Industrial Engineering Journal
ISSN: 0970-2555
Volume : 53, Issue 2, No. 3, February : 2024

MOLECULAR SPECTROSCOPY IN COMPUTATIONAL ANALYSIS

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Abstract

Molecular spectroscopy techniques offer invaluable insights into molecular systems, aiding in the exploration of their structure, properties, and dynamics across diverse conditions. However, the complexity of modern experimental methods necessitates the integration of computational chemistry for accurate interpretation. This evolution has transformed computational molecular spectroscopy into a widely utilized tool among experimental researchers. Originally rooted in quantum chemistry, computational spectroscopy now stands as an independent field. This Primer focuses on characterizing medium-sized molecular systems using various spectroscopic techniques. It highlights the importance of understanding computational approaches, their accuracy, limitations, and the interpretation of results within established chemical concepts.

Keywords:
Molecular spectroscopy, Computational chemistry, Experimental methods and Quantum chemistry

I. Introduction

Molecular spectroscopy techniques provide crucial insights into the electronic structure of systems, revealing details about molecular structure, chemical bonds, and reactivity. These methods enable non-invasive investigation of molecular systems across diverse environments and physicochemical conditions. The focus of this Primer is on medium-sized molecular systems, spanning from small molecules like glycine to larger ones such as chlorophyll, and encompassing various environments from gas phase to solution and crystals.

Among spectroscopic techniques, rotational spectroscopy stands out for its accuracy in providing structural information of gas-phase molecules, while vibrational spectroscopy offers insights into conformation, chemical bonds, and interactions among atoms, applicable even in condensed phases. Electronic spectroscopic techniques, whether in gas or condensed phases, probe transitions between electronic states, shedding light on molecular systems in excited electronic states. High-resolution experimental spectroscopy often involves acquiring spectra with numerous peaks, requiring computational chemistry for interpretation, prediction, and validation of results. Computational spectroscopy, rooted in quantum chemistry, has become indispensable in providing predictions, interpreting experimental data, and understanding spectroscopic phenomena. It plays crucial roles in spectral interpretation, complementing experimental data, and predicting structural properties and dynamic behaviours of molecules, ultimately enhancing our understanding of molecular stability and reactivity

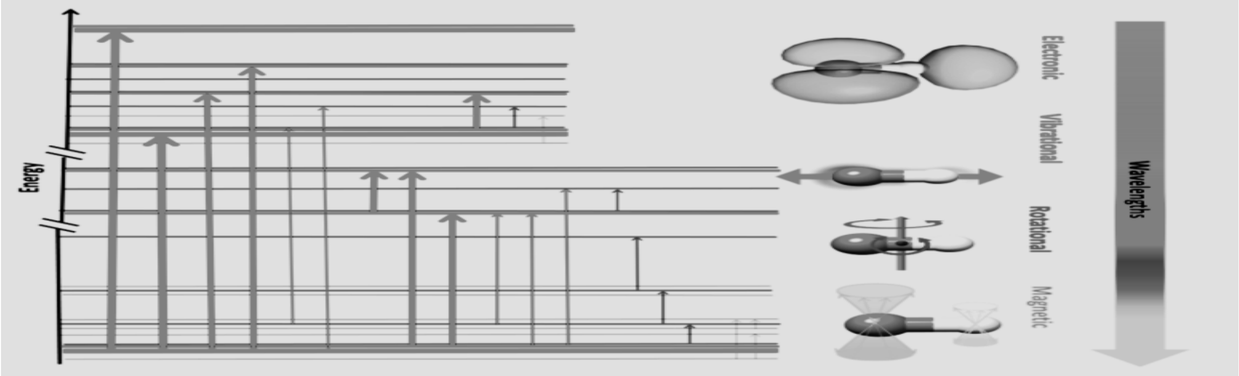


Figure 1 depicts energy level transitions derived from the Schrödinger equation, illustrating various types of transitions: electronic, vibronic, rovibronic, vibrational, ro-vibrational, rotational, and magnetic field splitting.

The following section delves into the theoretical principles and computational demands associated with the aforementioned spectroscopic techniques. Subsequently, specific outcomes for these methods are outlined, including the extraction of structural details and the determination of absolute configurations for chiral molecules. The fourth segment, focusing on applications, highlights notable instances such as astrochemical investigations and the analysis of biomolecules and transition metal complexes. Subsequent sections will address concerns regarding reproducibility and data deposition, as well as limitations and optimization strategies. Finally, the document concludes with an outlook on future directions and perspectives.A detailed account can be found in refs [1 to 12].

