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

UDC: 535.333

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 the molecule [12, 13, 14]. Here we assign the C–D and C–C bonds respectively to the U(2) Lie algebras U(2) and U(2) to U(2) and U(2), as represented in Fig. 1. Note that cyclobutane-d8 belongs to the point group D2d with the symmetry species A1, A2, B1, B2, E. It is characterized by 23 normal vibrational modes.

![Fig. 1. Structure of cyclobutane-d8.](image)

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

\[
H^{C-D} = E_0^{C-D} + \sum_{i=1}^{m_{C-D}} A_i^{C-D} C_i + \sum_{i<j}^{m_{C-D}} A_{ij}^{C-D} C_i C_j + \sum_{i<j}^{m_{C-D}} \left( k^1_{ij} + k^2_{ij} + k^3_{ij} + k^4_{ij} \right) \lambda_{ij}^{C-D} M_{ij},
\]

(1)

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

\[
\begin{align*}
    k^1_{ij} &= \begin{cases} 
        1, & (i, j) = (1,2), (2,3), (3,4), (4,5), (5,6), (6,7), (7,8), (1,8) \\
        0, & \text{otherwise}
    \end{cases} \\
    k^2_{ij} &= \begin{cases} 
        1, & (i, j) = (1,3), (2,4), (3,5), (4,6), (5,7), (6,8), (1,7), (2,8) \\
        0, & \text{otherwise}
    \end{cases} \\
    k^3_{ij} &= \begin{cases} 
        1, & (i, j) = (1,4), (2,5), (3,6), (4,7), (5,8), (1,6), (2,7), (3,8) \\
        0, & \text{otherwise}
    \end{cases} \\
    k^4_{ij} &= \begin{cases} 
        1, & (i, j) = (1,5), (2,6), (3,7), (4,8) \\
        0, & \text{otherwise}
    \end{cases}
\]


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

$$H^{C-C} = E_0^{C-C} + \sum_{i=1}^{n_{d4}} A_i^{C-C} C_i + \sum_{i<j}^{n_{d4}} A_{ij}^{C-C} C_i C_j + \sum_{i<j}^{n_{d4}} \left( l_{ij}^1 + l_{ij}^2 \right) \lambda_{ij}^{C-C} M_{ij}.$$  (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 term, $E_0^{C-D}$ 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 $A_i^{C-D}, A_i^{C-C}, A_{ij}^{C-D}, A_{ij}^{C-C}$ and $\lambda_{ij}^{C-C}$ 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]:

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

$$\langle N_i, v_i; N_j, v_j \rangle = 4 \left( v_i + v_j \right) \left( v_i + v_j - N_i - N_j \right),$$  (4)

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

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

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

$$\langle C_i \rangle = -4 \left( N - 1 \right), \quad \langle C_{ij} \rangle = -4 \left( 2N - 1 \right), \quad \langle M_{ij} \rangle = \begin{cases} -N \left( i \neq j \right) \\ N \left( i = j \right) \end{cases}.$$  (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...
\[
N = \frac{\omega_e}{\omega_e X_e} - 1, \tag{7}
\]

where \(\omega_e\) is equal to 2101.05193 and 1855.06630 respectively for the C–D and C–C bonds, and \(\omega_e X_e\) 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:

\[
E^{C-D} = -4A_i^{C-D} \left(N^{C-D} - 1\right),
\]

\[
E^{C-C} = -4A_i^{C-C} \left(N^{C-C} - 1\right). \tag{8}
\]

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 \(\lambda_{ij}^{C-D}\) and \(\lambda_{ij}^{C-C}\) can be guessed using the relations

\[
\lambda_{ij}^{C-D} = \left|\frac{E_s^{C-D} - E_{as}^{C-D}}{6N^{C-D}}\right|, \quad \lambda_{ij}^{C-C} = \left|\frac{E_s^{C-C} - E_{as}^{C-C}}{2N^{C-C}}\right|. \tag{9}
\]

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 \(A_i^{C-D}\) and \(A_i^{C-C}\).

### 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.**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N^{C-D}, N^{C-C}) (stretching)</td>
<td>60, 136</td>
</tr>
<tr>
<td>(A_i^{C-D}, A_i^{C-C}) (stretching)</td>
<td>(-9.2076, -1.2807)</td>
</tr>
<tr>
<td>(A_i^{C-D}, A_i^{C-C}) (stretching)</td>
<td>(1.0112, 0.1542)</td>
</tr>
<tr>
<td>(\lambda_{ij}^{C-D}, \lambda_{ij}^{C-C}) (stretching)</td>
<td>(0.3277, 0.8848)</td>
</tr>
<tr>
<td>(N) (bending)</td>
<td>36</td>
</tr>
<tr>
<td>(A_i) (bending)</td>
<td>(-6.4142)</td>
</tr>
<tr>
<td>(A_{ij}) (bending)</td>
<td>(0.4952)</td>
</tr>
<tr>
<td>(\lambda_{ij}) (bending)</td>
<td>(1.3449)</td>
</tr>
</tbody>
</table>
### Table 2. Fundamental vibrational frequencies calculated for \( C_4D_8 \).

