation $A_1$ is called the fundamental spurious state:
\[
\psi(A_1, 100000) = 6^{-1/2} \sum_{\mu=5}^{10} |1_\mu\rangle, 
\] (2.1)

where \(|1_\mu\rangle\) denotes the first excited state of the \(\mu\)th oscillator. This state introduces a spurious degree of freedom that should be removed.

Some methods for removing the spurious states were recently introduced. Iachello and Oss [9] placed the spurious states at the energies \(\geq 10\) times the energies of the physical states by projection operators. This method of removal is exact for harmonic bending vibrations and acquires a small error for anharmonic ones. Instead, Lemus and Frank [13] directly eliminated the spurious states from both the space and the Hamiltonian. They demanded the matrix elements of the Hamiltonian related to the fundamental spurious state \(\psi(A_1, 100000)\) vanishing. However, it is impossible to demand all the matrix elements of the Hamiltonian that related to the spurious states vanishing. In Ref. [14] a criterion for identifying the spurious states was introduced: a state is a spurious state if it contains \(\psi(A_1, 100000)\) as a factor. In addition, the bases of the physical states are chosen to be orthogonal with each other and with all the spurious states. In next section we will use this criterion to remove the spurious states from Hamiltonian and the symmetrized bases.

III. HAMILTONIAN

Studies of the vibrations in a tetrahedral molecule already exist in the literature. Its excited stretching vibrational states were explained in the local mode model [17] and a U(5) algebraic model [5]. A U(2) algebraic approach [13] was proposed for both stretching and bending modes, where the interactions between the stretch and the bend were neglected. In our previous papers [14,15] we studied the vibrational spectrum of methane in boson-realization model in terms of bosonic operators and q-deformed harmonic oscillators, however, intensities of infrared transitions were not involved. We will further research both the vibrational energy levels and intensities of a tetrahedral molecules in the two different models, and apply it to the spectrum of SiF\(_4\).

A. HARMONICALLY COUPLED BOSON-REALIZATION MODEL

First of all, we outline the boson-realization model that we recently introduced in [14], where the interactions between the stretch and the bend are described by a quadratic cross term. We here call it as the harmonically coupled boson-realization model (HCBM). Then, we calculate the energy levels of SiF\(_4\) in HCBM.

For simplicity we assume that all oscillators are the Morse ones with two parameters \(\omega\) and \(x\), so that the energies of those oscillators can be expressed in the operator form:

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

\[
E_b(n_\mu) = n_\mu \{\omega_b - x_b(n_\mu + 1)\}, \quad 5 \leq \mu \leq 10, 
\] (3.1)
where the null energy has been removed.

The vibrational Hamiltonian \( H \) of the molecule \( XY_4 \) is \( T_d \) invariant and is assumed to preserve the total number of quanta \( n = n_s + n_b \). Since \( a_j^\dagger \) (\( a_j \)) and \( a_\mu^\dagger \) (\( a_\mu \)) are the tensor operators belonging to \( A_1 \oplus F_2 \) and \( A_1 \oplus E \oplus F_2 \), respectively, and \( \sum \alpha_\mu \) (or \( \sum \alpha_\mu^\dagger \)) only annihilates (or creates) the spurious states, we can express Hamiltonian \( H \) as the \( T_d \) invariant combinations of the products of one creation operator and one annihilation operator [15]:

\[
H = \sum_{j=1}^{4} E_s(a_j^\dagger a_j) + \sum_{\mu=5}^{10} E_b(a_\mu^\dagger a_\mu) + \lambda_s \sum_{i \neq j} a_i^\dagger a_j
+ \lambda_b \sum_{\mu=5}^{7} (a_\mu^\dagger a_{\mu+3} + \text{H.c.}) + \lambda_{sb} \left\{ a_1^\dagger \sum_{\mu=5}^{7} (a_\mu - a_{\mu+3})
+ a_2^\dagger \left( a_5 - \sum_{\mu=6}^{8} a_\mu + a_9 + a_{10} \right)
+ a_3^\dagger \sum_{\mu=3}^{5} (a_{2\mu} - a_{2\mu-1})
+ a_4^\dagger \left( -a_5 - a_6 + \sum_{\mu=7}^{9} a_\mu - a_{10} \right) + \text{H.c.} \right\},
\]

(3.2)

where \( \lambda_s \) and \( \lambda_b \) are the coupling strength among stretching modes and bending ones, respectively. The term with \( \lambda_{sb} \) describes the interaction between stretching and bending vibrations, which was neglected in Ref. [13] for simplicity. The Hamiltonian \( H \) contains seven parameters: \( \omega_s, x_s, \omega_b, x_b, \lambda_s, \lambda_b, \) and \( \lambda_{sb} \).

