
Vibrational spectra of cyclobutane-d8 using symmetry-adapted one-dimensional Lie algebraic framework

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Abstract. We use a one-dimensional $U(2)$ Lie algebraic model to study fundamental and first-overtone vibrational frequencies, as well as their combination bands for cyclobutane-d8, C_4D_8 . The model preserves the point symmetry group D_{2d} , with the symmetry species A_1 , A_2 , B_1 , B_2 and E , and involves 23 normal vibrational modes. A comparison of the calculated vibrational frequencies and the available reference data results in the root-mean-square deviation as small as 1.557 cm^{-1} .

Keywords: vibrational Hamiltonian, Morse oscillator, $U(2)$ Lie algebras, cyclobutane-d8

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1. Introduction

The field of molecular spectroscopy addresses the problems of how light interacts with molecules. It involves various techniques, including infrared and Raman spectroscopy, in order to determine the vibrational modes of molecules and analyze their structure. By analyzing the vibrational-energy levels and the frequencies of molecules, one can determine their structure and gain insights into their properties and behaviour. In order to successfully develop novel methods of experimentation that enable deriving higher-order vibrational excitations in polyatomic molecules, one must first develop robust theoretical approaches for interpreting those excitations.

The experimental data for the rovibrational spectra of polyatomic molecules can be interpreted using two well-known theoretical frameworks. The first approach is a Dunham expansion, which studies the spectra of polyatomic molecules with some success, even though the number of coefficients required increases rapidly with increasing complexity of a molecule. One of the limitations of this expansion is that Dunham coefficients can be difficult to calculate, especially for higher-order terms, and may require sophisticated computational methods or extensive experimental data. The second approach, a Schrödinger equation with potentials, can be solved analytically for only a few simple cases, and so numerical methods are required for most systems. Nonetheless, a solution of the Schrödinger equation results in insights into allowed energy levels and associated wave functions in a quantum system. A critical drawback of this approach is that its computational complexity may represent a significant challenge in the case of large enough systems.

In order to address the challenges encountered in the traditional approaches, Iachello et al. [1, 2] have used Lie algebraic models to analyze the vibrational spectra of polyatomic molecules. This technique has been notably improved in subsequent studies to investigate the rotation-vibration spectra of different polyatomic molecules [3–8]. The Lie algebraic models are now used in molecular

spectroscopy to describe the symmetry properties of molecules and analyze their spectra. In particular, these approaches have been already employed to determine analytically the vibrational spectra, the gas-phase Raman spectra and the infrared spectra of cyclobutane-d8 [9–11].

It is worthwhile that the earlier studies have been performed with either *ab initio* theory or semi-empirical methods and have addressed mainly the fundamental vibrational frequencies. On the contrary, in the present work we model the vibrational Hamiltonian of cyclobutane-d8, using one-dimensional dynamical U(2) Lie algebras and calculate the fundamental vibrational frequencies more accurately than the previous works. Moreover, we predict the first-overtone frequencies and the frequencies of combination bands at a significantly lower computational cost.

2. Symmetry-adapted one-dimensional Lie algebraic framework for cyclobutane-d8

Our framework is based on the idea that the vibrational Hamiltonian of a molecule can be expressed in terms of the generators of the U(2) Lie algebra, and their eigenvalues correspond to the allowed vibrational frequencies of this molecule [12, 13, 14]. Here we assign the C–D and C–C bonds respectively to the U(2) Lie algebras $U_1(2)$ to $U_8(2)$ and $U_1^*(2)$ to $U_4^*(2)$, as represented in Fig. 1. Note that cyclobutane-d8 belongs to the point group D_{2d} with the symmetry species A_1, A_2, B_1, B_2, E . It is characterized by 23 normal vibrational modes.

