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Algebraic approach : study of vibrational spectra of some linear triatomic molecules

Nirmal Kumar Sarkar[1]*, Joydeep Choudhury[2] and Ramendu Bhattacharjee

[1]Department of Physics Karimganj College Karimganj 788 710 Assam India

[2]Department of Physics Assam University Silchar 788 011 Assam India

E mail nks sds@rediffmail com

Abstract Using the Lie algebraic method the vibrational energy levels of OCS and HCN are calculated for 35 vibrational bands each using the local Hamiltonian A comparative study is made between the two It has been shown that local Hamiltonian gives a much better fit to the HCN in comparison to that of OCS Better result for HCN compared to those published earlier also has been reported

Keywords Vibrational spectra Lie algebra OCS, HCN

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1. Introduction

Marius Sophus Lie introduced Lie algebras at the end of the 19th century However, Lie algebraic methods have been useful in the study of problems in Physics after the development of quantum mechanics in the first part of the 20th century The use of Lie algebras as a tool to systematically investigate physical systems (the so called spectrum generating algebras) did not however develop fully until the 1970's, when it was introduced in a systematic fashion by A Arima and F Iachello in the study of spectra of atomic nuclei (interacting boson model) [1,2] Wulfman played a great role in the introduction of the algebraic approach to molecules[3] He is the pioneer to publish the first paper on the algebraic approach to molecules (the algebraic approach to the Morse oscillator) in 1979[3] Later , in 1981, F. Iachello used Lie algebraic methods in the systematic study of spectra of molecules (vibron model) [4] After 1981, there was a rapid progress in the field The situation up to 1995 was reviewed in the study of F Iachello and R.D Levine[5] The study of F.Iachello and S Oss[6] presented a brief review of the work done in this field up

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Corresponding Author

to 2000 Moreover, the study[6] also provided perspectives for the algebraic method in the first decade of the 21st century

In the Lie algebraic method there is provision to study a molecule both by a normal and a local Hamiltonian Using Lie algebraic method, in this paper the vibrational energy levels of OCS and HCN (in cm^{-1}) are calculated by local Hamiltonian for 35 vibrational bands each On the basis of this study it has been shown that local Hamiltonian gives a much better fit to the HCN in comparison to that of OCS Better result for HCN compared to those published earlier also has been reported.

2. Theory : the Lie algebraic method [7]

In Lie algebraic method to study the vibrational spectra of triatomic molecules, there are two main ways in which the bonds can be coupled [8]

$$U_1(4)\otimes U_2(4) \supset O_1(4)\otimes O_2(4) \supset O_{12}(4) \supset O_{12}(3) \supset O_{12}(2) \quad \text{(I)} \tag{1}$$

$$U_1(4)\otimes U_2(4) \supset U_{12}(4) \supset O_{12}(4) \supset O_{12}(3) \supset O_{12}(2) \quad \text{(II)}$$

Which correspond to local and normal coupling respectively For these two situations the Hamiltonian operator can be diagonalized analytically

The local basis is characterized by the representations of chain I [5, 8],

$$\left.\begin{array}{lccccccc} & U_1(4) \otimes & U_2(4) \supset & O_1(4) \otimes & O_2(4) \supset & O_{12}(4) \supset & O_{12}(3) \supset & O_{12}(2) \\ \mathrm{I} & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow & \downarrow \\ & [N_1] & [N_2] & (\omega_1,0) & (\omega_2,0) & (\tau_1,\tau_2) & J & M_J \end{array}\right\} \tag{2}$$

The numbers N_1, N_2 are the vibron numbers of each bond They are related to the number of bound states for bonds 1 and 2 respectively For Morse rovibrators they are given by the following equation [5]

$$E'o = -A(2N+3) \tag{3}$$

($E'o,A \rightarrow$ algebraic parameters)

Equation (3) shows that the vibron numbers are related to the depth of the potentials.They are fixed numbers for a given molecules. The numbers $\omega_1, \omega_2, \tau_1, \tau_2$ are related to the vibrational quantum numbers, as discussed explicitly in the following sections We have written the $O_1(4)$ representations as $(\omega_1,0)$ and not simply as ω_1, since for coupled systems one can have representations of $O_1(4)$ in which the second quantum number is not zero[5]. The values of ω_1 and ω_2 are given by the rule

$$\omega_1 = N_1, N_1-2, \text{————————} 1 \text{ or } 0,\ N_1 = \text{odd or even.}$$

$$\omega_2 = N_2, N_2-2, \text{————————} 1 \text{ or } 0,\ N_2 = \text{odd or even} \tag{4}$$

The values of (τ_1, τ_2) are instead obtained from the direct product of representations [5]. They are given by [9]

$$\tau_1 = \omega_1 - \omega_2 - \mu - \nu, \tau_2 = \mu - \nu ,$$

$$\mu = 0,1, \text{———————}, \min(\omega_1, \omega_2), \nu = 0,1, \text{———————} \mu \tag{5}$$