Following the criterion in Sec. II for eliminating the spurious states from the bases and straight calculating, we find that for \( n = 1 \) and representation \( A_1 \), there is one physical state, for \( n = 1 \) and \( E \) there is only one set of physical states, for \( n = 1 \) and \( F_2 \) there are two sets of physical states, for \( n = 2 \) and \( F_2 \) there are seven sets of physical states, and for \( n = 3 \) and \( F_2 \), there are 25 sets of physical states, and for \( n = 4 \) and \( F_2 \), there are 69 sets of physical states. Those combinations for \( n = 1, 2 \) were given in Ref. [14], and others can be obtained from us upon request.

In those bases of the physical states the Hamiltonian becomes a symmetric block matrix. The energies of physical states can be calculated provided that the parameters of the Hamiltonian are known. A least-square fitting is adopted to get the parameters from the observed data. The observed energy levels from Ref. [20] and the corresponding calculated values are given in Table I, where the standard deviation (SD) in this fit (Fit A) is 1.956 cm\(^{-1}\). The seven parameters obtained are given in Table II. In terms of those parameters one can calculate the other energy levels. Since the infrared experimental dipole transitions energies correspond to \( F_2 \), we hereby only list the calculation results for other \( F_2 \) states in Table III.

![Table I](image1.png)

![Table II](image2.png)

![Table III](image3.png)
From Table II we see that the ratio \( w_s/w_s \) of the stretching modes is larger than that of the bending ones. It means that, contrary to the case in methane [14], the anharmonicity of bending modes in \( SiF_4 \) is larger than that of the stretching ones. At least, the anharmonicity of the vibrations depends upon the molecules discussed.

**B. FERMI RESONANCE BOSON-REALIZATION MODEL**

With the development and refinement of experimental techniques in high-resolution spectroscopy, measurements of high excited vibrational spectra for molecules become available [21]. One of important characters in highly excited states is appearance of anharmonic resonances. Fermi resonance (FR), one of these resonances, is taken into account for description of molecular vibrations. In the normal mode model, FR terms were treated as perturbative corrections [22], while they were described by the nondiagonal matrix elements of Majorana operators in U(4) algebraic model [23]. Recently, simple Fermi resonance-local mode models for bent triatomic molecules [24] and pyramidal \( XY_3 \) molecules [25] have been constructed by Halonen et al., where FR terms are expressed in terms of curvilinear internal valence coordinates. In addition, FR can be of central importance for intramolecular vibrational redistribution and kinetics [26]. Therefore, it is necessary for us to consider FR in the boson-realization model. We present an extended model, called Fermi resonance boson-realization model (FRBM), and it is pleasure to see that FRBM provides smaller standard deviation than HCBM in the energy level fits of \( SiF_4 \).

We introduce another vibrational Hamiltonian for a tetrahedral molecule, where the interactions between stretching and bending vibrations are described by the \( T_d \) symmetric FR terms that couple one creation (or, respectively, annihilation) operator of stretching vibrations with two annihilation (or, respectively, creation) operators of bending ones. Although \( a_\mu a_\nu \) belongs to \( 3A_1 \oplus 3E \oplus 3F_2 \oplus F_1 \), we find only four independent \( T_d \) invariant combinations related to physical states:

i) \( A_1 \otimes (E \otimes E)_{A_1} \),

\[
H_1 = \left( \sum_{j=1}^{4} a_j^\dagger \right) \left( \sum_{\mu=5}^{10} a_\mu^2 - \sum_{\mu<\nu=6}^{10} a_\mu a_\nu + 3 \sum_{\mu=5}^{7} a_\mu a_{\mu+3} \right) + H.c., \quad (3.3)
\]