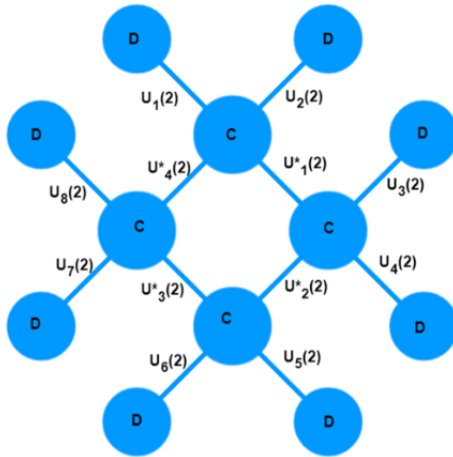


Fig. 1. Structure of cyclobutane-d8.

The vibrational Hamiltonian for the stretching C–D vibrations in cyclobutane-d8 is as follows [1, 2, 13, 14]:

$$H^{C-D} = E_0^{C-D} + \sum_{i=1}^{n=8} A_i^{C-D} C_i + \sum_{i < j}^{n=8} A_{ij}^{C-D} C_{ij} + \sum_{i < j}^{n=8} (k_{ij}^1 + k_{ij}^2 + k_{ij}^3 + k_{ij}^4) \lambda_{ij}^{C-D} M_{ij} \quad (1)$$

where the symmetry-adapted 1st, 2nd, 3rd and 4th neighbour couplings coefficients are given by

$$k_{ij}^1 = \begin{cases} 1, (i, j) = (1, 2), (2, 3), (3, 4), (4, 5), (5, 6), (6, 7), (7, 8), (1, 8) \\ 0, \text{ otherwise} \end{cases}$$

$$k_{ij}^2 = \begin{cases} 1, (i, j) = (1, 3), (2, 4), (3, 5), (4, 6), (5, 7), (6, 8), (1, 7), (2, 8) \\ 0, \text{ otherwise} \end{cases}$$

$$k_{ij}^3 = \begin{cases} 1, (i, j) = (1, 4), (2, 5), (3, 6), (4, 7), (5, 8), (1, 6), (2, 7), (3, 8) \\ 0, \text{ otherwise} \end{cases}$$

$$k_{ij}^4 = \begin{cases} 1, (i, j) = (1, 5), (2, 6), (3, 6), (3, 7), (4, 8) \\ 0, \text{ otherwise} \end{cases}$$

The vibrational Hamiltonian for the stretching C–C vibrations of cyclobutene-d8 can be represented as [1, 2, 13, 14]

$$H^{C-C} = E_0^{C-C} + \sum_{i=1}^{n=4} A_i^{C-C} C_i + \sum_{i<j}^{n=4} A_{ij}^{C-C} C_{ij} + \sum_{i<j}^{n=4} (l_{ij}^1 + l_{ij}^2) \lambda_{ij}^{C-C} M_{ij} . \quad (2)$$

Here the symmetry-adapted 1st and 2nd neighbour couplings coefficients read as

$$l_{ij}^1 = \begin{cases} 1, (i, j) = (1, 2), (2, 3), (3, 4), (1, 4) \\ 0, \text{otherwise} \end{cases}$$

$$l_{ij}^2 = \begin{cases} 1, (i, j) = (1, 3), (2, 4) \\ 0, \text{otherwise} \end{cases}$$

In Eqs. (1) and (2), the first terms, E_0^{C-D} and E_0^{C-C} , are the electronic ground-state energies of respectively the C–D and C–C single bonds. They will be taken as a reference for all the vibrational excitations. The second term is associated with the independent local oscillators represented in terms of the invariant Casimir operators C_i . The third term describes the cross anharmonicities between the pairs of distinct local oscillators in terms of the coupled Casimir operators C_{ij} . Finally, the last term implies the anharmonic non-diagonal interactions involving the pairs of local oscillators in terms of the coupled Majorana operators M_{ij} .