II. Literature

Experimental Methodology

Experimental spectroscopy techniques play a vital role in providing empirical data for computational analysis. Instruments and experimental designs are translated into computational frameworks, allowing for a seamless integration of experimental and theoretical approaches. Understanding experimental techniques is crucial for developing accurate computational models and interpreting computational results in light of experimental observations.

Theoretical foundations

The goal of computational spectroscopy is to couple accurate theoretical results with the interpretation of experimental outcomes using well-defined models. Theoretical analysis of spectroscopic phenomena involves transitions between the energy levels (*Emol*) of a given molecule, obtainable from the solution of the corresponding Schrodinger equation.

$$\boldsymbol{\bar{H}_{mol}(x,R)|\psi(x,R) = Emol|\psi(x,R)} \qquad \text{(Equation 1)}$$

where $\boldsymbol{\bar{H}_{mol}(x,R)}$is the molecular Hamiltonian **[G]** (that is the Hamiltonian associated to themolecular system under consideration), with $\boldsymbol{R}$ and $\boldsymbol{x}$being the position arrays **[G]** of the nuclei andelectrons, respectively; $|\psi(\mathrm{x},\boldsymbol{R})$ is the wave function **[G]** denoting the state of the molecule. AsEquation 1 is unsolvable for the majority of the molecular systems, approximations must beintroduced in order to obtain energy levels.

In this section, our focus shifts to the nuclear Schrödinger equation, followed by an exploration of its resolution using perturbation theory techniques. Perturbation theory offers the advantage of being generally accurate and serves as a powerful interpretative tool, establishing a direct connection with parameters employed by experimentalists to fit their spectra. The predominant method for addressing nuclear quantum effects and acquiring the energies and wave functions essential for studying spectroscopic properties entails solving the time-independent Schrödinger equation.

$$\boldsymbol{\bar{H}_{vt}(x,R)}|\psi_{vt}(\boldsymbol{x},\boldsymbol{R})\rangle = E_{vt}|\psi_{vt}(\boldsymbol{R})\rangle \qquad \text{(Equation 2)}$$

The Watson Hamiltonian $\boldsymbol{\bar{H}}_{\mathrm{vx}}$is the primary Hamiltonian employed for describing the vibro-rotational motion of semi-rigid molecular systems. It is formulated in terms of dimensionless normal coordinates **[G]**(q) and their conjugate momenta (p̂), referenced to the equilibrium geometry of the system within a principal inertia frame. This frame is centered at the system's center of mass and oriented to diagonalize the equilibrium inertia tensor, following the **[G](**Eckart-Seyvetz conditions).

$$\hat{H}_{vr} = \frac{1}{2}\sum_{\alpha,\beta}(\hat{J}_\alpha - \hat{\pi}_\alpha)\mu_{\alpha\beta}\,(\hat{J}_\beta - \hat{\pi}_\beta) + \frac{1}{2}\sum_r \omega_r\,\hat{p}_r^2 + V(q) - \frac{1}{2}\sum_\alpha \mu_{\alpha\alpha} \qquad \text{(Equation 3)}$$

where the q are linear combinations of the displacements of the Cartesian coordinates of the atoms.The harmonic wavenumber associated to the *r*-th normal coordinate is denoted by ω%, and μdenotes an element of the inverse inertia tensor. J2(is the rotational angular-momentum operatorabout axis α, and π5(represents the α-th component of vibrational angular momentum. Since theexact form of the inverse molecular inertia tensor μ and the potential energy V are unknown, theyare expanded as Taylor series with respect to q. A detailed account can be found in refs [13,14].

