

Calculating Vibrational Spectra Of Silane Using Vibron Model



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Abstract

In this paper, vibrational spectra (infrared and Raman) of Silane (SiH₄) is calculated using theoretical method, Vibron model. The determined vibrational energy levels by Vibron model are compared with experimental results. The obtained results from our method are consistent with experimental results.

Key words: Lie algebras, vibrational spectra, Silane, Vibron model

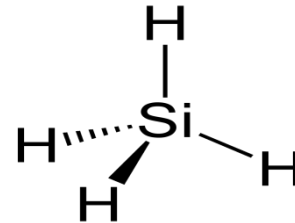


Figure: Structure of Silane

I. INTRODUCTION

Vibrational spectroscopy is one of the important methods for the structural identification of molecular systems and measuring their interactions. Until now there are two approaches are used to understand the vibrational spectra of molecules. Dunham approach is based on expansion of energy levels in terms of rotational and vibrational quantum numbers and second approach is by solving the Schrodinger equation with interatomic variables and potential coefficients. These two approaches are tedious because of huge number of parameters are introduced in order to obtain the result. To overcome the difficulties arised in mentioned two approaches, Iachello introduced Vibron model in which Hamiltonian operator can express in terms of invariant operators characterizing the local, normal mode of the system. In the last few years Vibron model has been used extensively by Karumuri and co-workers to calculate the vibrational spectra of different polyatomic molecules [1,2,3].

II. STRUCTURE OF SILANE (SiH₄)

Silane (SiH₄) containing one silicon and four hydrogen atoms with four (Si-H) bonds. Silane is a tetrahedral structure molecule with the Point group, T_d. Symmetry species of this point group are A₁, E, T₁ and T₂.

III. VIBRON MODEL

The Hamiltonian operator which is used in Vibron model [5,6] for four interacting bonds of Silane is

$$H = E_0 + \sum_{i=1}^4 A_i C_i + \sum_{i<j}^4 A_{ij} C_{ij} + \sum_{i<j}^4 \lambda_{ij} M_{ij}.$$

In the Hamiltonian, the second term is related to the four independent local oscillators in terms of invariant operators C_i. The third term associated with cross-anharmonicities between pairs of dissimilar local oscillators in terms of the operators C_{ij}. The last term express anharmonic, non diagonal interactions involving pairs of local oscillators in terms of the Majorana operators M_{ij}

Where, C_i and C_{ij} are invariant operators of the uncoupled and coupled bonds respectively and are given by

$$\langle C_i \rangle = -4(N_i v_i - v_i^2),$$

$$\langle N_i, v_i; N_j, v_j | C_{ij} | N_i, v_i; N_j, v_j \rangle = 4 \left[(v_i + v_j)^2 - (v_i + v_j)(N_i + N_j) \right].$$

The Majorana operators M_{ij} is used to explain the local mode interactions in pairs and contains both diagonal and non-diagonal matrix elements and given by

$$\langle N_i, v_i; N_j, v_j | M_{ij} | N_i, v_i; N_j, v_j \rangle = (N_j v_j + N_j v_i - 2v_i v_j)$$

$$\langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle = -[v_j (v_i + 1)(N_i - v_i)(N_j - v_j + 1)]^{1/2}$$

$$\langle N_i, v_i - 1; N_j, v_j + 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle = -[v_i (v_j + 1)(N_j - v_j)(N_i - v_i + 1)]^{1/2}.$$

Where, V_i, V_j are vibrational quantum numbers of bonds i and j respectively. The Vibron number N_i is calculated by

$$N_i = \frac{\omega_i}{\omega_i x_i} - 1, i = 1, 2, \dots (\omega_i \text{ and } \omega_i x_i \text{ are the spectroscopic constants [6]})$$

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We consider a mathematical fitting procedure to adjust the parameters, $A_i, A_{ij}, \lambda_{ij}$ over an experimental data base of vibrational energy levels.

The starting guess for the parameter A_i will be calculated by using the energy equation for the single-oscillator fundamental mode as

$$E(v=1) = -4A_i(N_i - 1).$$

The parameter λ_{ij} can be evaluated from the relation,

$$\lambda_{ij} = \frac{|E_i - E_j|}{3N}.$$

IV. RESULTS

Table. Vibrational frequencies (in cm-1) of Silane

Symmetry	Mode number	Experimental [7]	Calculated
A ₁	1	2187	2186.923
E	2	975	976.021
T ₁	3	2191	2190.743
T ₂	4	914	915.219

Fitted Parameters:

$$A_i (A_1 = A_2 = A_3 = A_4) = -9.940$$

$$\lambda_{ij} (\lambda_{12} = \lambda_{23} = \lambda_{34} = \lambda_{14} = \lambda_{13} = \lambda_{14} = \lambda_{24}) = -4.234$$

$$A_{ij} (A_{12} = A_{23} = A_{34} = A_{14} = A_{13} = A_{14} = A_{24}) = 0.375$$

$$N (N_1 = N_2 = N_3 = N_4) = 56$$

V. CONCLUSIONS

The obtained fundamental vibrational frequencies of Silane from Vibron model are consistent with available experimental data. The obtained results are useful for the experimentalists and theorists to develop the vibrational frequencies of Silane in higher overtones.

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