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$U(2)$ Algebraic Model Applied to Stretching Vibrational Spectra of Tetrahedral Molecules

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The highly excited stretching vibrational energy levels and the intensities of infrared transitions in tetrahedral molecules are studied in a $U(2)$ algebraic model. Its applications to silane and silicon tetrafluoride are presented, with smaller standard deviations than those of other models.

1. INTRODUCTION

In recent years, algebraic models, such as Lie algebraic methods (Iachello and Levine, 1995; Bijker *et al.*, 1995) and the boson-realization model (Ma *et al.*, 1996), have been proposed for descriptions of vibrations, rotations, and rotation–vibration interactions in polyatomic molecules. Lie algebraic methods for diatomic molecules have been modified by the corresponding quantum algebra (Alvarez *et al.*, 1994; Chang, 1995), and the boson-realization model has been developed for the higher vibrational states of polyatomic molecules in terms of q-deformed oscillators (Xie *et al.*, 1996; Hou *et al.*, 1997a,b).

In Lie algebraic approaches, $U(4)$ and $U(2)$ algebraic models have been extensively used. The $U(4)$ model took the rotation and the vibration into account simultaneously, but became quite complicated when the number of atoms in a molecule increased to larger than four. The $U(2)$ model was particularly successful in explaining stretching vibrations of polyatomic molecules such as benzene-like and octahedral systems (Iachello and Oss, 1991; Chen *et al.*, 1996). This model was extended to deal with both stretching and bending vibrations in triatomic molecules (Frank *et al.*, 1996). Recently,

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a $U(5)$ algebraic model was introduced for higher excited stretching modes and infrared intensities of tetrahedral molecules (Leroy *et al.*, 1996; Leroy and Boujut, 1997). However, the $U(5)$ model was less feasible than the $U(2)$ model when the bending vibrations were considered.

In this paper, we will use the $U(2)$ algebraic model to study the stretching vibrations and intensities of infrared transition of silane, SiH_4, and silicon tetrafluoride, SiF_4. Our results are quite good in comparison with those of the $U(5)$ algebraic model for SiH_4 (Leroy *et al.*, 1996) and the local mode model (Della Valle, 1988). Results for stretching and bending vibrations in the $U(2)$ model and the boson-realization model will be presented in a subsequent publication.

2. $U(2)$ ALGEBRAIC MODEL

For a tetrahedral molecule XY_4, we introduce four $U(2)$ algebras to describe the vibrations of four X–Y bonds. The molecular dynamical group is

$$U_1(2) \otimes U_2(2) \otimes U_3(2) \otimes U_4(2)$$

where each $U_i(2)$ $(1 \leq i \leq 4)$ is generated by the operators $\{\hat{N}_i, \hat{J}_{+,i}\hat{J}_{-,i}, \hat{J}_{0,i}\}$, satisfying the following commutation relations (Frank *et al.*, 1996):

$$[\hat{J}_{0,i}, \hat{J}_{\pm,j}] = \pm\delta_{ij}\hat{J}_{\pm,i}, \qquad [\hat{J}_{+,i}, \hat{J}_{-,j}] = 2\delta_{ij}\hat{J}_{0,i}$$

$$[\hat{N}_i, \hat{J}_{0,j}] = 0, \qquad [\hat{N}_i, \hat{J}_{\pm,j}] = 0$$

where $\hat{N}_i$ is related with the Casimir operator of $U(2)$:

$$2\hat{J}_{0,i}^2 + \hat{J}_{+,i}\hat{J}_{-,i} + \hat{J}_{-,i}\hat{J}_{+,i} = \hat{N}_i(\hat{N}_i/2 + 1)$$

Denote by v_i the number of quanta in the ith bond. The local basis states for each bond are labeled by the eigenvalue N_i of $\hat{N}_i$ and v_i, and written as $|N_i, v_i\rangle$. Their products provide the local bases:

$$|N_1, v_1\rangle|N_2, v_2\rangle|N_3, v_3\rangle|N_4, v_4\rangle \equiv |N_i, v_i\rangle$$

where those N_i are equal to each other, $N_i = N$, due to equivalent bonds.

There are three kinds of $O(2)$-invariant combinations of those generators:

$$\begin{aligned} \hat{H}_i &= (\hat{J}_{+,i}\hat{J}_{-,i} + \hat{J}_{-,i}, \hat{J}_{+,i})/2 - \hat{N}_i/2 \\ \hat{H}_{ij} &= 2\hat{J}_{0,i}\hat{J}_{0,j} - \hat{N}_i\hat{N}_j/2, \qquad i \neq j \\ \hat{V}_{ij} &= \hat{J}_{+,i}\hat{J}_{-,j} + \hat{J}_{-,i}\hat{J}_{+,j}, \qquad i \neq j \end{aligned} \tag{1}$$

Their matrix elements in the local bases are given by Frank *et al.* (1996). The operator $\hat{H}_i$ corresponds to the energy of the ith Morse oscillator. The operators $\hat{H}_{ij}$ describe the anharmonic terms with the type $v_i v_j$, while the operators $\hat{V}_{ij}$ describe the interbond couplings which, in configuration space, are of the type $\mathbf{r}_i\mathbf{r}_j$, where $\mathbf{r}_i$ and $\mathbf{r}_j$ are the displacement vectors of bonds i and j from their equilibrium positions.

