
Vibrational energies of silylene, difluorosilylene and dichlorosilylene, using U(2) Lie algebraic model

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Abstract. We have applied one-dimensional Lie algebraic model to estimate fundamental vibrations, their higher-order overtones (up to the tenth vibrational excitation) and combinational bands (up to the fourth excitation) of silylene (SiH_2), difluorosilylene (SiF_2) and dichlorosilylene (SiCl_2). A vibrational Hamiltonian maintaining the point symmetry group C_{2v} of each of these silylene molecules is modelled using three interacting Morse oscillators. Comparison of the calculated fundamental vibrational energies (the wave numbers) with the available reference experimental data confirms that our results are consistent with the experiment.

Keywords: vibrational energies, silylene, difluorosilylene, dichlorosilylene, Lie algebraic model

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1. Introduction

Studies of vibrational spectra of molecules is one of the most challenging directions of contemporary mathematical physics. Development of novel experimental techniques producing higher-order vibrational excitations in polyatomic molecules requires reliable theoretical methods for their interpretation. There have been two conventional theoretical frameworks for studying the experimental data that involves rovibrational spectra of polyatomic molecules. The first approach is a Dunham expansion [1] which deals with expansion series of energy levels in terms of rotation–vibration quantum numbers. The Dunham expansion is not advisable for rigorous modelling due to a number of limitations. First of all, it does not involve a correspondence to the wave functions of individual states and, hence, operator matrix elements cannot be calculated directly. Second, the number of parameters required to consider large polyatomic molecules within the Dunham expansion is large enough and the same is true of the experimental database needed to optimize these parameters. The latter is not feasible in any practical situation [2].

The second approach, which has been proven to be better than the Dunham expansion, lies in solving the Schrodinger equation with some potentials using an improved *ab initio* method [3] and providing the wave functions to calculate the matrix elements of Hamiltonian. Note however that, since all the manipulations involved in this approach are either differentiation or integration, it encounters some problems for the cases of large molecules or highly excited levels.

In our opinion, a one-dimensional symmetry-adapted Lie algebraic model represents, probably, a more interesting alternative to the conventional techniques mentioned above. Iachello *et al.* [4] have already applied a U(2) Lie algebraic method to study the vibrational spectra of small-size molecules. The method has been improved to consider the rotation–vibration spectra of medium-size molecules, including the case of higher-order overtones [5–12]. It is believed that the Lie algebraic approach enables estimating the vibrational energies at a less computational cost and provides higher accurately if compared to the other theoretical techniques.

The vibrational spectra of silane and its fluoro- and chloro-derivatives represent an interesting and important topic. Upon decomposition, they form stable SiH₂, SiF₂ and SiCl₂ compounds. It would be tempting to find the appropriate vibrational parameters, which are associated with highly toxic natural phenomena. Up to now, there has been no attempt to calculate the vibrational energies of these molecules corresponding to higher-order overtones and combination frequencies. In the present work we apply the Lie algebraic model and calculate the vibrational energies up to the ninth overtone with tenth vibrational excitation and third overtone with fourth excitation.

2. One-dimensional Lie algebraic model

Silylene, difluorosilylene and dichlorosilylene are bent triatomic molecules with the equilibrium structure belonging to the point symmetry group C_{2v}. These molecules are nonlinear and have three vibrational degrees of freedom, with the symmetry species A₁ (symmetric stretching), B₂ (antisymmetric stretching) and A₁ (bending). Each of the vibrating bonds in a bent triatomic molecule XY₂ (SiH₂: X = Si and Y = H, SiF₂: X = Si and Y = F, and SiCl₂: X = Si and Y = Cl) is effectively described by a one-dimensional Morse oscillator. The corresponding U(2) Lie algebras can be assigned as shown schematically in Fig. 1.

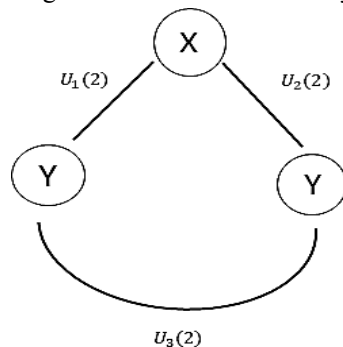


Fig. 1. Assignment of U(2) Lie algebras to different bonds in XY₂ molecule.