ii) \( A_1 \otimes (F_2 \otimes F_2)_{A_1} \),

\[
H_2 = \left( \sum_{j=1}^{4} a_j^\dagger \right) \left( \sum_{\mu=5}^{10} a_\mu^2 - 2 \sum_{\mu=5}^{7} a_\mu a_{\mu+3} \right) + H.c., \quad (3.4)
\]

iii) \( F_2 \otimes (E \otimes F_2)_{F_2} \),

\[
H_3 = \left( a_1^\dagger - a_2^\dagger + a_3^\dagger - a_4^\dagger \right) (a_6 - a_9) \left( 3a_6 + 3a_9 - \sum_{\mu=5}^{10} a_\mu \right) \\
+ \left( a_1^\dagger - a_2^\dagger - a_3^\dagger + a_4^\dagger \right) (a_7 - a_{10}) \left( 3a_7 + 3a_{10} - \sum_{\mu=5}^{10} a_\mu \right)
\]

\[6\]
\[ + \left( a_1^+ + a_2^+ - a_3^+ - a_4^+ \right) (a_5 - a_8) \left( 3a_5 + 3a_8 - \sum_{\mu=5}^{10} a_\mu \right) + H.c., \]  
(3.5)

iv) \( F_2 \otimes (F_2 \otimes F_2)_{F_2} \),

\[ H_4 = \left( a_1^+ - a_2^+ + a_3^+ - a_4^+ \right) (a_5 - a_8) (a_7 - a_{10}) \]
\[ + \left( a_1^+ - a_2^+ - a_3^+ + a_4^+ \right) (a_5 - a_8) (a_6 - a_9) \]
\[ + \left( a_1^+ + a_2^+ - a_3^+ - a_4^+ \right) (a_6 - a_9) (a_7 - a_{10}) + H.c. \]  
(3.6)

Now, we obtain the following \( T_d \) invariant Hamiltonian with ten parameters:

\[ H = \sum_{j=1}^{4} E_s(a_j^+a_j) + \sum_{\mu=5}^{10} E_b(a_\mu^+a_\mu) + \lambda_s \sum_{i\neq j=5}^{10} a_i^+a_j + \lambda_b \sum_{\mu=5}^{7} \left( a_\mu^+a_{\mu+3} + a_{\mu+3}^+a_\mu \right) \]
\[ + \lambda f_1 H_1 + \lambda f_2 H_2 + \lambda f_3 H_3 + \lambda f_4 H_4, \]  
(3.7)

where the Hamiltonian preserve the quantum number \( N = 2n_s + n_b \).

The symmetrized bases are also used in the calculation. Using the same method for removing the spurious states as described in Sec. II, we find that there are 1 set of states with \( N = 1 \) for representation \( E \) (no spurious state), and 3 states with \( N=2 \) for \( A_1 \) (removing 1 spurious state), and for the representation \( F_2 \) there are 1 set of states with \( N = 1 \) (no spurious state), 3 sets of states with \( N = 2 \) (removing 1 set of spurious state), 8 sets of states with \( N = 3 \) (removing 4 sets of spurious states), 20 sets of states with \( N = 4 \) (removing 12 sets of spurious states), 43 sets of states with \( N = 5 \) (removing 32 sets of spurious states), and 90 sets of states with \( N = 6 \) (removing 75 sets of spurious states). The physical states and the Hamiltonian matrices in those physical states are evaluated with the help of the computer algebra program MATHEMATICA [27].

For comparison, we also list the ten parameters determined by fitting the same 16 experimental data (Fit B) in Table II and the calculated results in Table I, respectively. The standard deviation in this fit is 0.908 cm\(^{-1}\). Other calculation results for the spectrum only for \( F_2 \) are given in Table IV.

| From Table II we see that the parameters \( \lambda f_2 \), \( \lambda f_3 \) and \( \lambda f_4 \) are quite small. It provides us a possibility to set those three parameters vanishing. In this way another fitting (Fit C) is obtained with the standard deviation 0.989 cm\(^{-1}\), where it contains the same number of parameters as in Fit A. This standard deviation is about one half of that in Fit A. The seven parameters and the calculated values obtained in Fit C are given in the corresponding tables.

