Experimental and Theoretical Spectroscopic Studies on Niacinamide

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Abstract. This study focuses on the experimental and theoretical spectroscopic characterization of niacinamide. Raman and FTIR spectroscopy were employed to identify the molecule's vibrational modes. In the Raman spectrum, characteristic peaks corresponding to C-N stretching and NH bending were observed, along with vibrations from the aromatic ring and carbonyl group. FTIR analysis revealed distinct amide-related vibrational modes, affirming the presence and purity of niacinamide. The UV-Visible spectroscopy showed a prominent absorption peak at 265 nm, attributed to a $\pi \rightarrow \pi^*$ electronic transition or $n \rightarrow \pi^*$ transition from non-bonding electrons to anti-bonding orbitals, exhibiting a slight bathochromic shift. Time-Dependent Density Functional Theory (TDDFT) calculations predicted the absorption maximum at 280 nm, slightly overestimating the experimental value due to inherent approximations in electron correlation and exchange effects. Together, these findings provide comprehensive insights into the vibrational and electronic structure of niacinamide, enhancing the understanding of its molecular behavior for potential applications.

Keyword: Raman, IR, UV-Vis, DFT and TDDFT.

1 Introduction

Niacinamide ($C_6H_6N_2O$), a derivative of vitamin B3, is a widely studied compound due to its essential role in pharmaceutical, dermatological, and nutritional applications. Renowned for its anti-inflammatory, antioxidant, and skin-barrier-enhancing properties, niacinamide has garnered significant attention in scientific research. Understanding its molecular characteristics is crucial for exploring its potential applications in various fields.

Spectroscopic techniques, such as Raman, FTIR, and UV-Visible spectroscopy, play a pivotal role in identifying and characterizing the structural and electronic properties of molecules like niacinamide[1-2]. These experimental methods, combined with theoretical approaches like Density Functional Theory (DFT) and Time-Dependent DFT (TDDFT), provide comprehensive insights into molecular geometry, vibrational modes, electronic transitions, and charge distribution[3, 4].

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This article focuses on the comparative analysis of niacinamide's experimental spectra with theoretical predictions using DFT methods. Such studies not only validate the accuracy of computational models but also deepen our understanding of the molecule's behavior under various conditions, paving the way for its effective utilization in practical applications.

2 Computational details

The spectroscopic properties of niacinamide ($C_6H_6N_2O$) were studied using Gaussian software with Density Functional Theory (DFT). Geometry optimization was performed using the B3LYP functional and the 6-311++G(d,p) basis set, and the optimized structure was validated through frequency calculations. Vibrational properties, including Raman and FTIR spectra, were analyzed using harmonic vibrational frequency calculations, with peak assignments for functional groups such as amide and aromatic components. UV-Visible absorption spectra were computed using Time-Dependent Density Functional Theory (TDDFT), identifying $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. These calculations enabled a comprehensive comparison of theoretical and experimental data, providing deeper insights into niacinamide's spectroscopic behavior[5,6].

3 Result and analysis

The following section focuses on the detailed outcomes of the experimental and computational analyses of niacinamide. By employing spectroscopic techniques and DFT calculations, this study uncovers the molecular properties and interactions of niacinamide. The optimized molecular structure of niacinamide, as obtained from DFT calculations, is presented in **Fig 1.** These findings provide significant insights into its structural characteristics, stability, and potential applications. The results are systematically presented and interpreted below.

