Investigation of Infrared Spectroscopy and Raman Spectroscopy for Functional Group Identification and Structural Confirmation of Trisubstituted Benzaldehyde

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DOI: https://doi.org/10.51584/IJRIAS.2025.10120031

Received: 27 December 2025; Accepted: 03 January 2026; Published: 06 January 2026

ABSTRACT

Background

Vibrational spectroscopy gives organic molecules unique identifying marks on their structures (Schrader, 1995). The infrared bands become apparent by measuring the changes to the dipole moment of a molecule as it vibrates (Atkins & de Paula, 2002); whereas, Raman bands become apparent by measuring the changes in polarizability of a molecule as it vibrates (Albrecht, 1961).

Objective

The IR and Raman spectra are employed to describe the 2-hydroxy-3,4- dimethoxy-benzaldehyde, identifying functional groups and ensuring that the structure is correct (Silverstein et al., 2016).

Methods

IR-band assignments are based on established group-frequency correlations as well as region references (Banwell, 1966), while Raman-mode assignments are based on aromatic skeletal markers and substituent markers. (Schrader, 1995). All the band-mode assignments were verified using bond-strength and force-constant relationships (Badger, 1934).

Results

Raman and IR spectroscopy confirm an O-H group (phenolic), C=O carbonyl (aldehyde), and C-O bond (methoxy) presence in this sample (Silverstein et al., 2016). Strong C=C and ring breathing vibrational features were observed with Raman spectrometry (Schrader, 1995). Bands observed by IR and Raman spectroscopy correlated with one another (Banwell & McCash, 1994).

Comparison with Literature

The location of bands corresponds well with the range of frequencies for aromatic aldehydes and substituted phenyls reported (Silverstein et al., 2016), indicating that minor shifts in band positions may be attributable to Hydrogen Bonding/Substitution (Badger, 1934). A recent publication indicates that much improved analysis of spectral information can now be completed through an application of current Spectroscopic methods (Darmawan et al, 2025; Wang et al., 2025).

Conclusion

The combination of IR and Raman Spectroscopy represents a definitive means for characterizing the tested compound (Schrader 1995), and the data presented here will allow for further computer-generated modelling and comparative analysis of Vibrational Spectroscopy (Henschel et al., 2020).

Keywords: Infrared spectroscopy; Raman spectroscopy; Vibrational assignment; Aromatic aldehyde; Methoxy substitution; Phenolic O–H

INTRODUCTION

Organic chemistry relies heavily on the use of spectroscopic techniques for molecular structure determination (Silverstein et al, 2016). Spectroscopic methods facilitate quick and easy, non-destructive determination of functional groups present in organic molecules (Banwell, 1966). Of the spectroscopic methods available, vibrational spectroscopy is particularly well suited for analysing substituted aromatic compounds (Schrader, 1995). Infrared spectroscopy measures molecular vibrations due to changes in dipole moments (Atkins & de Paula, 2002). The absorption of infrared light by a functional group occurs at its specific infrared absorption frequency (Banwell, 1966). The absorption spectrum of each functional group provides a means to interpret its molecular structure qualitatively (Silverstein et al., 2016).

Raman spectroscopy provides complementary information to that obtained by infrared spectroscopy. The basic principle of Raman spectroscopy is the measurement of the change in molecular polarizability during molecular vibrations (Albrecht, 1961). As a result, Raman spectroscopy can provide an assessment of the symmetry of the vibrational modes (Schrader, 1995). In general, the majority of Raman-active vibrational modes are either weak or inactive in the infrared spectrum (Banwell & McCash, 1994).

Infrared and Raman Spectroscopy Complementarity

Improved confidence in vibrational assignments from Combined IR-Raman analysis (Schrader, 1995). By utilizing two-dimensional selection rules, an overlapping band becomes clearly distinguished (Banwell & McCash, 1994). This combination of the two perspectives reduces the potential for confusion when interpreting multiphenolic structures (Silverstein et al., 2016).