It is interesting to compare the obtained parameters in the three fits. From Table II, when FR terms (Fit B) is replaced with the harmonical coupling (Fit A) between the stretch and the bend, the biggest change of the parameters is that of the anharmonic constant \( x_s \) in Morse oscillator of the stretch, while parameter \( \lambda_b \) for the interactions between the bending vibrations gets the least change. |
When the three small FR parameters are set to be zero (Fit C), other parameters change very little in comparison with those in Fit B. Fit C provides less standard deviation than Fit A with the same number of parameters. To our knowledge, it may be the model with the least parameters that well fits the observed vibrational spectrum of SiF$_4$. In principle, the physical meaning of those obtained parameters can be explained in terms of internal coordinate.

It is worth mentioning that McDowell et al. [20] described the same vibrational spectrum of SiF$_4$ by the normal mode model with more parameters. This model provides the normal mode labels for small amplitude polyatomic molecular vibrational spectra. However, it becomes less appropriate at higher levels of vibrational excitation. In particular, the assignment of sets of normal mode quantum numbers to give spectral absorption features becomes inherently ambiguous [28]. This model does not provide explicitly wave functions so that some physical properties such as transition intensities are hard to be calculated.

### IV. INTENSITIES OF INFRARED TRANSITION

Having completed calculations for the vibrational energy levels of SiF$_4$, we are now able to compute the intensities of infrared transition for all active modes. This information can be used to check the assignments and in the study of intramolecular energy relaxation in SiF$_4$. For stretching vibrations of tetrahedral molecules, Leroy et al. [29] recently constructed an electric dipole moment operator through unitary algebra and point group symmetry. However, their dipole function is not feasible for treating other vibrational modes. Intensities of infrared and Raman transition of stretching modes in octahedral molecules were analyzed by Chen et al. [30] in terms of U(2) algebra. In this section, intensities of infrared transition for all active modes of SiF$_4$ will be computed in the two approaches presented in Sec. III.

The absolute absorption intensities from state $n'$ to $n$ in the infrared active mode $F_2$ are given by

$$I_{nn'} = \nu_{nn'} P_{nn'},$$

$$P_{nn'} = |\langle n| \hat{T}_x |n'\rangle|^2 + |\langle n| \hat{T}_y |n'\rangle|^2 + |\langle n| \hat{T}_z |n'\rangle|^2,$$

(4.1)

where $\nu_{nn'}$ is the frequency of the observed transition, and $\hat{T}_x$, $\hat{T}_y$, and $\hat{T}_z$ correspond to the three components of the infrared transition operator $\hat{T}$. All other constants are absorbed in the normalization of the operator $\hat{T}$. The three components of $\hat{T}$ are

$$\hat{T}_x = \gamma_s (\hat{t}_1 - \hat{t}_2 + \hat{t}_3 - \hat{t}_4) + \gamma_b (\hat{t}_6 - \hat{t}_9) + \gamma_{sb} (\hat{t}_1 + \hat{t}_2 + \hat{t}_3 + \hat{t}_4)(\hat{t}_6 - \hat{t}_9),$$

$$\hat{T}_y = \gamma_s (\hat{t}_1 - \hat{t}_2 - \hat{t}_3 + \hat{t}_4) + \gamma_b (\hat{t}_7 - \hat{t}_{10}) + \gamma_{sb} (\hat{t}_1 + \hat{t}_2 + \hat{t}_3 + \hat{t}_4)(\hat{t}_7 - \hat{t}_{10}),$$

$$\hat{T}_z = \gamma_s (\hat{t}_1 + \hat{t}_2 - \hat{t}_3 - \hat{t}_4) + \gamma_b (\hat{t}_5 - \hat{t}_8) + \gamma_{sb} (\hat{t}_1 + \hat{t}_2 + \hat{t}_3 + \hat{t}_4)(\hat{t}_5 - \hat{t}_8),$$

(4.2)

where $\gamma_s$, $\gamma_b$, and $\gamma_{sb}$ are parameters, and $\hat{t}_\alpha$ is the local operator on the $\alpha$th bond. The term with $\gamma_{sb}$ is the higher order contribution of $\hat{T}$, which is necessary for describing both the stretching and
the bending active modes in SiF$_4$. Following [9] we take the matrix elements of $\hat{t}_\alpha$ as follows:

$$
\langle n | \hat{t}_j | n' \rangle = \exp(-\eta_j |n_j - n'_j|), \quad 1 \leq j \leq 4,
$$

$$
\langle n | \hat{t}_\mu | n' \rangle = \exp(-\eta_\mu |n_\mu - n'_\mu|), \quad 5 \leq \mu \leq 10,
$$

(4.3)

where the coefficients $\eta_j$ should be equal for the equivalent bonds $\eta_j \equiv \eta_s$, and $\eta_\mu \equiv \eta_b$.