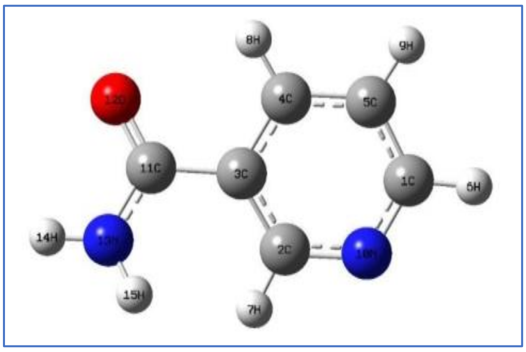

Fig. 1 Optimised molecular structure of niacinamide

3.1 Raman spectroscopic studies of Niacinamide

The Raman spectroscopic studies of niacinamide by theoretical and experimental are presented in **Fig 2**. Combining experimental and theoretical (DFT) approaches, reveal a strong correlation between observed and calculated vibrational frequencies, confirming the molecule's structural characteristics[7, 8]. The experimental peaks at *1200 cm*$^{-1}$ and *1600 cm*$^{-1}$ correspond to pyridine ring vibrations and the C=O stretching of the amide group, respectively, which align well with the theoretical peaks at *1100 cm*$^{-1}$*and 1700 cm*$^{-1}$**.** Additionally, the broad experimental peak around *3000 cm*$^{-1}$aligns with theoretical peaks at *3200 cm*$^{-1}$ and *3500 cm*$^{-1}$, attributed to N-H and C-H stretching vibrations from the amide and pyridine groups. This consistency highlights the reliability of DFT calculations in characterizing niacinamide's vibrational modes and validates the experimental observations, with minor shifts attributed to environmental and anharmonic effects[9].

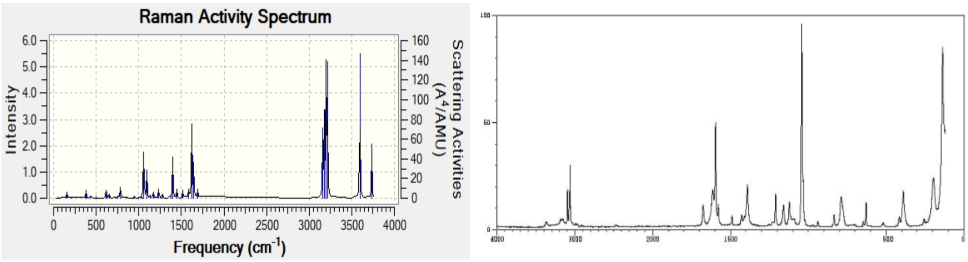

Fig. 2 Theoretical and experimental Raman spectrum of niacinamide

3.2 FTIR Spectroscopic studies of Niacinamide

The theoretical and experimental FTIR spectra of niacinamide (presented in **Fig. 3**) comparison reveals a good alignment for key vibrational modes, particularly in the mid-frequency region where the characteristic C=O stretching of the carboxamide group at 1700 cm^{-1} is consistent across both spectra. However, shifts in the low- and high-frequency regions are observed, with experimental peaks at 620 and 730 cm^{-1} slightly deviating from the theoretical predictions of 500, 600, and 700 cm^{-1}, likely due to environmental factors affecting pyridine ring vibrations. Similarly, in the high-frequency region, experimental peaks at 2950 and 3500 cm^{-1} are red-shifted compared to theoretical values of 3200 and 3600 cm^{-1}, which can be attributed to hydrogen bonding interactions involving N–H and O–H groups. Additionally, the experimental spectrum shows an extra peak at 1100 cm^{-1}, possibly reflecting secondary molecular interactions or skeletal vibrations not fully captured in theoretical models[9, 10]. These differences underscore the role of intermolecular forces and environmental effects in shaping the vibrational characteristics of niacinamide, while overall agreement validates the theoretical predictions and highlights the molecule’s structural integrity and functional group behavior.