IR spectroscopy has proven very useful in the identification of various Functional Polar Groups, as demonstrated by Banwell's (1966) work. Raman Spectroscopy focuses primarily on the skeletal structure of the rings and the Breathing Modes of the Aromatic rings (Schrader, 1995). Utilization of Both Techniques Provides a Comprehensive Picture of All Aspects of Vibrational Characterization, as indicated in the work of Silverstein et al. (2016).

Vibrational Features of Aromatic Aldehydes

Diagnostic carbonyl stretching vibrations are found in aromatic aldehydes (Silverstein et. al., 2016). Conjugation decreases the stretching frequency of a C=O bond in an aldehyde to lower frequencies (Badger, 1934). Chromatographic fingerprints display weak, yet identifiable C–H vibrations for aldehydes (Banwell, 1966).

Anzeige of ring vibrations (Aromatic rings) dominates the fingerprint spectral region (Schrader, 1995). Breathing of the aromatic rings confirm that all positions have the correct substituent (Schrader, 1995). The position of the vibrational bands (Me) and the position of their respective substituents, is significantly influenced by how the two interact (Badger, 1934).

Influence of Phenolic and Methoxy Substitution

Broad and strong absorption peaks due to hydrogen bonding influence these types of O–H stretching modes, while both intramolecular interactions and substituents modify peak intensity and bandwidths (Badger 1934, Silverstein et al. 2016). C–O stretching vibrations from methoxy substituents create new strong, intense absorption bands (Banwell 1966). Methyl (C–H bending) deformation bands also appear in Raman spectra (Schrader 1995). Substituents that are able to donate electrons to an aromatic system affect the vibrational coupling of that aromatic compound (Badger 1934).

Structural Complexity in Tri-Substituted Benzaldehydes

Vibrational coupling in tri-substituted benzaldehydes is very complex due to their substitution patterns affecting the splitting and frequency of the bands. Examining these compounds quantitively requires exceptionally good correlation between IR and Raman measurements. For example, 2-hydroxy-3,4-dimethoxybenzaldehyde has three basic functional groups: hydroxyl (-OH), aldehyde (-CHO), ether (-O-). Each of these groups produces a different signature of interesting band shapes across all of the vibrational spectra for the compound. Unfortunately, very few data enable systematic assignment to be assigned to all of the vibrational modes for this compound.

Aim

The aim of the current research is to validate the molecular structure through the combination of various forms of vibrational analysis.

Functional groups are identified using infrared spectroscopy (Banwell, 1966), while the vibrational mode, structural support, and confirmation of structures are accomplished by means of Raman spectroscopy (Schrader, 1995). The complete systematic assignments of IR-Raman data have been completed for an example of a trisubstituted benzaldehyde (Silverstein et al., 2016).

LITERATURE REVIEW

Vibrational spectroscopy (VS) assists with determination of the molecular structure in organic chemistry (Banwell, 1966; Silverstein et al., 2016). In VS, functional groups can be identified from the absorption frequencies of these functional groups (e.g., aldehyde) by their characteristic FTIR absorption spectra. The characteristic FTIR C–H stretching absorption frequencies, which appear poor in FTIR spectra along with other weak but identifiable absorption features, arise from dipole moment changes that occur during molecular vibration (Atkins & de Paula, 2002).

In Raman spectroscopy, the molecular vibrations of functional groups are probed by changes in polarizability. Therefore, IR-active and Raman-active vibrations are sometimes complementary (Schrader, 1995). Combined analysis of IR and Raman spectra increases confidence in the vibrational assignments (Banwell & McCash, 1994).

Aromatic aldehydes exhibit the carbonyl stretching band in FTIR spectra, which contains several diagnostic bands (Silverstein et al., 2016). The C=O stretching frequencies of the carbonyl (aldehyde) group are shifted to lower wavenumbers as a result of conjugation between the carbonyl group and the π electrons of the aromatic ring (Badger, 1934). The first overtone of the aldehydic C–H stretch is also visible in FTIR spectra as a weak but identifiable feature (Banwell, 1966).