Since calculations are done in the symmetrized bases it is sufficient to consider only the $z$ component, $\hat{T}_z$. All others can be obtained by making use of the Wigner-Eckart theorem. The relative intensities calculated in Fit A and Fit B are given in Table I, where they are compared with experiment. The corresponding parameters and the standard deviations (SD) are listed in Table V. In the two fits, the obtained parameters in the operator of infrared transition have a little difference, but the calculated intensities for a few energy levels are quite different. This is owing to the different wave functions and the same transition operator in the two models.

| Table V |

In Table I most of calculated intensities for the two models are in good agreement with the experimental values, but a few are not. Those differences may come from two sources. The observed intensities are only approximately accurate [20], and the other higher order contributions to the operator $\hat{T}$ are neglected. The more accurate experimental data are needed to improve the models.

In order to complete the spectroscopic study of vibrational overtone of SiF$_4$, we should also calculate the intensities of Raman transition in the two models. Unfortunately, we have to postpone this calculation due to lack of the observed values.

V. CONCLUSION

For studying the stretching and bending spectrum of a tetrahedral molecule, we have presented a harmonically coupled boson-realization model (HCBM) and a Fermi resonance boson-realization model (FRBM), where the coupling between the stretch and the bend is described by a quadratic cross term and by Fermi resonance terms, respectively. The two models have been applied to the complete vibrations of silicon tetrafluoride SiF$_4$. HCBM with seven parameters and FRBM with ten parameters provide fits to the published experimental vibrational eigenvalues with standard deviations $1.956$ cm$^{-1}$ and $0.908$ cm$^{-1}$, respectively. This is based on our new method for constructing symmetrized bases [14] and for removing both the spurious states in the wavefunction space and the spurious components in Hamiltonian [15]. This method is particularly useful for highly excited states in large molecules. In another FRBM, we decrease the number of parameters and obtain the standard deviation $0.989$ cm$^{-1}$ that is about half of that in HCBM with the same number of parameters. To our knowledge, FRBM may be the model for a good description of vibrational spectrum of SiF$_4$ with the least parameters. We believe that FRBM will be better suitable for describing highly excited vibrations in molecules.

The intensities of infrared transitions of the complete vibrations in this molecule have been calculated in those two models. The model transition operator with five parameters well reproduces the
observed data. The more satisfactory results can be obtained if more accurate experimental values are available.

Finally, we remark that our models can be extended in several ways. The Fermi resonances may be taken into account as perturbative terms in HCBM, or the harmonically coupled term appears in FRBM as a perturbative one. Other anharmonic resonances such as Darling-Dennison resonances can be included in the models by adding higher-order terms of bosonic operators [16]. The rotational degrees of freedom can be incorporated by coupling the vibrational wave functions to rotational states carrying the appropriate point symmetries [31]. Our algebraic Hamiltonian can be written down in the coset space representation to study the dynamics of stationary eigenstates and inter-mode energy transfer [32]. Work on those subjects is in progress.