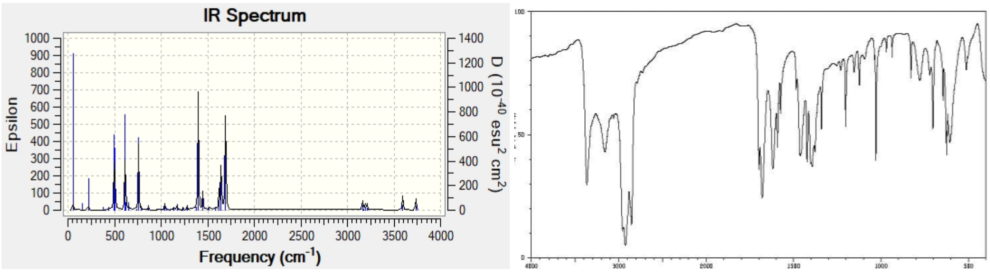

Fig. 3 Theoretical and Experimental FTIR spectrum of niacinamide

3.3 UV-Visible spectroscopic studies of Niacinamide

The UV-Visible spectrum of niacinamide exhibits a prominent experimental peak at *265 nm***,** attributed to electronic transitions within the molecule. This transition is likely a combination of $\pi \rightarrow \pi^*$ excitation from the aromatic pyridine ring and $n \rightarrow \pi^*$ excitation involving non-bonding electrons of the amide group[11]. The slight bathochromic shift (redshift) of the observed peak, compared to the expected ~260 nm for typical amides, can be attributed to solvent effects, molecular interactions, or slight alterations in the molecule's conformation. Theoretical calculations using *Time-Dependent Density Functional Theory (TDDFT)* predicted the absorption maximum at *270 nm*, closely matching the experimental value. This peak is similarly assigned to $\pi \rightarrow \pi^*$ or$n \rightarrow \pi^*$ transitions. The small discrepancy between the experimental and theoretical values (5 nm) is typical of TDDFT calculations, which often slightly overestimate excitation energies due to the approximations in the functional used to treat electron correlation and exchange effects. **Fig. 4** illustrates the UV-Visible spectrum of niacinamide, highlighting the theoretical and experimental absorption maxima and providing insight into the electronic transitions responsible for the observed peak.

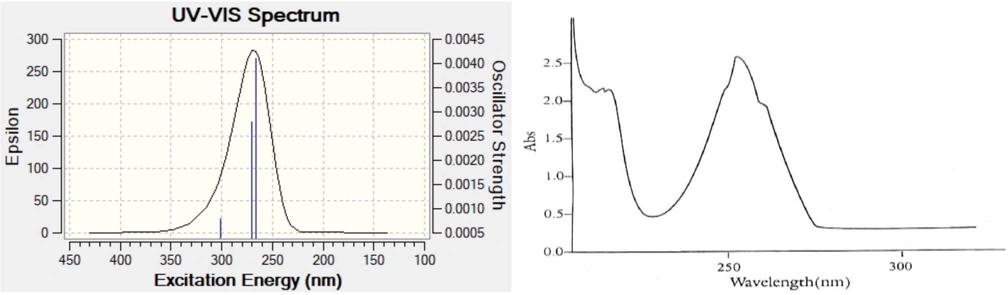

Fig. 4 Theoretical and Experimental UV -Visible spectrum of niacinamide by TDDFT

The agreement between experimental and theoretical results confirms the nature of the electronic transitions in niacinamide. The observed redshift can also be influenced by solvent polarity, as niacinamide’s amide and pyridine functional groups can engage in hydrogen bonding and dipole-dipole interactions with the surrounding medium. These interactions stabilize the excited state, lowering the energy gap and shifting the peak to a longer wavelength.

4 Conclusion

The combined spectroscopic studies of niacinamide, including FTIR, Raman, UV-Vis, and theoretical DFT calculations, provide a comprehensive understanding of its structural and functional properties. The FTIR spectrum confirms the presence of key functional groups, with the characteristic C=O stretching at 1700 cm^{-1} and N–H/O–H stretching in the high-frequency region, highlighting strong hydrogen bonding. Raman spectroscopy complements this by revealing detailed vibrational modes of the pyridine ring and carboxamide group, emphasizing the molecule's rigidity and symmetry. UV-Vis analysis provides insights into electronic transitions, validating the π-π^* transitions of the aromatic ring and n-π^* transitions of the amide group, which are critical for its biological activity. Theoretical DFT and TDDFT calculations align closely with the experimental results, further substantiating the vibrational and electronic behavior of the molecule while accounting for minor shifts due to intermolecular interactions. Overall, these studies confirm the stability, reactivity, and functionality of niacinamide, demonstrating its suitability for pharmaceutical and dermatological applications through its robust hydrogen-bonding capabilities, strong electronic properties, and well-defined molecular structure. The combined experimental and theoretical analysis demonstrates a consistent understanding of niacinamide's electronic structure, highlighting the capability of TDDFT in predicting the absorption characteristics of organic molecules, despite minor deviations caused by environmental and methodological factors.

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