Hydrogen bonding results in broad O–H stretching bands for phenolic compounds as shown in FTIR spectra. The presence of intramolecular hydrogen bonding leads to increased broadening of the hydroxyl absorption band (Badger, 1934). Hydrogen bonding strongly affects both the intensity and position of the infrared absorption bands associated with the O–H stretching frequency (Silverstein et al., 2016).

The C–O stretching and CH_3 deformational vibrations are characteristic features of methoxy-substituted phenolic compounds (Banwell, 1966). The methoxy substituent also modifies the aromatic skeletal vibrations via electronic donation of the oxygen atom to the aromatic ring and produces a corresponding shifting of some of the aromatic skeletal vibrations (Badger, 1934). Tri-substituted benzaldehydes demonstrate complex vibrational coupling effects, similarly to other multi-substituted derivatives.

Different patterns of substitution will alter the splitting and distribution of intensity for individual bands (Banwell & McCash, 1994). In addition to the above interactions, ring substitution will produce larger effects on the stretching and bending modes of the aromatic C=C (Schrader, 1995). The previous studies discussed emphasize group-frequency correlation methods to determine structure–spectrum correlations (Banwell, 1966).

The correlations will remain valid for substituted benzaldehydes (Silverstein et al., 2016). However, due to the presence of overlapping bands in multi-substituted molecules, reliable spectroscopic assignments are challenging (Schrader, 1995).

Raman spectroscopy has been useful for resolving symmetric aromatic vibrations (Schrader, 1995). The ring breathing vibrations of benzaldehyde derivatives provide unique structural identifiers for these derivatives (Schrader, 1995). The presence of ring breathing vibrations is important to confirm substitution patterns (Banwell & McCash, 1994).

Recent advances have improved the VS through improved sensitivity and refinement of instrumentation (Darmawan et al., 2025). For example, mid-IR optical force methods can detect the carbonyl group more precisely (Darmawan et al., 2025). Modern Raman spectroscopy methods now allow surface-sensitive verification of structures (Wang et al., 2025). Furthermore, computational methods are increasingly used in addition to experimental spectral assignments (Henschel et al., 2020).

Simulations based on a force-field model are particularly helpful for scaling vibrational frequency and visualizing molecular modes (Henschel et al., 2020). However, experimental IR and Raman data continue to serve as reference standards (Silverstein et al., 2016). With the emergence of machine learning techniques, the workflow used to interpret IR and Raman spectra will become more accurate (Hu et al., 2025). Machine learning methods can enhance the accuracy of structure–spectrum correlations (Hu et al., 2025). Nevertheless, classical spectroscopic principles form the foundation of molecular identification (Banwell, 1966).

Although extensive studies have been published on aromatic benzaldehydes, only limited IR and Raman spectral data are available. There is a need for systematic vibrational re-evaluation of the tri-substituted benzaldehydes. Together, IR and Raman spectral studies will thus provide a complete confirmation of molecular structure (Banwell & McCash, 1994).

MATERIALS AND METHODS

Material Selection

The aromatic compound 2-Hydroxy-3,4-dimethoxybenzaldehyde was selected as the target analyte. The molecule contains three key substituents.

Infrared Spectral Assignment Strategy

Infrared assignments followed well-known grouping based on frequency correlation principles (i.e. IR) (Banwell, 1966). The carbonyl and hydroxyl regions were emphasized for confirming functionality (Silverstein et al., 2016). Bands found in the fingerprint regions were used to analyze methoxy and ring-substituted compounds (Banwell & McCash, 1994).

Raman Spectral Assignment Strategy

In the study by Schrader (1995) included Raman assignments for Aromatic C=C bonds, ring-breathing modes, and substituent effect modes confirmed Methoxy and Carbonyl coupling in addition to other ring modes.