The two possible chains of dynamical symmetry groups in the XY₂ molecule, which correspond to local and normal couplings in the stretching vibrations, are given by

$$U_1(2) \otimes U_2(2) \supset O_1(2) \otimes O_2(2) \rightarrow \text{Local coupling}$$

$$U_1(2) \otimes U_2(2) \supset U_{12}(2) \supset O_{12}(2) \rightarrow \text{Normal coupling}$$

The Hamiltonian operator describing the vibrational spectra of the two single interacting bonds (X–Y) in the XY₂ molecule are expressed mathematically as [13, 14]

$$H = E_0 + \sum_{i=1}^n p_i b_i + \sum_{i < j}^n p_{ij} b_{ij} + \sum_{i < j}^n q_{ij} f_{ij} \dots \quad (1)$$

In Eq. (1), E_0 is the term corresponding to the Schrodinger-equation eigenvalue associated with the electronic ground state of bond vibrations, which will be used as a zero reference for all the other excitations, p_i, p_{ij} and q_{ij} are the algebraic parameters, and b_i and b_{ij} denote the physically invariant operators of uncoupled and coupled bonds, respectively. Besides, we have

$$\langle b_i \rangle = -4(N_i^{X-Y} v_i - v_i^2), \quad (2)$$

$$\begin{aligned} & \langle N_i^{X-Y}, v_i; N_j^{X-Y}, v_j | b_{ij} | N_i^{X-Y}, v_i; N_j^{X-Y}, v_j \rangle \\ & = 4 \left[(v_i + v_j)^2 - (v_i + v_j)(N_i^{X-Y} + N_j^{X-Y}) \right]. \end{aligned} \quad (3)$$

The Majorana operator f_{ij} , which contains both diagonal and off-diagonal matrix elements, is used to express the local-mode interactions in pairs. In particular, we obtain

$$\begin{aligned} & \langle N_i^{X-Y}, v_i; N_j^{X-Y}, v_j | f_{ij} | N_i^{X-Y}, v_i; N_j^{X-Y}, v_j \rangle = \\ & \quad (N_i^{X-Y} v_j + N_j^{X-Y} v_i - 2v_i v_j), \\ & \langle N_i^{X-Y}, v_i + 1; N_j^{X-Y}, v_j - 1 | f_{ij} | N_i^{X-Y}, v_i; N_j^{X-Y}, v_j \rangle = \\ & \quad - \left[v_j (v_i + 1) (N_i^{X-Y} - v_i) (N_j^{X-Y} - v_j + 1) \right]^{1/2}, \\ & \langle N_i^{X-Y}, v_i - 1; N_j^{X-Y}, v_j + 1 | f_{ij} | N_i^{X-Y}, v_i; N_j^{X-Y}, v_j \rangle = \\ & \quad - \left[v_i (v_j + 1) (N_j^{X-Y} - v_j) (N_i^{X-Y} - v_i + 1) \right]^{1/2}. \end{aligned} \quad (4)$$

Here v_i and v_j are the vibrational quantum numbers respectively of the bonds i and j , and N_i^{X-Y} and N_j^{X-Y} imply the vibron numbers describing the stretching vibrations of the two $X-Y$ bonds in the XY_2 molecule. Since the two stretching $X-Y$ bonds are equivalent, the vibron numbers N_i^{X-Y} and N_j^{X-Y} must be the same. Finally, note that the algebraic parameters and the operators vary from molecule to molecule.

The vibron number N^{X-Y} ($= N_i^{X-Y} = N_j^{X-Y}$) for the stretching bonds of the molecule can be calculated using the relation $N^{X-Y} = \omega_e / \omega_e x_e - 1$, with ω_e and $\omega_e x_e$ being the harmonic and anharmonic spectroscopic constants of the bond $X-Y$ [15]. Finally, the algebraic parameter p is estimated from the energy equation for the single-oscillator fundamental mode,

$$E(v=1) = -4p(N^{X-Y} - 1), \quad (5)$$

and the parameter q_{12} from the relation

$$q_{12} = \frac{|E_1 - E_2|}{2N^{X-Y}}, \quad (6)$$

where E_1, E_2 are respectively the symmetric and antisymmetric vibrational energies of the molecule. Here the initial p_{ij} values are taken to be zero.

The Hamiltonian for the two stretching vibrations of the XY_2 molecule reads as

$$H = E_0 + p_1 b_1 + p_2 b_2 + p_{12} b_{12} + q_{12} f_{12}. \quad (7)$$

In Eq. (7), p_1, p_2, p_{12} and q_{12} are the algebraic parameters (in cm^{-1}) which can be found from the available spectroscopic data. The vibrational energies of the molecule can be determined issuing from the Hamiltonian matrix (i.e., the first two local oscillators):

$$H = \begin{bmatrix} -4p(N^{X-Y} - 1) - 4p_{12}(2N^{X-Y} - 1) + q_{12}N^{X-Y} & -q_{12}N^{X-Y} \\ -q_{12}N^{X-Y} & -4p(N^{X-Y} - 1) - 4p_{12}(2N^{X-Y} - 1) + q_{12}N^{X-Y} \end{bmatrix}. \quad (8)$$

The interactions result in three normal-mode (stretching and bending) vibrations, which correspond to λ_1, λ_2 and λ_3 , i.e. to the symmetry species A_1 (symmetric stretching), A_1 (bending), and B_1 (asymmetric stretching), respectively.

