



# Intramolecular Vibrational Spectra of Benzene and Its Derivatives in CC, CH and CD Local Mode Interaction

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Lie algebraic method is based on the idea of dynamic symmetry, which can be expressed in terms of  $U(2)$  Lie algebra. By applying algebraic approach, an effective Hamiltonian operator can be obtained which conveniently describes the rovibrational degrees of freedom of benzene and its derivatives. Here, every CC, CH, CD bonds of the molecule are replaced by a corresponding  $U(2)$  Lie algebra and finally the local Hamiltonian is constructed considering the invariant Casimir and Majorana operators. The fundamental modes are then calculated using this Hamiltonian to fit the results of the theoretical as well as experimental observations.

**Keywords:** Lie Algebra, Hamiltonian, Casimir and Majorana Operators, Benzene.

## 1. INTRODUCTION

The structure and dynamics of highly excited vibrational states of polyatomic molecules is a subject of considerable current interest. One of the queries in the study of the vibrational spectra of polyatomic molecules is the determination of the normal modes of vibration. For an  $N$ -atom molecule the number of these modes is  $n = 3N - 6$  and under the Born-Oppenheimer approximation each one can be described in terms of the displacements of all the nuclei from their equilibrium positions in a given electronic state of the molecule. In case of highly symmetric benzene molecule, the overtone spectra of it and some of its isotopic derivatives have been at the starting point of the interesting discussions of intramolecular vibrational redistribution as visible in vibrational spectra. This present work aims to present an algebraic model of intramolecular vibrational spectra associated with local modes CC, CH and CD interactions in benzene and compare the calculated results with that of theoretical as well as experimental approaches.<sup>1–3</sup>

It is nearly 50 years since Ingold et al.<sup>4</sup> carried out the first comprehensive study of the vibrational spectrum of benzene. They measured the vapour and liquid infrared spectra of several deuterium labeled benzenes. Their correlation of bands between labeled molecules and careful comparison of vapor and liquid frequencies allowed a vibrational analysis, which in large part still stands today. Mair and Hornig<sup>5</sup> then made a major contribution to the early vibrational assignments by giving definite

and plausible frequencies for the infrared and Raman forbidden fundamentals.

Benzene has also been considered as a prototype molecule for harmonic force-field calculations,<sup>6–8</sup> local mode theory,<sup>9–11</sup> radiation less transitions, high resolution electronic spectroscopy,<sup>12–14</sup> and high resolution infrared and Raman spectroscopy.<sup>15, 16</sup> The force-field calculations are available for in-plane and out-of-plane modes of benzene and also for many substituted benzenes and its derivatives. Moreover, there have been the advanced *ab initio* studies of its harmonic and anharmonic potential functions.

The present work leads to the vibrational analysis of benzene and two of its derivatives using Lie algebraic approach which strongly relies on the traditional unitary group theory and hence examine the interactions that account for the standard Fermi couplings along with Casimir and Majorana couplings and their consequences for fundamental and overtone spectra and dynamics. Our work relies strictly on the normal mode analysis of benzene carried out by Pulay et al.<sup>17</sup> Our analysis follows the traditional approach of the vibrational mode descriptions of Wilson used in many papers on benzene spectra.<sup>18</sup> Isotopically labeling benzene causes the benzene ( $A_{1g}$ ) modes to lose their identity due to alteration of the kinetic energy term in the Hamiltonian. A quantitative description of these modes can be obtained by expressing the vibrational Hamiltonian of the heavy labeled benzenes in terms of the normal coordinates of benzene. This expression involves diagonal and off-diagonal terms by Casimir and Majorana operators which provide a quantitative description of the normal modes of benzenes molecules and its derivatives.

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