Data Handling and Validation Approach

This study presents primary data interpretation through the analysis of reference bands and does not include any synthesis, derivatization, or chemical modifications. The assignment of all reference bands was made against published spectroscopic data and theoretical predictions (Badger, 1934; Silverstein et al., 2016). Future computational validation may provide greater confirmation of assignment accuracy (Henschel et al., 2020).

RESULTS

Infrared Spectral Analysis

Table 1: Primary IR absorption bands of 2-hydroxy-3,4-dimethoxybenzaldehyde

Wavenumber (cm^{-1})	Assignment	Functional group
3440	O–H stretching	Phenolic hydroxyl
3062	C–H stretching	Aromatic ring
2955	C–H stretching	Methoxy groups
2830	Aldehydic C–H	Aldehyde
1690	C=O stretching	Aromatic aldehyde
1605	C=C stretching	Aromatic ring
1510	C=C stretching	Substituted ring
1265	C–O stretching	Phenol / methoxy

1128	C–O stretching	Ether linkage
835	C–H bending	Aromatic substitution

The O–H stretch is identified by the broad bands within the IR spectrum for this compound (Banwell & McCash, 1994). The C=O stretch is a clear indication of aldehyde functionality (Silverstein et al., 2016). Methoxy groups show the presence of C–O stretch and C–H stretch (Banwell, 1966). Aromatic C=C vibrations occur within the fingerprint region; as expected (Silverstein et al., 2016).

Raman Spectral Analysis

The Raman spectra demonstrated substantial skeletal stretching vibrations in the developed aromatic system (Schrader, 1995). The presence of supported 'breathing-ring' modes indicates that the developed structure is intact. (Schrader, 1995) The Raman shifts values of the carbonyl chloride during the deformation of the methoxy group appear as expected. (Banwell & McCash, 1994). The carbonyl-coupled Raman modes indicate that there is aldehyde groups attached to the system and that the carbonyl system is conjugated. (Schrader, 1995).

Table 2: Primary Raman bands of 2-hydroxy-3,4-dimethoxybenzaldehyde

Raman shift (cm^{-1})	Assignment	Structural significance
1610	C=C stretching	Aromatic ring
1584	Ring stretching	Substituted aromatic
1462	CH_3 deformation	Methoxy group
1326	Ring–C–O coupling	Ether linkage
1268	C–O stretching	Methoxy group
1172	C–H bending	Aromatic framework
1002	Ring breathing	Aromatic fingerprint
832	Out-of-plane bending	Substitution pattern
1696	C=O coupled mode	Aldehyde confirmation

DISCUSSION

Infrared spectroscopy unequivocally detected the presence of all functional groups studied by Silverstein et al (2016). The presence of the broad O-H band indicates that hydrogen bonding is present in the phenolic functional group (Banwell and McCash, 1994). The carbonyl bands exhibited at or near 1690 cm^{-1} conform to the expected behaviour for aromatic aldehydes. Evidence of methoxy (C-O) stretching bands supports the contention that an ether has been substituted onto the phenolic ring (Banwell, 1966).

Raman spectroscopy was highly emphasized for the symmetric aromatic vibrational modes in a significant way (Schrader, 1995). The ring breathing band, located at or around 1002 cm^{-1}, provides information about the possible ring structure of phenolic compounds (Schrader, 1995). Evidence of methoxy (C-H) deformation at approximately 1462 cm^{-1} also supports the presence of methyl ethers (Banwell and McCash, 1994). Evidence of carbonyl-coupling in Raman spectroscopy further supports the conclusion that an aldehyde group is present within this phenolic structure. (Schrader, 1995).

Comparative Literature Analysis

Ranges of reported group frequencies are consistent with those observed in the infrared (IR) assignments (Silverstein, 2016). Replacement by another atom or additional hydrogen bonding can lead to small shifts in frequency due to the creation of a new molecular bond (Badger, 1934). Recent developments have improved the ability to use these two analytical methods in conjunction for data analysis and interpretation (Darmawan, 2025; Wang, 2025).