3. Results

The parameters of the Hamiltonian obtained on the basis of fitting of the experimental data are reported in Table 1. The fundamental vibrational energies have been calculated using the Hamiltonian operator, as explained above. The results obtained theoretically are compared with the experimental data in Table 2. Finally, the calculated vibrational energies corresponding to the higher overtones and the combinations are displayed in Table 3 and Table 4, respectively.

Table 1. Algebraic parameters involved in our model (found upon fitting the experimental data).

Parameter	SiH ₂	SiF ₂	SiCl ₂
N ^{X-Y} (<i>stretching</i>)	56	172	246
N ^{Y-X-Y} (<i>bending</i>)	32	98	152
p ₁ , p ₂ (<i>stretching</i>)	-9.0653	-1.2612	-0.5408
p ₃ (<i>bending</i>)	-8.056	-0.6214	-0.3443
p ₁₂ (<i>stretching</i>)	0.0034	0.0055	0.0025
p ₁₃ , p ₂₃ (<i>bending</i>)	-0.0239	-0.2143	-1.2913
q ₁₂ (<i>stretching</i>)	0.0277	0.0447	0.0203
q ₁₃ , q ₂₃ (<i>bending</i>)	0.9213	1.2361	-0.6542

Table 2. Fundamental vibrational energies (in cm⁻¹) obtained from experiments and calculated for SiH₂, SiF₂ and SiCl₂.

Vibrational mode	Symmetry	Experimental [16–19]			Calculated		
		SiH ₂	SiF ₂	SiCl ₂	SiH ₂	SiF ₂	SiCl ₂
λ ₁ (symmetric)	A ₁	1995.93	855.01	525	1995.958	855.114	525.074
λ ₂ (bending)	A ₁	999.03	345	208	997.237	343.601	206.613
λ ₃ (antisymmetric stretching)	B ₁	1992.82	870.40	535	1992.856	870.491	535.061

Table 3. Vibrational energies (in cm⁻¹) corresponding to higher-order overtones.

Vibrational mode	Symmetry	Vibrational energy		
		SiH ₂	SiF ₂	SiCl ₂
1	2	3	4	5
2λ ₁	A ₁	3986.130	1706.810	1042.011
2λ ₂	A ₁	1986.401	676.263	408.420
2λ ₃	B ₁	3973.926	1736.322	1058.105
3λ ₁	A ₁	5983.231	2559.112	1563.213
3λ ₂	A ₁	2931.121	1012.003	613.003
3λ ₃	B ₁	5964.198	2591.921	1591.211
4λ ₁	A ₁	7975.631	3417.111	2088.315
4λ ₂	A ₁	3949.612	1327.891	803.921
4λ ₃	B ₁	7952.250	3432.632	2087.093
5λ ₁	A ₁	9968.359	4261.103	2603.463
5λ ₂	A ₁	4912.261	1684.198	1021.996

1	2	3	4	5
$5\lambda_3$	B ₁	9948.129	4302.730	2551.619
$6\lambda_1$	A ₁	11946.037	5114.585	3109.662
$6\lambda_2$	A ₁	5909.621	2019.205	1187.173
$6\lambda_3$	B ₁	11939.237	5182.774	3161.624
$7\lambda_1$	A ₁	13945.410	5963.534	3587.321
$7\lambda_2$	A ₁	6906.112	2372.419	1398.254
$7\lambda_3$	B ₁	13912.096	6036.138	3670.321
$8\lambda_1$	A ₁	15921.161	6824.087	4123.519
$8\lambda_2$	A ₁	7923.536	2709.129	1573.023
$8\lambda_3$	B ₁	15891.531	6892.229	4161.855
$9\lambda_1$	A ₁	17893.204	7631.850	4672.752
$9\lambda_2$	A ₁	8916.392	3064.005	1723.732
$9\lambda_3$	B ₁	17881.582	7741.403	4639.112
$10\lambda_1$	A ₁	19742.409	8480.612	5173.518
$10\lambda_2$	A ₁	9923.443	3342.451	1968.374
$10\lambda_3$	B ₁	19873.985	3617.722	5114.008

Table 4. Vibrational energies (in cm^{-1}) corresponding to combinational bands.