Finally for each representation (τ_1, τ_2) the values of the allowed angular momenta and parities are

$$J^P = 0^+, 1^-, 2^+, \text{—————} \left(\tau_1^+ \text{ or } \tau_1^-\right), \text{ when } t_2 = 0 \text{ and } (\tau_1 = \text{even or odd})$$

$$J^P = \tau_2^\pm, (\tau_2 + 1)^\pm, \text{—————} \tau_1^+ \text{ When } \tau_2 \neq 0 \tag{6}$$

The z components of the angular momentum is given by the usual rule

$$-J \leq M_J \leq +J . \tag{7}$$

3. Local-mode Hamiltonian for linear triatomic molecules

Whenever the Hamiltonian can be written in terms of invariant(Casimir) operators of a chain, its eigen value problem can be solved analytically. This method can be applied to the construction of both local and normal Hamiltonians. For local Hamiltonians, one writes H in terms of Casimir invariants of equation (2)

$$H^{local} = Eo + A_1 C(O(4_1)) + A_2 C(O(4_2)) + A_{12} C(O(4_{12})) + BC(O(3_{12})) \tag{8}$$

Here we have dropped the subscript 2 from the Casimir invariant operators in order to simplify the notation [5]. The Hamiltonian (8) is diagonal in the local basis with eigen values

$$E(N_1, N_2, \omega_1, \omega_2, \tau_1, \tau_2, J, M_J) = Eo + A_1\omega_1(\omega_2 + 2) + A_2\omega_2(\omega_2 + 2)$$

$$+ A_{12}\left[\tau_1(\tau_1 + 2) + \tau_2^2\right] + BJ(J + 1) . \tag{9}$$

The last term in the right hand side of the above equation representing the rotational part. We can now convert equation (9) into the usual form by introducing the local vibrational quantum numbers[5],

$$\omega_1 = N_1 - 2v_a$$

$$\omega_2 = N_2 - 2v_c$$

$$\tau_1 = N_1 + N_2 - 2v_a - v_b - 2v_c$$

$$\tau_2 = 1_h \tag{10}$$

The quantum number v_a, v_c denote local stretching vibrations, while the quantum numbers, v_b^{lb}, denote the doubly degenerate bending vibrations. Eq. (9) can be converted, using eq. (10) to

$$E\left(v_a, v_b{}^{lb}, v_c\right) = E_0' - 4A_1\left[(N_1+1)v_a - v_a^2\right] - 4A_2\left[(N_1+1)v_c - v_c^2\right]$$

$$-A_{12}\left[2(N_1+N_2+1)(2v_a+v_b+2v_c) - (2v_a+v_b+2v_c)^2 + 1_b^2\right] \tag{11}$$

In this expression we have dropped the rotational part and written only the vibrational part. In this (purely local) limit, vibrational energy levels are determined by five parameters(A_1,A_2,A_{12} and N_1,N_2).

4. Results and discussion

Vibrational energy levels of OCS and those calculated in the strict local limit for 35 vibrational bands are shown in Table 1. Vibrational energy levels of HCNand those calculated in the strict local limit for 35 vibrational bands are shown in Table 2. Using the established norms[5, 8] the vibron numbers N_1,N_2 and other algebraic parameters A_1,A_2,A_{12} were determined. A_1, A_2, A_{12} all in cm^{-1}, except N_1 and N_2, which are dimensionless.

Table 1 shows that in the calculation of vibrational energy levels, local Hamiltonian gives a poor fit to the OCS. Table 2 shows that local Hamiltonian gives a much better fit to the HCN in comparison to that of OCS [10]. Result reported here for HCN[7] is better with respect to the results published earlier [5, 8, 14]. RMS deviations(Δ(r.m.s.)) here we reported for OCS and HCN were 90.816 cm^{-1}and 11.057 cm^{-1} respectively.

5. Conclusion

(i) On the basis of the cited data it may be concluded that result reported in this study is better with respect to the results published earlier for the vibrational spectra of HCN(using local model).

(ii) In the comparative study of the vibrational spectra of OCS and HCN in the local mode limit we conclude : Local model is a poor approximation for OCS compared to that of HCN. Only HCN could be very well approximated by a local Hamiltonian but not OCS.