Concerning the other notation, the terms A_i^{C-D} , A_i^{C-C} , A_{ij}^{C-D} , A_{ij}^{C-C} , λ_{ij}^{C-D} and λ_{ij}^{C-C} are the algebraic parameters, while C_i and C_{ij} represent the (invariant) Casimir operators of the associated Lie algebras. The Majorana (invariant) operators M_{ij} are related to the coupling schemes involving the Lie algebras of n interacting one-dimensional Morse oscillators. The spectroscopic data can be used for determining the algebraic parameters, whereas the expressions for determining the algebraic operators are as follows [1, 2]:

$$\langle C_i \rangle = -4(N_i v_i - v_i^2), \quad (3)$$

$$\langle N_i, v_i; N_j, v_j | C_{ij} | N_i, v_i; N_j, v_j \rangle = 4(v_i + v_j)(v_i + v_j - N_i - N_j), \quad (4)$$

$$\left. \begin{aligned} \langle N_i, v_i; N_j, v_j | M_{ij} | N_i, v_i; N_j, v_j \rangle &= v_i N_j + v_j N_i - 2v_i v_j \\ \langle N_i, v_i + 1; N_j, v_j - 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle &= -[v_j(v_i + 1)(N_i - v_i)(N_j - v_j + 1)]^{1/2} \\ \langle N_i, v_i - 1; N_j, v_j + 1 | M_{ij} | N_i, v_i; N_j, v_j \rangle &= -[v_i(v_j + 1)(N_j - v_j)(N_i - v_i + 1)]^{1/2} \end{aligned} \right\} . \quad (5)$$

Here v_i and v_j are the vibrational quantum numbers respectively of the bonds i and j , and N_i and N_j are the vibron numbers linked to the numbers of bound states of the one-dimensional Morse oscillators.

The following mathematical expressions for the matrix elements $\langle C_i \rangle$, $\langle C_{ij} \rangle$ and $\langle M_{ij} \rangle$ describe the fundamental vibrations:

$$\langle C_i \rangle = -4(N - 1), \quad \langle C_{ij} \rangle = -4(2N - 1), \quad \langle M_{ij} \rangle = \begin{cases} -N (i \neq j) \\ N (i = j) \end{cases} . \quad (6)$$

The (dimensionless) vibron number N corresponding to the maximum number of bound states of the Morse potential in each vibrating bond species is given by

$$N = \frac{\omega_e}{\omega_e \chi_e} - 1, \tag{7}$$

where ω_e is equal to 2101.05193 and 1855.06630 respectively for the C–D and C–C bonds, and $\omega_e \chi_e$ amounts to 34.72785 for the C–D bonds, and 13.6007 for the C–C bonds. They represent the spectroscopic constants of the bonds determined from the experimental data obtained for diatomic molecules [15].

The initial values for A_i^{C-D} and A_i^{C-C} can be obtained from the energy expression for the single-oscillator fundamental mode:

$$\begin{aligned} E^{C-D} &= -4A_i^{C-D} (N^{C-D} - 1), \\ E^{C-C} &= -4A_i^{C-C} (N^{C-C} - 1) \end{aligned} \tag{8}$$

Here N^{C-D} and N^{C-C} are the vibron numbers corresponding to the numbers of bound states of the one-dimensional Morse oscillators, which describe the vibrations in the C–D and C–H single bonds.

The initial values for λ_{ij}^{C-D} and λ_{ij}^{C-C} can be guessed using the relations

$$\lambda_{ij}^{C-D} = \frac{|E_s^{C-D} - E_{as}^{C-D}|}{6N^{C-D}}, \lambda_{ij}^{C-C} = \frac{|E_s^{C-C} - E_{as}^{C-C}|}{2N^{C-C}}. \tag{9}$$

Here E_s and E_{as} are the energies corresponding to symmetric and antisymmetric combinations of the two local modes. The parameter values can be optimized by a least-square fitting, starting from the initial values given by Eqs. (8) and (9). Finally, we take zero initial values for A_{ij}^{C-D} and A_{ij}^{C-C} .

3. Results

Table 1 lists the optimized values of the algebraic parameters and vibron numbers involved in our model. Tables 2–4 display the calculated frequencies corresponding respectively to the fundamental, first-overtone and combination bands. It is noteworthy that the calculated vibrational frequencies are very close to the experimental data taken from Ref. [16]. In particular, the root-mean-square deviation is as small as 1.5566 cm⁻¹.

Table 1. Optimized parameters found for our Lie algebraic framework.