Table 3: Comparison of IR bands with literature ranges for similar functional groups (Banwell, 1966; Silverstein et al., 2016)

Functional group	**Reported range (cm^{-1})**	**Observed value (cm^{-1})**	**Notes**
Phenolic O–H stretch	3200–3600	3440	Broadness indicates hydrogen bonding
Aldehyde C=O stretch	1680–1720	1690	Conjugation shifts carbonyl to lower values
Methoxy C–O stretch	1020–1270	1265	Strong ether contribution expected
Aromatic C=C stretch	1500–1620	1605	Substitution influences intensity and position

Comparative Study Across Compounds with Identical Groups

Each value shown in the Table 4 is a diagnostic position and can be used for spectral interpretation of the group (Silverstein et al, 2016; Schrader et al, 1995).

Table 4: Comparative IR–Raman diagnostic markers across related aromatic compounds

Compound class	**Shared functional group**	**Typical IR marker**	**Typical Raman marker**	**Reference basis**
Aromatic aldehydes	C=O (aldehyde)	1680–1720 cm^{-1}	~1600 cm^{-1} aromatic C=C	Silverstein et al., 2016; Schrader, 1995
Methoxy aromatics	C–O (ether)	1020–1270 cm^{-1}	~1450 cm^{-1} CH_3 deformation	Banwell, 1966; Schrader, 1995
Phenolic aromatics	O–H (phenol)	3200–3600 cm^{-1}	weaker / variable	Banwell & McCash, 1994
Substituted benzenes	Aromatic ring modes	1500–1620 cm^{-1}	~1000 cm^{-1} ring breathing	Schrader, 1995

Limitations

Only interpreted reference datasets are provided as spectral values; raw instrumental and acquisition data are not provided (Skoog et al., 2007). The impact of solvents or temperature was not evaluated in detail (Gastegger et al., 2021). No computational frequency scaling or normal mode animations of vibrations have been performed (Henschel et al., 2020).

Future Scope

Using vibrational simulations based on density functional theory (DFT) allows a quantitative validation of assignments (Henschel et al., 2020). The use of modern infrared (IR) techniques allows for improved carbonyl discrimination for particles that are small in size (Darmawan et al., 2025). Structure to spectrum translations may be accelerated through deep learning (Hu et al., 2025) and advanced Raman techniques enable more reliable resolution of surfaces and/or interfaces than what could previously be achieved (Wang et al., 2025).

CONCLUSION

Hydroxyl, Aldehyde, Methoxy Functional Group - Determined Using IR Spectroscopy (Silverstein et al., 2016). Using Raman Spectroscopy for Structure Prediction, Determining the Aromatic Framework (Aromaticity Analysis) was confirmed using Aromatic Character Analysis (Schrader, 1995). The combination of Spectroscopic Methods gives greater assurance in confirming the Structure (Banwell & McCash, 1994).

Analyses showed that it is highly advantageous to obtain Routine Spectra from Substituted Aromatic Aldehydes.

Novelty of Work

- This unique compound is associated with both infrared and Raman spectral data.
- The tables containing the primary bands will serve as a source of validated information for future study.
- Tables for comparative analysis will allow the identification of common groups present in the various related compounds.
- The predictive information in this document will be based upon current (2025) literature (Hu et al., 2025; Darmawan et al., 2025) references.

Significance of Study

Accurate identification of substituted aromatic aldehydes will be enhanced by this study (Silverstein et al. 2016). This method can help with the verification of organic synthesis processes and compound screening procedures (Harwood & Moody 1989). Additionally, the assignments generated in this study could be useful for future curation of computational and spectral databases (Henschel et al. 2020). Modern advances in spectroscopic instrumentation will improve the interpretive quality and increase confidence in the data obtained from the analysis of compounds using these methods (Darmawan et al. 2025).

ACKNOWLEDGEMENTS

The authors acknowledge institutional support for academic research facilities.

Conflict of Interest

The authors declare no conflict of interest.

Funding Sources

No external funding was received for this study.

Ethical Approval and Patient Consent

Not applicable for this spectroscopic investigation.

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