6. Algebraic approach in the study of molecular spectra in near future

Using the Lie algebraic methods many molecules(small and medium) have been analyzed in the last twenty five years. At present challenges for the Lie algebraic methods are the larger and more complex molecules (macromolecules, polymers, biomolecules and biopolymers). Introduction of anharmonicities gives the Lie algebraic methods an advantageous position. Some physical systems are known where anharmonicities play a role.Liquids and surfaces are the two important sectors belongs to this category[6]. It is

Table 1. Vibron Model Fits of OCS (in cm ^{1})[10]

v_1	v_2^{12}	v_3	Expt.[a]	Calc.[b]	Δ^c
1	0^0	0	859	867 24	-8 24
0	2^0	0	1047	1102 84	55 84
0	0^0	1	2062 2	2075 92	-13 72
2	0^0	0	1711 1	1730 64	-19 54
1	2^0	0	1892 2	1963 76	-71 56
0	4^0	0	2104 8	2199 36	-94 56
1	0^0	1	2918 1	2936 84	-18 74
0	2^0	1	3095 6	3172 44	76 84
0	0^0	2	4101 4	4133 28	-31 88
3	0^0	0	2556	2590 2	-34 2
2	2^0	0	2731 4	2820 84	-89 44
1	4^0	0	2937 2	3053 96	-116 76
0	6^0	0	3170 6	3289 56	-118 96
2	0^0	1	3768 5	3793 92	-25 42
1	2^0	1	3937 4	4027 04	-89 64
0	4^0	1	4141 2	4262 64	-121 44
1	0^0	2	4953 9	4987 88	-33 98
0	2^0	2	5121	5223 48	102 48
0	0^0	3	6117 6	6172 08	-54 48
4	0^0	0	3394	3445 92	51 92
3	2^0	0	3564 5	3674 08	-109 58
2	4^0	0	3762 8	3904 72	-141 92
3	0^0	1	4609 9	4647 16	-37 26
1	4^0	1	4970 4	5110 92	-140 52
0	6^0	1	5196	5346 52	-150 52
2	0^0	2	5801 9	5838 64	-36 74
1	2^0	2	5959 3	6071 76	-112 46
0	4^0	2	6154 7	6307 36	-152 66
1	0^0	3	6966 2	7020 36	-54 16
5	0^0	0	4224 9	4297 8	-72 9
4	2^0	0	4391 4	4523 48	-132 08
4	0^0	1	5445	5496 56	-51 56
2	4^0	1	5792	5955 3	-163 36
3	0^0	2	6640 1	6685 56	-45 46
2	2^0	2	6791 6	6916 2	-124 6

Δ (r m.s.) = 90 816

[a] Ref. [11]

[b] N_1=190, N_2=159, A_1=0 31, A_2=-1 53, A_{12}=-0 79 ,

[c] Δ = (Expt - Cal)

Table 2. Vibron Model Fits of HCN (in cm ^{1})[7]

v_1	v_2^{12}	v_3	Expt[a]	Calc[b]	Δ^c
1	2^0	0	1411 43	1412 972	1 542
1	0^0	0	2096 85	2104 012	7 162
0	0^0	1	3311 48	3299 364	+12 116
0	4^0	0	2802 85	2810 832	7 982
1	2^0	0	3501 13	3501 872	-0 742
2	0^0	0	4173 07	4183 040	9 97
0	2^0	1	4684 32	4697 224	12 904
1	0^0	1	5393 70	5388 264	+5 436
0	0^0	2	6519 61	6503 344	+16 266
2	2^0	0	5571 89	5565 788	+6 102
1	2^0	1	6761 33	6771 012	-9 682
1	0^0	2	8585 57	8577 132	+8 438
0	0^0	3	9627 02	9611 94	+15 08
1	2^0	2	9914 41	9944 768	30 358
1	0^0	3	11674 46	11670 616	+3 844
0	0^0	4	12635 90	12625 152	+10 748
0	0^0	5	15551 94	15542 98	+8 96
3	0^0	3	15710 53	15713 016	-2 486
2	0^0	4	16674 21	16687 296	13 086
1	0^0	5	17550 39	17571 432	-21 042
0	0^0	6	18377 01	18365 424	+11 586
5	0^0	2	16640 31	16622 444	+17 866
0	1^1	0	711 98	710 264	+1 716
0	3^1	0	2113 46	2115 68	-2 22
1	1^1	0	2805 58	2806 72	-1 14
0	1^1	1	4004 17	4002 072	+2 098
1	3^1	0	4201 29	4197 024	+ 4 266
2	1^1	0	4878 27	4878 192	+0 078
0	3^1	1	5366 86	5392 376	-25 516
1	1^1	1	6083 35	6083 416	-0 066
0	1^1	2	7194 75	7198 496	-3 746
0	2^2	0	1426 53	1420 528	+6 002
0	4^2	0	2818 16	2818 388	-0 288
1	2^2	0	3516 88	3509 428	+7 452
0	2^2	1	4699 21	4704 78	-5 57

Δ (r m s) = 11 057

[d] References [12] and [13]

[e] N_1=140, N_2=47, A_1=-1 234, A_2=-10 034, A_{12}=-1 889,

[f] Δ = (Expt - Cal)

another challenge for the Lie algebraic methods to expand its kingdom in to these regions in near future.

In view of the many possible applications it is hoped that present momentum of the Lie algebraic method will stimulate further research, especially in the spectroscopy of higher-energy states of molecules[5] and new areas of complex systems for which alternative methods of analysis are difficult to apply. In this regard we are optimistic to hope that in near future the Lie algebraic methods will be able to open many new windows in the field of spectroscopy.

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