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[1] F. Iachello, Chem. Phys. Lett. 78 (1981), 581; F. Iachello and R. D. Levine, J. Chem. Phys. 77 (1982), 3046.
[2] O. S. van Roosmalen, F. Iachello, R. D. Levine, and A. E. L. Dieperink, J. Chem. Phys. 79 (1983), 2515; F. Iachello, S. Oss, and R. Lemus, J. Mol. Spectrosc. 146 (1991), 56; 149 (1991), 132.
[3] F. Iachello, S. Oss, and L. Viola, Mol. Phys. 78 (1993), 561; J. Chem. Phys. 101 (1994), 3531.
[4] R. Bijker, A. E. L. Dieperink, and A. Leviatan, Phys. Rev. A 52 (1995), 2786.
[5] C. Leroy and F. Michelot, J. Mol. Spectrosc. 151 (1992), 71.
[6] F. Iachello and S. Oss, Phys. Rev. Lett. 66 (1991), 2976; Chem. Phys. Lett. 187 (1991), 500.
[7] R. N. Alvarez, D. Bonatsos, and Y. F. Smirnov, Phys. Rev. A 50 (1994), 1088.
[8] R. K. Gupta and I. L. Cooper, J. Chem. Phys. 102 (1995), 3123; D. Bonatsos, C. Daskaloyannis, and K. Kokkotas, Phys. Rev. A 45 (1992), R6153.
[9] F. Iachello and S. Oss, J. Chem. Phys. 99 (1993), 7337; Chem. Phys. Lett. 205 (1993), 285.
[10] F. Iachello and S. Oss, J. Chem. Phys. 104 (1996), 6956.
[11] A. Frank, R. Lemus, R. Bijker, F. Pérez-Bernal, and J. M. Arias, Ann. Phys. (N.Y.) 252 (1996), 211.
[12] F. Pérez-Bernal, R. Bijker, A. Frank, R. Lemus, and J. M. Arias, Chem. Phys. Lett. 258 (1996), 301.
[13] R. Lemus and A. Frank, J. Chem. Phys. 101 (1994), 8321.

[14] Z. Q. Ma, X. W. Hou, and M. Xie, Phys. Rev. A 53 (1996), 2173.

[15] M. Xie, X. W. Hou, and Z. Q. Ma, Chem. Phys. Lett. 262 (1996), 1.

[16] X. W. Hou, M. Xie, and Z. Q. Ma, Phys. Rev. A 55 (1997), 3401; Inter. J. Theor. Phys. 36 (1997), 1153; Nuov. Cim. D 19 (1997), 1.

[17] L. Halonen and M. S. Child, Mol. Phys. 46 (1982), 239; J. Chem. Phys. 79 (1983), 559.

[18] J. Q. Chen, A. Klein, and J. L. Ping, J. Math. Phys. 37 (1996), 2400; J. Q. Chen and J. L. Ping, ibid. 38 (1997), 387; J. L. Ping and J. Q. Chen, Ann. Phys. (N.Y.) 255 (1997), 75.

[19] P. R. Bunker, "Molecular symmetry and spectroscopy", Academic Press, New York, 1979.

[20] R. S. McDowell, M. J. Reisfeld, C. W. Patterson, B. J. Krohn, M. C. Vasquez, and G. A. Laguna, J. Chem. Phys. 77 (1982), 4337; R. J. H. Clark and D. M. Rippon, J. Mol. Spectrosc. 44 (1972), 479.

[21] R. H. Page, Y. R. Shen, and Y. T. Lee, J. Chem. Phys. 88 (1988), 4621, 5362.

[22] J. L. Duncan, A. M. Ferguson, and S. Mathews, J. Chem. Phys. 91 (1989), 783.

[23] F. Iachello and S. Oss, J. Mol. Spectrosc. 142 (1990), 85.

[24] L. Halonen and T. Carrington, Jr., J. Chem. Phys. 88 (1988), 4171.

[25] T. Lukka, E. Kauppi, and L. Halonen, J. Chem. Phys. 102 (1995), 5200; E. Kauppi and L. Halonen, ibid. 103 (1995), 6861; J. Lummila, T. Lukka, L. Halonen, H. Bürger, and O. Polanz, ibid. 104 (1996), 488.

[26] Faraday Discussions Chem. Soc. 75 (1983), 7.

[27] S. Wolfram, "Mathematica", Addison-Wesley, Redwood City, California, 1988.

[28] M. M. Law and J. L. Duncan, Mol. Phys. 83 (1994), 757.

[29] C. Leroy, F. Collin, and M. Loëte, J. Mol. Spectrosc. 175 (1996), 289; C. Leroy and V. Boujut, ibid. 181 (1997), 127.

[30] J. Q. Chen, F. Iachello, and J. L. Ping, J. Chem. Phys. 104 (1996), 815.

[31] J. K. G. Watson, J. Mol. Spectrosc. 103 (1984), 350.