Parameter	Value
N^{C-D}, N^{C-C} (<i>stretching</i>)	60, 136
A_i^{C-D}, A_i^{C-C} (<i>stretching</i>)	-9.2076, -1.2807
$A_{ij}^{C-D}, A_{ij}^{C-C}$ (<i>stretching</i>)	1.0112, 0.1542
$\lambda_{ij}^{C-D}, \lambda_{ij}^{C-C}$ (<i>stretching</i>)	0.3277, 0.8848
N (<i>bending</i>)	36
A_i (<i>bending</i>)	-6.4142
A_{ij} (<i>bending</i>)	0.4952
λ_{ij} (<i>bending</i>)	1.3449

Table 2. Fundamental vibrational frequencies calculated for C₄D₈.

Vibrational mode	Symmetry species	Experimental frequency, cm ⁻¹ [16]	Calculated frequency, cm ⁻¹
<i>v</i> ₁ (<i>CD</i> ₂ <i>s-str</i>)	A ₁	2124	2124.4224
<i>v</i> ₂ (<i>CD</i> ₂ <i>scis</i>)	A ₁	1160	1160.2816
<i>v</i> ₃ (<i>CD</i> ₂ <i>scis</i>)	A ₁	882	882.6176
<i>v</i> ₄ (<i>CD</i> ₂ <i>a-str</i>)	A ₁	2224	2223.7912
<i>v</i> ₅ (<i>CD</i> ₂ <i>rock</i>)	A ₁	632	633.5910
<i>v</i> ₆ (<i>ring puck</i>)	A ₁	158	156.2691
<i>v</i> ₇ (<i>CD</i> ₂ <i>wag</i>)	A ₂	1010	1008.9803
<i>v</i> ₈ (<i>CD</i> ₂ <i>twist</i>)	A ₂	889	891.2123
<i>v</i> ₉ (<i>CD</i> ₂ <i>wag</i>)	B ₁	1078	1077.0012
<i>v</i> ₁₀ (<i>ring deform</i>)	B ₁	746	745.6011
<i>v</i> ₁₁ (<i>CD</i> ₂ <i>twist</i>)	B ₁	864	865.9003
<i>v</i> ₁₂ (<i>CD</i> ₂ <i>s-str</i>)	B ₂	2115	2115.8925
<i>v</i> ₁₃ (<i>CD</i> ₂ <i>scis</i>)	B ₂	1040	1038.4426
<i>v</i> ₁₄ (<i>ring deform</i>)	B ₂	938	939.6622
<i>v</i> ₁₅ (<i>CD</i> ₂ <i>a-str</i>)	B ₂	2242	2241.7001
<i>v</i> ₁₆ (<i>CD</i> ₂ <i>rock</i>)	B ₂	483	482.0208
<i>v</i> ₁₇ (<i>CD</i> ₂ <i>a-str</i>)	E	2230	2231.4450
<i>v</i> ₁₈ (<i>CD</i> ₂ <i>twist</i>)	E	938	939.9182
<i>v</i> ₁₉ (<i>CD</i> ₂ <i>rock</i>)	E	556	553.5000
<i>v</i> ₂₀ (<i>CD</i> ₂ <i>s-str</i>)	E	2103	2102.3219
<i>v</i> ₂₁ (<i>CD</i> ₂ <i>scis</i>)	E	1078	1075.6621
<i>v</i> ₂₂ (<i>CD</i> ₂ <i>wag</i>)	E	1048	1045.4372
<i>v</i> ₂₃ (<i>ring deform</i>)	E	734	732.2029

Notation: *s-str* = symmetric stretch, *a-str* = asymmetric stretch, *scis* = scissor, *rock* = rocking, *ring deform* = ring deformation, *ring puck* = ring puckering, *twist* = twisting and *wag* = wagging.

Table 3. First-overtone vibrational frequencies calculated for C₄D₈.