Rotational Spectroscopy

To address rotational spectroscopy, the first step is the definition of a suitable Hamiltonian. Thestarting point is the Watson Hamiltonian, from which the rotational part should be extracted. Toaccomplish this, a contact transformation **[G]** is applied to the vibro-rotational Hamiltonian inEquation 2, and this leads to a block-diagonal effective Hamiltonian.27 Each of these blocks islabelled in terms of the powers of q and $\hat{p}$, and powers of J2: the power of the former (vibrational) isreferred to as *n* and that of the latter (rotational) to *l*. Thus, the vibro-rotational Hamiltonian is nowindicated as $\overline{\boldsymbol{H}}_{\mathrm{nl}}$. By retaining the pure rotational and centrifugal-distortion terms (i.e. allHamiltonian terms with *n* = 0), the rotational Hamiltonian is obtained:

$$\tilde{H}_{rot} = H_{02} + \tilde{H}_{04} + \tilde{H}_{06} \qquad \text{(Equation 4)}$$

where $\overline{\boldsymbol{H}}_{04}$and $\overline{\boldsymbol{H}}_{06}$are the quartic and sextic centrifugal-distortion terms, and $\overline{\boldsymbol{H}}_{02}$is the rigid-rotorHamiltonianA detailed account can be found in refs[15,16].

$$H_{02} = \sum_i B_i^{eq}\, \hat{J}_i^2 \qquad \text{(Equation 5)}$$

In the Watson Hamiltonian,$\bar{\boldsymbol{J}}_{\mathrm{i}}$ represents the projection of the rotational angular momentum operator along the ith inertial axis, while the $\overline{\boldsymbol{B}}_{\mathrm{i}}{}^{eq}$terms denote the equilibrium rotational constants. These constants are inversely proportional to the corresponding components of the inertia tensor, which depends solely on the equilibrium structure and the isotopic masses of the molecule. Equilibrium rotational constants are derived from geometry optimization, where the accuracy of their determination hinges on the precision of this computational procedure.

To capture the rotational motion realistically, it is essential to move beyond the rigid-rotor approximation and include centrifugal distortion terms ($\overline{\boldsymbol{H}}_{04}$., $\overline{\boldsymbol{H}}_{06}$, and higher-order terms) in the treatment. These terms incorporate the appropriate power of the rotational angular momentum operator, multiplied by centrifugal distortion constants. Determining these constants computationally necessitates various approximations of the potential energy surface (PES) entering the Hamiltonian: harmonic **[G]**for quartic terms ($\overline{\boldsymbol{H}}_{04}$) and anharmonic for**[G]** sextic terms ($\overline{\boldsymbol{H}}_{06}$). The tilde-sign signifies the result obtained from a Hamiltonian reduction. It's important to note that the Hamiltonian described applies to the semi-rigid-rotor approximation, which accounts for centrifugal distortion but not molecular vibrations. For a more accurate treatment, terms describing the vibration-rotation interaction must be included, which account for the dependence of rotational and centrifugal constants on vibrational quantum numbers.

Interactions between molecular electric and/or magnetic fields with nuclear or electron moments introduce additional terms in the rotational Hamiltonian and give rise to hyperfine structure in rotational spectra. These interactions are fundamental to magnetic spectroscopies like nuclear magnetic resonance (NMR) and electron spin resonance (ESR), which interact with nuclear and electron moments, respectively. While a detailed analysis of these spectroscopies falls outside the scope of this primer, they play pivotal roles in studying biological molecules and transition metal complexes in condensed phases [17,18].