[32] G. Wu, Chem. Phys. Lett. 227 (1994), 682; 248 (1996), 77; G. Wu and X. Ding, ibid. 262 (1996), 421.
Table I. Observed and calculated energy levels and relative intensities for SiF\(_4\)

| \(\Gamma\) | \(E\) (cm\(^{-1}\)) | Intensity | \(n\) | \(E\) (cm\(^{-1}\)) | Intensity | \(N\) | \(E\) (cm\(^{-1}\)) | Intensity |
|---|---|---|---|---|---|---|---|---|
| \(E\) | 264.2 | | 1 | 262.593 | | 1 | 262.616 | | 263.043 |
| \(F\) | 776.3 | 0.9 | 2 | 776.028 | 0.968 | 2 | 776.196 | 0.413 | 775.104 |
| \(A\) | 800.8 | | 1 | 803.333 | | 2 | 800.195 | | 799.847 |
| \(F\) | 1031.3968 | 5000 | 1 | 1031.338 | 4999.989 | 2 | 1030.951 | 5000.031 | 1030.818 |
| \(E\) | 1064.2 | | 2 | 1065.926 | | 3 | 1064.486 | | 1064.411 |
| \(F\) | 1164.2 | 1.4 | 3 | 1164.348 | 4\times10^{-4} | 3 | 1164.939 | 4.117 | 1165.115 |
| \(F\) | 1189.7 | 40 | 2 | 1190.361 | 40.073 | 3 | 1190.236 | 39.631 | 1190.531 |
| \(F\) | 1294.05 | 2.4 | 2 | 1293.938 | 1\times10^{-4} | 3 | 1294.308 | 0.009 | 1293.861 |
| \(F\) | 1418.75 | 0.1 | 2 | 1418.367 | 2\times10^{-4} | 3 | 1418.989 | 1\times10^{-5} | 1418.370 |
| \(F\) | 1804.5 | 0.7 | 3 | 1805.405 | 2\times10^{-6} | 4 | 1804.941 | 0.002 | 1805.922 |
| \(F\) | 1828.17 | 7 | 2 | 1828.908 | 3.820 | 4 | 1828.219 | 3.999 | 1828.083 |
| \(F\) | 2059.1 | 1.2 | 2 | 2056.461 | 3.653 | 4 | 2059.016 | 4.193 | 2059.998 |
| \(F\) | 2602.55 | 0.007 | 4 | 2602.163 | 2\times10^{-9} | 6 | 2601.910 | 2\times10^{-6} | 2602.273 |
| \(F\) | 2623.8 | 0.015 | 3 | 2621.531 | 0.002 | 6 | 2624.028 | 0.007 | 2624.067 |
| \(F\) | 3068.5 | 0.015 | 3 | 3071.082 | 0.004 | 6 | 3068.276 | 0.005 | 3068.251 |

Table II. Parameters in the Hamiltonian obtained by the least square fitting (cm\(^{-1}\))

| \(\omega_s\) | \(x_s\) | \(\lambda_s\) | \(\omega_b\) | \(x_b\) | \(\lambda_b\) | \(\lambda_{sb}\) (\(\lambda_{f_k}\), \(k = 1, 4\)) | SD |
|---|---|---|---|---|---|---|---|
| Fit A | 987.106 | 6.395 | -56.995 | 135.205 | -94.810 | -62.232 | | 1.486 | 1.956 |
| Fit B | 978.898 | 2.930 | -57.661 | 133.656 | -95.854 | -62.748 | 1.274 | 0.431 | 0.772 | 0.635 | 0.908 |
| Fit C | 978.043 | 2.567 | -57.909 | 132.979 | -96.159 | -62.255 | 1.167* | | 0.989 |

* \(\lambda_{f2} = \lambda_{f3} = \lambda_{f4} = 0\).
Table III. The calculated energy levels in Fit A for other $F_2$ states without observed data (in cm$^{-1}$)