Vibrational mode	Symmetry species	Calculated frequency, cm ⁻¹	Vibrational mode	Symmetry species	Calculated frequency, cm ⁻¹
1	2	3	4	5	6
<i>2v</i> ₁ (<i>CD</i> ₂ <i>s-str</i>)	A ₁	4123.0290	<i>2v</i> ₁₃ (<i>CD</i> ₂ <i>scis</i>)	B ₂	1949.3104
<i>2v</i> ₂ (<i>CD</i> ₂ <i>scis</i>)	A ₁	2240.4700	<i>2v</i> ₁₄ (<i>ring deform</i>)	B ₂	1812.1618
<i>2v</i> ₃ (<i>CD</i> ₂ <i>scis</i>)	A ₁	1683.1616	<i>2v</i> ₁₅ (<i>CD</i> ₂ <i>a-str</i>)	B ₂	4279.3026
<i>2v</i> ₄ (<i>CD</i> ₂ <i>a-str</i>)	A ₁	4259.2293	<i>2v</i> ₁₆ (<i>CD</i> ₂ <i>rock</i>)	B ₂	904.3229

1	2	3	4	5	6
$2\nu_5$ (CD_2 rock)	A ₁	1132.4631	$2\nu_{17}$ (CD_2 a-str)	E	4350.7692
$2\nu_6$ (ring puck)	A ₁	305.1328	$2\nu_{18}$ (CD_2 twist)	E	1807.3180
$2\nu_7$ (CD_2 wag)	A ₂	1933.0454	$2\nu_{19}$ (CD_2 rock)	E	1024.5521
$2\nu_8$ (CD_2 twist)	A ₂	1641.2831	$2\nu_{20}$ (CD_2 s-str)	E	4112.0219
$2\nu_9$ (CD_2 wag)	B ₁	2021.0015	$2\nu_{21}$ (CD_2 scis)	E	2043.6419
$2\nu_{10}$ (ring)	B ₁	1413.2005	$2\nu_{22}$ (CD_2 wag)	E	1886.4504
$2\nu_{11}$ (CD_2 twist)	B ₁	1640.9732	$2\nu_{23}$ (ring deform)	E	1265.0216
$2\nu_{12}$ (CD_2 s-str)	B ₂	4085.8001			

Table 4. Frequencies of the combination bands calculated for C₄D₈.

Vibrational mode	Calculated frequency, cm ⁻¹	Vibrational mode	Calculated frequency, cm ⁻¹
$\nu_1 + \nu_{12}$	4248.4045	$2\nu_1 + 2\nu_{12}$	8216.9187
$\nu_1 + \nu_{20}$	4235.8339	$2\nu_1 + 2\nu_{20}$	8243.1405
$\nu_{12} + \nu_{20}$	4227.3040	$2\nu_{12} + 2\nu_{20}$	8205.9116
$\nu_4 + \nu_{15}$	4474.5809	$2\nu_4 + 2\nu_{15}$	8546.6215
$\nu_4 + \nu_{17}$	4463.3258	$2\nu_4 + 2\nu_{17}$	8618.0881
$\nu_{15} + \nu_{17}$	4482.2347	$2\nu_{15} + 2\nu_{17}$	8638.1614
$\nu_1 + 2\nu_{12}$	6218.3121	$2\nu_1 + \nu_{12}$	6247.0111
$\nu_1 + 2\nu_{20}$	6244.5339	$2\nu_1 + \nu_{20}$	6234.4405
$\nu_{12} + 2\nu_{20}$	6236.004	$2\nu_{12} + \nu_{20}$	6197.2116
$\nu_4 + 2\nu_{15}$	6511.1834	$2\nu_4 + \nu_{15}$	6510.019
$\nu_4 + 2\nu_{17}$	6582.65	$2\nu_4 + \nu_{17}$	6498.7639
$\nu_{15} + 2\nu_{17}$	6601.5589	$2\nu_{15} + \nu_{17}$	6518.8372

4. Conclusion

In the present work, we have developed the symmetry-adapted one-dimensional Lie algebraic framework, which is adapted for cyclobutane-d8 in its gas phase. The appropriate vibrational frequencies can be calculated with the root-mean-square deviation as small as 1.5566 cm⁻¹, if compared with the experimental data. Hence, our results demonstrate that the vibrational Hamiltonian reproduces successfully the fundamental vibrational frequencies and predicts the first-overtone and combination bands of cyclobutane-d8 at a much lower computational cost, if compared to the alternative techniques.