Combinational band	Vibrational energy		
	SiH ₂	SiF ₂	SiCl ₂
1	2	3	4
$\lambda_1 + \lambda_2$	2992.169	1197.879	726.532
$\lambda_1 + \lambda_3$	3988.842	1725.649	1060.155
$\lambda_2 + \lambda_3$	2989.070	1213.256	736.519
$2\lambda_1 + 2\lambda_2$	5972.452	2382.237	1445.275
$2\lambda_1 + 2\lambda_3$	7960.083	3443.176	2100.136
$2\lambda_2 + 2\lambda_3$	5960.245	2411.749	1461.369
$3\lambda_1 + 3\lambda_2$	8914.271	3570.279	2171.060
$3\lambda_1 + 3\lambda_3$	11947.457	5151.077	3154.444
$3\lambda_2 + 3\lambda_3$	8895.238	3603.088	2199.058
$4\lambda_1 + 4\lambda_2$	11925.161	4744.166	2892.256
$4\lambda_1 + 4\lambda_3$	15927.908	6849.787	4170.252
$4\lambda_2 + 4\lambda_3$	11901.780	4759.687	2885.858
$\lambda_1 + 2\lambda_1$	5982.116	2561.968	1567.105
$\lambda_1 + 2\lambda_2$	3982.278	1530.541	928.338
$\lambda_1 + 2\lambda_3$	5969.912	2591.480	1578.023
$\lambda_2 + 2\lambda_1$	4982.344	2049.575	1243.469
$\lambda_2 + 2\lambda_2$	2982.506	1018.122	604.702
$\lambda_2 + 2\lambda_3$	4970.140	2079.087	1259.563
$\lambda_3 + 2\lambda_1$	5979.014	2577.345	1577.092
$\lambda_3 + 2\lambda_2$	3979.175	1545.918	938.326
$\lambda_3 + 2\lambda_3$	5966.809	2606.857	1593.186
$\lambda_1 + 3\lambda_1$	7979.217	3414.270	2088.307
$\lambda_1 + 3\lambda_2$	4926.998	1866.281	1132.921

	1	2	3	4
$\lambda_1 + 3\lambda_3$		7960.184	3447.079	2116.305
$\lambda_2 + 3\lambda_1$		6979.446	2902.1392	1764.671
$\lambda_2 + 3\lambda_2$		3927.226	1355.412	809.285
$\lambda_2 + 3\lambda_3$		6960.412	2935.440	1792.669
$\lambda_3 + 3\lambda_1$		7976.115	3429.521	2098.294
$\lambda_3 + 3\lambda_2$		4923.895	1882.412	1142.909
$\lambda_3 + 3\lambda_3$		7957.082	3462.439	2126.292
$\lambda_1 + 4\lambda_1$		9971.617	4272.252	2613.409
$\lambda_1 + 4\lambda_2$		5945.488	2182.813	1323.839
$\lambda_1 + 4\lambda_3$		9948.236	4287.79	2612.187
$\lambda_2 + 4\lambda_1$		8971.845	3759.876	2289.773
$\lambda_2 + 4\lambda_2$		4945.716	1669.777	1000.203
$\lambda_2 + 4\lambda_3$		8948.464	3775.397	2288.551
$\lambda_3 + 4\lambda_1$		9968.514	4287.646	2623.396
$\lambda_3 + 4\lambda_2$		5942.386	2197.546	1333.827
$\lambda_3 + 4\lambda_3$		9945.133	4303.167	2622.174

4. Conclusion

We have calculated the vibrational energies of silylene, difluorosilylene and dichlorosilylene, using the one-dimensional Lie algebraic model. Our results indicate that the model based upon the Lie algebra represents a successful technique. We have found that the calculated energies agree well with the fundamental experimental references. For instance, the root-mean-square deviations obtained for the both stretching and bending fundamental vibrational energies are equal to 1.03, 0.81 and 0.80 cm^{-1} respectively for SiH_2 , SiF_2 and SiCl_2 .

As a consequence, one can believe that the approach adopted in the present work can predict accurately the vibrational energy levels for the small and medium-size molecules, as well as the higher-order overtones and the combinational bands. In particular, we have calculated the higher-order vibrational energies up to the ninth overtone with tenth vibrational excitation and third overtone with fourth excitation.

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Анотація. Ми застосували одновимірну алгебраїчну модель Лі до оцінок фундаментальних коливань, а також їхніх обертонів вищого порядку (аж до десятого коливального збудження) та комбінаційних смуг (до четвертого збудження) для силілену (SiH₂), дифторсилілену (SiF₂) та дихлорсилілену (SiCl₂). Коливальний гамільтоніан, який утримує точкову групу симетрії C_{2v}, кожної з цих молекул силілену, змодельовано за допомогою трьох взаємодіючих осциляторів Морзе. Порівняння розрахованих нами фундаментальних коливальних енергій (хвильових чисел) із наявними експериментальними довідковими даними підтверджує, що наші результати добре узгоджуються з експериментом.