The Hamiltonian, if restricted at the quadratic terms, is expressed in terms of those three kinds of operators as follows:

$$\begin{aligned} H = {} & \lambda_1 \sum_{i=1} \hat{H}_i + \lambda_2 \sum_{i \neq j} \hat{H}_{ij} + \lambda_3 \sum_{i \neq j} \hat{V}_{ij} + \lambda_4 \sum_{i=1} (\hat{H}_i)^2 \\ & + \lambda_5 \sum_{i,j \neq k} \hat{H}_i \hat{H}_{jk} + \lambda_6 \sum_{i \neq j} \hat{H}_i \hat{H}_j + \lambda_7 \sum_{i \neq j} \hat{H}_i \hat{H}_{ij} + \lambda_8 \sum_{i \neq j} \hat{H}_i \hat{V}_{ij} \\ & + \lambda_9 \sum_{i,j \neq k} \hat{H}_i \hat{V}_{jk} + \lambda_{10} \sum_{i \neq j} (\hat{H}_{ij})^2 + \lambda_{11} \sum_{i \neq j \neq k} \hat{H}_{ij} \hat{H}_{ik} + \lambda_{12} \sum_{i \neq j, k \neq l} \hat{H}_{ij} \hat{H}_{kl} \\ & + \lambda_{13} \sum_{i \neq j} (\hat{V}_{ij})^2 + \lambda_{14} \sum_{i \neq j \neq k} \hat{V}_{ij} \hat{V}_{ik} + \lambda_{15} \sum_{i \neq j, k \neq l} \hat{V}_{ij} \hat{V}_{kl} \\ & + \lambda_{16} \sum_{i \neq j} \hat{H}_{ij} \hat{V}_{ij} + \lambda_{17} \sum_{i \neq j \neq k} \hat{H}_{ij} \hat{V}_{ik} + \lambda_{18} \sum_{i \neq j, k \neq l} \hat{H}_{ij} \hat{V}_{kl} \end{aligned} \tag{2}$$

where all λ's are coupling parameters. The Hamiltonian preserves the quantum number $V = \sum v_i$.

We now apply this model to study the stretching vibrational spectra of SiH_4 and SiF_4. The calculation for energy levels has been greatly simplified since the symmetrized bases are used. The boson number N is taken to be 60 for SiH_4 and 100 for SiF_4.

For SiH_4, we choose five parameters, the same as the number of parameters used by Leroy *et al.* (1996), to calculate the vibrational levels. It was found that these five parameters λ_j, $1 \leq j \leq 5$, can give better results. This means setting $\lambda_i = 0$, $6 \leq i \leq 18$. Fitting the observed data for SiH_4 from the compilation of Leroy *et al.* (1996), we obtain the parameter values and the calculated energy levels listed in Table I. For SiF_4, better results can be obtained in terms of only three parameters λ_1, λ_2, and λ_3. The observed data from McDowell *et al.* (1982), calculated values, and corresponding parameters are also listed in Table I. For comparison, the levels for the two molecules calculated by the local mode model (LMM) (Della Valle, 1988) and the recently calculated results for SiH_4 by the $U(5)$ model [$U(5)$M, Leroy *et al.* (1996)] are given in Table I, together with their standard deviations (SD). The calculated vibrational energy levels given in Table I are the differences between the observed values and the calculated ones.

3. INTENSITIES OF INFRARED TRANSITION

In the following we will introduce the infrared transition operator. The calculated intensities can be used to check assignments and to study the intramolecular energy relaxation in tetrahedral molecules.