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References

1. Oss S, 1996. Algebraic models in molecular spectroscopy. *Adv. Chem. Phys.* **93**: 455–649.
2. Iachello F and Levine R D. Algebraic Theory of Molecules. Oxford: Oxford University Press, 1995.
3. Frank A, Lemus R, Bijker R, Péilez Bernal F and Arias J M, 1996. A general algebraic model for molecular vibrational spectroscopy. *Ann. Phys.* **252**: 211–238.
4. Choudhury J, Karumuri S R, Rupali Sinha, Sarkar N K and Bhattacharjee R, 2010. Vibrational spectra of H₂O and CF₄ molecules using Lie algebraic approach. *Indian J. Phys.* **84**: 659–664.
5. Srinivasa Rao K and Girija Sravani K, 2016. Calculation of vibrational spectra of some tetraphenyl porphyrins. *Mol. Phys.* **114**: 643–649.
6. Balla M R and Vijayasekhar J, 2021. Vibrational Hamiltonian of methylene chloride using U(2) Lie algebra. *Mol. Phys.* **115**: e1828634.
7. Balla M R, Venigalla S and Vijayasekhar J, 2021. Calculation of vibrational frequencies of sulfur dioxide by Lie algebraic framework. *Acta Phys. Polon. A.* **140**: 138–140.
8. Vijayasekhar J, 2022. Vibrational energies of silylene, difluorosilylene and dichlorosilylene, using U(2) Lie algebraic mode. *Ukr. J. Phys. Opt.* **23**: 126–132.
9. Lord R C and Nakagawa I, 1963. Normal vibrations, potential constants, and vibration–rotation interaction constants in cyclobutane and cyclobutane-d₈. *J. Chem. Phys.* **39**: 2951–2965.
10. Miller F A and Capwell R J, 1971. The ring-puckering vibration of cyclobutane and cyclobutane-d₈ in their gas phase Raman and infrared spectra. *Spectrochim. Acta A.* **27**: 947–956.
11. Miller F A, Capwell R J, Lord R C and Rea D G, 1972. Infrared and Raman spectra of cyclobutane and cyclobutane-d₈. *Spectrochim. Acta A.* **28**: 603–618.
12. Bijker R, Frank A, Lemus R, Arias J M and Pérez-Bernal F, 1998. A comparison between algebraic models of molecular spectroscopy. In: *Symmetries in Science X*, Ed. by Gruber B and Ramek M (Boston: Springer). pp. 37–46.
13. Balla M R and Vijayasekhar J, 2022. Vibrational Hamiltonian of naphthalene (C₁₀H₈) using dynamical U(2) Lie algebras. *Polycycl. Aromat. Compd.* **42**: 4684–4699.
14. Vijayasekhar J and Balla M R, 2022. Vibrational Hamiltonian of tetrachloro-, tetrafluoro-, and mono-silanes using U(2) Lie algebras. *Spectrochim. Acta A.* **264**: 120289.
15. Irikura K K, 2007. Experimental vibrational zero-point energies: diatomic molecules. *J. Phys. Chem. Ref. Data.* **36**: 389–397.
16. Shimanouchi T, 1972. Tables of Molecular Vibrational Frequencies Consolidated, National Bureau of Standards. Vol. I: pp. 1–60.

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Анотація. У цій статті ми використовуємо одновимірну U(2) алгебраїчну модель Лі для дослідження основних коливальних частот першого обертона та їх комбінованих смуг циклобутану-d₈ (C₄D₈), який має точкову групу симетрії D_{2d} із незвідними представленнями A₁, A₂, B₁, B₂ і E і складається з 23 нормальних коливальних мод. Проведено порівняння між розрахованими частотами коливань і доступними довідковими даними, і виявлено, що середньоквадратичне відхилення становить 1,5566 см⁻¹.

Ключові слова: коливальний гамільтоніан, осцилятор Морзе, U(2) алгебра Лі, циклобутан-d₈.