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Symmetry species</th>
<th>Experimental frequency, cm(^{-1} ) [16]</th>
<th>Calculated frequency, cm(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( v_1 ) (CD(_2) s-str)</td>
<td>A(_1)</td>
<td>2124</td>
<td>2124.4224</td>
</tr>
<tr>
<td>( v_2 ) (CD(_2) scis)</td>
<td>A(_1)</td>
<td>1160</td>
<td>1160.2816</td>
</tr>
<tr>
<td>( v_3 ) (CD(_2) scis)</td>
<td>A(_1)</td>
<td>882</td>
<td>882.6176</td>
</tr>
<tr>
<td>( v_4 ) (CD(_2) a-str)</td>
<td>A(_1)</td>
<td>2224</td>
<td>2223.7912</td>
</tr>
<tr>
<td>( v_5 ) (CD(_2) rock)</td>
<td>A(_1)</td>
<td>632</td>
<td>633.5910</td>
</tr>
<tr>
<td>( v_6 ) (ring puck)</td>
<td>A(_1)</td>
<td>158</td>
<td>156.2691</td>
</tr>
<tr>
<td>( v_7 ) (CD(_2) wag)</td>
<td>A(_2)</td>
<td>1010</td>
<td>1008.9803</td>
</tr>
<tr>
<td>( v_8 ) (CD(_2) twist)</td>
<td>A(_2)</td>
<td>889</td>
<td>891.2123</td>
</tr>
<tr>
<td>( v_9 ) (CD(_2) wag)</td>
<td>B(_1)</td>
<td>1078</td>
<td>1077.0012</td>
</tr>
<tr>
<td>( v_{10} ) (ring deform)</td>
<td>B(_1)</td>
<td>746</td>
<td>745.6011</td>
</tr>
<tr>
<td>( v_{11} ) (CD(_2) twist)</td>
<td>B(_1)</td>
<td>864</td>
<td>865.9003</td>
</tr>
<tr>
<td>( v_{12} ) (CD(_2) s-str)</td>
<td>B(_2)</td>
<td>2115</td>
<td>2115.8925</td>
</tr>
<tr>
<td>( v_{13} ) (CD(_2) scis)</td>
<td>B(_2)</td>
<td>1040</td>
<td>1038.4426</td>
</tr>
<tr>
<td>( v_{14} ) (ring deform)</td>
<td>B(_2)</td>
<td>938</td>
<td>939.6622</td>
</tr>
<tr>
<td>( v_{15} ) (CD(_2) a-str)</td>
<td>B(_2)</td>
<td>2242</td>
<td>2241.7001</td>
</tr>
<tr>
<td>( v_{16} ) (CD(_2) rock)</td>
<td>B(_2)</td>
<td>483</td>
<td>482.0208</td>
</tr>
<tr>
<td>( v_{17} ) (CD(_2) a-str)</td>
<td>E</td>
<td>2230</td>
<td>2231.4450</td>
</tr>
<tr>
<td>( v_{18} ) (CD(_2) twist)</td>
<td>E</td>
<td>938</td>
<td>939.9182</td>
</tr>
<tr>
<td>( v_{19} ) (CD(_2) rock)</td>
<td>E</td>
<td>556</td>
<td>553.5000</td>
</tr>
<tr>
<td>( v_{20} ) (CD(_2) s-str)</td>
<td>E</td>
<td>2103</td>
<td>2102.3219</td>
</tr>
<tr>
<td>( v_{21} ) (CD(_2) scis)</td>
<td>E</td>
<td>1078</td>
<td>1075.6621</td>
</tr>
<tr>
<td>( v_{22} ) (CD(_2) wag)</td>
<td>E</td>
<td>1048</td>
<td>1045.4372</td>
</tr>
<tr>
<td>( v_{23} ) (ring deform)</td>
<td>E</td>
<td>734</td>
<td>732.2029</td>
</tr>
</tbody>
</table>

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 \( C_4D_8 \).

<table>
<thead>
<tr>
<th>Vibrational mode</th>
<th>Symmetry species</th>
<th>Calculated frequency, cm(^{-1} )</th>
<th>Vibrational mode</th>
<th>Symmetry species</th>
<th>Calculated frequency, cm(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>( 2v_1 ) (CD(_2) s-str)</td>
<td>A(_1)</td>
<td>4123.0290</td>
<td>( 2v_{13} ) (CD(_2) scis)</td>
<td>B(_2)</td>
<td>1949.3104</td>
</tr>
<tr>
<td>( 2v_2 ) (CD(_2) scis)</td>
<td>A(_1)</td>
<td>2240.4700</td>
<td>( 2v_{14} ) (ring deform)</td>
<td>B(_2)</td>
<td>1812.1618</td>
</tr>
<tr>
<td>( 2v_3 ) (CD(_2) scis)</td>
<td>A(_1)</td>
<td>1683.1616</td>
<td>( 2v_{15} ) (CD(_2) a-str)</td>
<td>B(_2)</td>
<td>4279.3026</td>
</tr>
<tr>
<td>( 2v_4 ) (CD(_2) a-str)</td>
<td>A(_1)</td>
<td>4259.2293</td>
<td>( 2v_{16} ) (CD(_2) rock)</td>
<td>B(_2)</td>
<td>904.3229</td>
</tr>
</tbody>
</table>
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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Vibrational spectra

References


Анотація. У цій статті ми використовуємо одномірну U(2) алгебраїчну модель Лі для дослідження основних коливальних частот першого обертону та їх комбінованих смуг циклобутану-d8 (C4D8), який має точкову групу симетрії D2d із незвідними представленнями A1, A2, B1, B2 і E і складається з 23 нормальних коливальних мод. Проведено порівняння між розрахованими частотами коливань і доступними даними, і виявлено, що середньоквадратичне відхилення становить 1,5566 см⁻¹.

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