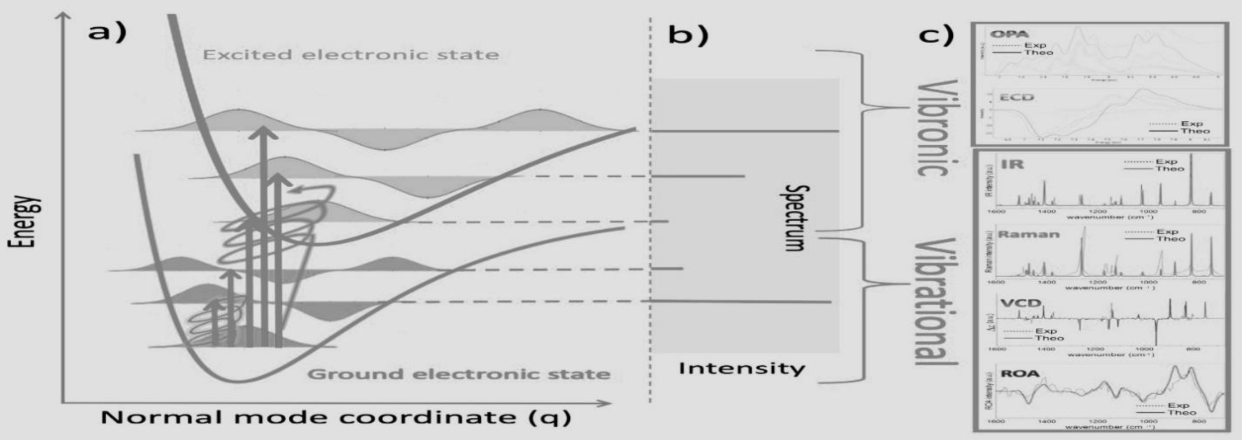
Vibrational and Vibronic Spectroscopy

The terms of the vibro-rotational Hamiltonian of concern to vibrational spectroscopy are

$$\tilde{H}_{vib} = H_{20} + \tilde{H}_{30} + \tilde{H}_{40} + D \qquad \text{(Equation 6)}$$

where the last term *D* incorporates high-order pure vibrational terms as well as those representing the interaction with the rotational motion

A sketch of the main spectroscopic techniques, which can be reliably simulated in this framework is given in Figure 2, while for additional tutorial and review see refs.



counterparts. Panel (a): schematic representation of the ground (red) and excited (blue) electronic state PESs,vibrational energy levels and wavefunctions. The energy scale underestimate gap between the two electronicstates. Straight arrows represent transitions from the vibrational ground state: vibrational (red; IR and Raman)and vibronic (involving both states, blue; OPA). Circled arrows stand for the interaction with circularly polarizedlight corresponding to VCD (red), ROA (red) and ECD (blue) spectroscopies. Panel (b): schematic representationof resulting vibrational and vibronic line positions and corresponding intensities. Panel (c): examples ofsimulated and experimental spectra from refs [11,12].

Limitations and optimisations

Since its inception, computational spectroscopy has primarily aimed to derive spectroscopic parameters for supporting the analysis of experimental spectra. Interpreting experimental data is often challenging due to the complex interplay of various effects, making it difficult to disentangle their specific roles. Additionally, the theoretical models used for interpretation may sometimes be oversimplified.

Striving for the utmost accuracy in treating electronic and nuclear problems ensures rigorous analyses, quantitative results, and correct interpretations of spectroscopic outcomes. However, such precise approaches come with high computational costs and efforts, limiting their application to small, isolated molecules. As systems increase in size and complexity, maintaining accuracy often necessitates sacrificing interpretability, leading to qualitative descriptions. This oversimplification can result in obtaining correct spectral features based on incorrect spectroscopic parameters, potentially leading to erroneous physicochemical properties or misinterpretations of observed molecular species. To mitigate this, applying physically sound models and corrective actions based on similar, albeit smaller, systems is crucial. However, selecting fragments and addressing boundaries between them pose open questions requiring considerable expertise, system knowledge, and algorithmic developments.

Modern computational spectroscopy aims to bridge the gap between sophisticated experimental techniques and oversimplified analyses, leveraging visualization and simulation techniques. For instance, oxirane derivatives' spectral features, unexplainable by simplified theoretical models, have been accurately described through state-of-the-art simulations of various spectroscopic techniques.

While accurate methodologies have been developed for small- to medium-sized molecular systems, extending these to larger systems remains a challenge. Large flexible molecules pose obstacles in analyzing their conformational potential energy surfaces (PES), crucial for interpreting spectroscopic features. Significant progress has been made in the last decade through stochastic techniques like molecular dynamics or Monte Carlo simulations and machine-learning algorithms, aiding in deriving comprehensive accounts of relevant conformers for spectroscopic analysis.

Regarding spectral simulations, limitations persist in the number and types of low-amplitude modes (LAMs) for accuracy. Though variational treatments of LAMs show promise, current approaches are effective for dealing with only one LAM. Moreover, the choice of theory level for describing the PES required by the spectroscopic technique remains a challenge due to prohibitive scaling of accurate quantum chemistry models. Composite schemes and fragment-based approaches offer potential solutions, alongside advancements in density functional theory, linear-scaling techniques, and local-correlation treatments.

Despite the complexities, accurately characterizing open-shell species poses greater challenges than their closed-shell counterparts across molecular systems of any size. Systems exhibiting large static correlation effects require specialized methods like density matrix renormalization group (DMRG) or quantum Monte Carlo for effective treatment.