| n=2   | 774.058  |
|-------|----------|
| n=3   | 3088.993 2846.495 2449.719 2443.500 2440.189 2319.058 2215.126 2090.697 |
|       | 1990.429 1920.150 1909.535 1807.367 1680.964 1599.793 1579.359 1578.813 |
|       | 1577.390 1489.258 1275.125 1099.854 944.679 |
| n=4   | 4097.150 4082.620 3873.222 3853.713 3633.127 3476.023 3468.264 3462.928 |
|       | 3458.116 3411.629 3351.604 3343.735 3333.687 3240.262 3233.533 3229.815 |
|       | 3109.090 3008.558 2945.283 2934.648 2884.130 2838.738 2836.739 2832.567 |
|       | 2830.527 2829.199 2827.224 2787.228 2716.908 2712.270 2706.295 2706.110 |
|       | 2624.924 2604.126 2603.943 2520.595 2477.722 2444.796 2432.932 2396.553 |
|       | 2379.427 2377.458 2375.573 2306.477 2302.174 2292.589 2257.637 2195.687 |
|       | 2192.434 2168.875 2164.824 2131.252 2086.635 2078.458 1976.028 1967.680 |
|       | 1941.916 1910.947 1903.186 1896.622 1845.473 1748.012 1663.632 1651.223 |
|       | 1634.084 1581.540 1448.531 1385.549 |
Table IV. The calculated energy levels in Fit B for other $F_2$ states without observed data (in cm$^{-1}$)

| N  | Energy Levels       |
|----|---------------------|
| 2  | 778.309             |
| 3  | 1496.547 1279.868   |
|    | 1102.618 945.771    |
| 4  | 2177.309 1925.826   |
|    | 1918.702 1911.620   |
|    | 1855.411 1809.079   |
|    | 1682.927 1669.183   |
|    | 1655.980 1644.807   |
|    | 1588.721 1578.839   |
|    | 1575.762 1569.344   |
|    | 1451.455 1388.306   |
| 5  | 3092.260 2722.565   |
|    | 2649.070 2592.144   |
|    | 2526.968 2462.997   |
|    | 2310.335 2296.747   |
|    | 2272.404 2257.953   |
|    | 2228.585 2218.677   |
|    | 2195.354 2193.315   |
|    | 2173.913 2157.729   |
|    | 2132.698 2102.615   |
|    | 2092.409 2089.835   |
|    | 2080.143 2073.023   |
|    | 2039.092 1990.464   |
|    | 1976.180 1963.068   |
|    | 1956.843 1938.327   |
|    | 1906.334 1897.406   |
|    | 1848.606 1824.641   |
|    | 1748.271 1655.093   |
| 6  | 4078.063 3543.827   |
|    | 3517.840 3426.476   |
|    | 3261.511 3258.607   |
|    | 3217.764 3207.488   |
|    | 3203.984 3090.515   |
|    | 3082.210 3046.639   |
|    | 2992.877 2977.422   |
|    | 2955.982 2952.235   |
|    | 2946.590 2941.518   |
|    | 2939.587 2928.298   |
|    | 2903.491 2901.129   |
|    | 2894.450 2886.484   |
|    | 2853.321 2846.446   |
|    | 2841.328 2838.193   |
|    | 2835.863 2835.647   |
|    | 2832.926 2831.058   |
|    | 2828.552 2806.848   |
|    | 2793.846 2789.674   |
|    | 2760.970 2742.810   |
|    | 2741.421 2725.766   |
|    | 2719.000 2715.320   |
|    | 2714.351 2708.920   |
|    | 2701.105 2698.761   |
|    | 2693.801 2685.015   |
|    | 2678.378 2672.708   |
|    | 2660.143 2655.004   |
|    | 2647.133 2638.670   |
|    | 2630.250 2615.894   |
|    | 2607.824 2598.092   |
|    | 2585.833 2582.730   |
|    | 2555.568 2535.720   |
|    | 2505.022 2487.403   |
|    | 2480.529 2477.413   |
|    | 2470.023 2468.413   |
|    | 2454.484 2444.678   |
|    | 2425.891 2414.598   |
|    | 2409.308 2398.143   |
|    | 2383.593 2380.054   |
|    | 2373.934 2363.527   |
|    | 2341.447 2321.627   |
|    | 2311.420 2307.632   |
|    | 2297.550 2241.223   |
|    | 2226.891 2190.736   |
|    | 2144.527           |

Table V. Obtained parameters for infrared transition intensities of SiF$_4$

|       | $\gamma_s$ | $\gamma_b$ | $\gamma_{sb}$ | $\eta_s$ | $\eta_b$ | SD   |
|-------|------------|------------|----------------|----------|----------|------|
| Fit A | 39.276     | 21.642     | 61.850         | 3.578    | 3.281    | 1.745|
| Fit B | 37.472     | 21.441     | 61.944         | 3.527    | 3.285    | 2.015|