Table I. Observed and Calculated Energy Levels, and Parameters (in cm^{-1})

SiH_4			
E_{obs}	LMM	$U(5)$M	$U(2)$M
2186.8730	0.5339	0.7378	0.4476
2189.1901	−0.0652	−0.5527	−0.0765
4374.5600	0.3247	−0.1007	−0.0503
4308.3800	−1.4258	−0.8963	−0.6650
4380.2800	1.7690	0.2231	−0.4878
4378.4000	1.3154	0.1421	−0.6465
4309.3485	−0.5244	0.0617	0.2095
6496.1300	0.7661	−0.0028	0.0190
6361.9800	−2.1182	0.1450	0.5381
6500.3000	2.5976	1.4384	1.3330
6502.8800	2.2612	0.4108	0.4409
6362.0800	−2.0186	0.2448	0.6372
6497.4810	0.9458	−0.4104	−0.0605
6500.6000	1.0278	−0.1297	−0.0578
8347.4000	−3.8164	0.1031	0.2949
10267.2200	−3.9023	0.4100	0.1748
12121.2000	−2.7061	−0.6399	−0.1973
13914.4000	4.8506	0.2227	0.3037
SD	2.465	0.610	0.573

SiF_4		
E_{obs}	LMM	$U(2)$M
800.6	−5.1243	−1.5226
1031.3968	−3.1250	1.7942
2059.1	−0.2942	4.4876
1828.17	−1.5378	−0.0686
2623.8	4.2976	0.9521
3068.5	0.5720	−4.1160
SD	3.090	2.066

Parameter	SiH_4	SiF_4
λ_1	30.2883	1.1974
λ_2	−2.2592	−2.8473
λ_3	−0.0147	−0.5687
λ_4	−0.0021	
λ_5	−0.0003	

For the considered systems, the infrared-active mode is F_2. The absolute absorption intensities from a state v' to v are given by

$$I_{vv'} = \nu_{vv'} P_{vv'} \tag{3}$$
$$P_{vv'} = |\langle v|\hat{T}_x|v'\rangle|^2 + |\langle v|\hat{T}_y|v'\rangle|^2 + |\langle v|\hat{T}_z|v'\rangle|^2$$

where $\nu_{vv'}$ is the frequency of the observed transition, $\hat{T}_x$, $\hat{T}_y$, and $\hat{T}_z$ correspond to the three components of the infrared transition operator $\hat{T}$, and the state $|v\rangle$ denotes $|N_i, v_i\rangle$ for short. All other constants are absorbed in the normalization of the operator $\hat{T}$. The three components of $\hat{T}$ are

$$\begin{aligned} \hat{T}_x &= \alpha(\hat{t}_1 - \hat{t}_2 + \hat{t}_3 - \hat{t}_4) \\ \hat{T}_y &= \alpha(\hat{t}_1 - \hat{t}_2 - \hat{t}_3 + \hat{t}_4) \\ \hat{T}_z &= \alpha(\hat{t}_1 + \hat{t}_2 - \hat{t}_3 - \hat{t}_4) \end{aligned} \tag{4}$$

where α is a parameter. The matrix elements of $\hat{t}_i$ are taken to be (Iachello and Oss, 1993)

$$\langle \hat{N}_i, v_i|\hat{t}_i|\hat{N}_i, v_i'\rangle = \exp(-\beta_i|v_i - v_i'|) \tag{5}$$

Those β_i for equivalent bonds are equal to each other, and denoted by a common symbol β.

Table II. Observed and Calculated Relative Intensities

	SiH_4					SiF_4				
	α	8.130		β	0.866	α	37.977		β	3.540
E_{calc}	10267.04	12121.40	13914.10	15645.57	17318.60	1029.60	1828.24	2054.60	2622.84	3072.62
Obs.[a]	—	100	21	2.4	0.6	5000	7	1.2	0.015	0.015
Calc.[b]	530	100	20.18	4.2	0.9					
Calc.	479	100	20.33	4.04	0.79	5000	3.79	4.14	0.005	0.003

[a] Observed data for SiH_4 from Bernheim *et al.* (1984), and for SiF_4 from McDowell *et al.* (1982).
[b] Calculated by Leroy *et al.* (1996).

The two parameters in the transition operator of (4) and (5) will be determined by fitting observed data. Due to the Wigner–Eckart theorem, it is sufficient to calculate only the z component of the transition operator, $\hat{T}_z$, in the symmetrized bases. In Table II we only list part of the calculated intensities to compare with known observed data, from which the two parameters are determined. The standard deviation in our fitting is 1.265 for SiH_4 and 2.512 for SiF_4, while it is 1.415 for SiH_4 by Leroy *et al.* (1996).

4. CONCLUSION

We have used a $U(2)$ algebraic model for studying the stretching vibrations and infrared intensities of a tetrahedral molecule. The model Hamiltonian and the model transition operator have provided better fits to the published experimental data of silane and silicon tetrafluoride than the local mode model (Della Valle, 1988) and the $U(5)$ algebraic approach (Leroy *et al.*, 1996) to silane. In addition, the $U(2)$ algebraic model can be applied to the stretching and bending vibrations of other medium-size and large molecules. Furthermore, this model can be studied by the corresponding quantum algebra (Bonatsos and Daskaloyannis, 1993). Investigations on those subjects are underway.

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