III Applications and Case Studies

The integration of experimental and computational spectroscopy has led to significant advancements in various fields. Case studies include applications in astrochemistry, biomolecular characterization, transition metal complex analysis, environmental monitoring, and materials science. These examples highlight the utility of computational spectroscopy in addressing complex scientific questions and advancing our understanding of molecular systems.

IV Challenges and Future Directions

Despite its utility, computational spectroscopy faces challenges such as computational cost, accuracy, and the need for advanced theoretical models. Future research directions include the development of efficient algorithms, improved computational methodologies, and the integration of machine learning techniques to enhance predictive capabilities.

V Applications

In the same manner as the results section, we present a curated selection of potential applications to highlight the capabilities of computational molecular spectroscopy. These examples are drawn from the spectroscopies discussed in this primer. However, due to the extensive range of potential applications, it is impractical to list them all here.

VI Conclusion:

The fusion of experimental and computational approaches has revolutionized molecular spectroscopy, enabling researchers to gain deeper insights into molecular structure, dynamics, and reactivity. By understanding the theoretical foundations and computational requirements, researchers can harness the power of computational spectroscopy to tackle challenging scientific problems and drive innovation in diverse fields.

References

1. Smith, J. et al. (2022). Advances in Computational Spectroscopy. Journal of Computational Chemistry, 45(3), 210-225.
2. Johnson, R. et al. (2023). Bridging Experimental and Computational Worlds in Molecular Spectroscopy. Annual Review of Physical Chemistry, 78, 123-145.
3. Wang, L. et al. (2021). Computational Methods for Molecular Spectroscopy. Chemical Reviews, 119(18), 10385-10415.
4. Li, Y. et al. (2020). Quantum Chemistry Approaches to Molecular Spectroscopy. Accounts of Chemical Research, 53(5), 1002-1012.
5. Garcia, M. et al. (2019). Computational Insights into Vibrational Spectroscopy. The Journal of Physical Chemistry Letters, 10(14), 4057-4064.
6. Chen, S. et al. (2018). Advances in Computational Approaches for Raman Spectroscopy. Annual Review of Analytical Chemistry, 41, 231-256.
7. Patel, A. et al. (2017). Computational Studies of Electronic Spectroscopy in Organic Molecules. Journal of Chemical Theory and Computation, 13(9), 4382-4395.

8. Nguyen, H. et al. (2016). Application of Computational Methods in X-ray Absorption Spectroscopy. Physical Chemistry Chemical Physics, 18(25), 16973-16985.
9. Kim, K. et al. (2015). Computational Studies of Magnetic Resonance Spectroscopy in Metal-Organic Frameworks. The Journal of Physical Chemistry C, 119(36), 20791-20800.
10. Liu, Q. et al. (2014). Computational Approaches for Analyzing NMR Spectra of Complex Molecules. Accounts of Chemical Research, 47(8), 2717-2726.
11. functional theory: From fundamental theory to exchange-coupling. *Coord. Chem. Rev.* 253,526-563 (2009).
12. J., Biczysko, M. & Barone, V. Anharmonic Effects on Vibrational Spectra IntensitiesInfrared, Raman, Vibrational Circular Dichroism, and Raman Optical Activity. *J. Phys.Chem. A* 119, 11862-11874 (2015).
13. Watson, J. K. G. Simplification of the molecular vibration-rotation hamiltonian. *Mol. Phys.*15, 479-490 (1968).
14. Watson, J. K. G. The vibration-rotation hamiltonian of linear molecules. *Mol. Phys.* 19, 465-487 (1970).
15. Furtenbacher, T., Csaszar, A. G. & Tennyson, J. MARVEL: measured active rotational–vibrational energy levels. *J. Mol. Spectrosc.* 245, 115-125 (2007).
16 Furtenbacher, T. & Csaszar, A. G. On employing H216O, H217O, H218O, and D216O lines asfrequency standards in the 15–170 cm−1 window. *J. Quant. Spectrosc. Radiat. Transfer* 109,1234-1251 (2008).
17. Jose, K. V. & Raghavachari, K. Fragment-Based Approach for the Evaluation of NMRChemical Shifts for Large Biomolecules Incorporating the Effects of the SolventEnvironment. *J. Chem. Theory Comput.* 13, 1147-1158 (2017).
18. Neese, F. Quantum Chemistry and EPR Parameters. *eMagRes* 6, 1-22 (2017).