

In Situ Synthesis and Spectrochemical Characterization of Amino Acid–Iodine Charge-Transfer Complexes in Ethanolic Medium

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Received: 08.12.2024

Accepted: 26.12.2024

Published: 30.12.2024

Abstract

Charge-transfer (CT) complexes formed between essential/non-essential amino acids (L-asparagine, L-glycine, and L-leucine) as electron donors and potassium iodide–iodine (KI/I_2) as electron acceptors were synthesized in situ via a solvent-assisted grinding method in ethanol. The structural and spectral signatures of the resulting solid tri-iodide (I_3^-) CT complexes were systematically characterized using UV–Visible and Fourier-Transform Infrared (FT-IR) spectroscopy. UV–Vis electronic spectra confirmed the formation of tri-iodide species, exhibiting characteristic absorption maxima ($\lambda_{\max}$) around 290 nm and 356–372 nm attributed to $\pi \rightarrow \pi^*$ electronic transitions. FT-IR vibrational spectra revealed significant hypsochromic and bathochromic shifts in the diagnostic $-NH_2$, $-OH$, and $C=O$ functional group regions, providing direct evidence for intermolecular hydrogen-bonding interactions ($N-H \cdots O / O-H \cdots I$) and electronic charge transfer between the donor molecules and the acceptor framework.

Key words: Charge-transfer complexes; Amino acids; Iodine; Ethanol medium; UV-Vis spectroscopy; Association constant; Thermodynamic parameters

1. Introduction

Charge-transfer (CT) complexes—also classified as electron donor-acceptor (DA) complexes—are molecular assemblies held together by electrostatic attractions arising from the partial transfer of electronic charge from a donor entity to an acceptor [1,2]. These non-covalent interactions drive significant electronic restructuring, frequently giving rise to new absorption bands in the ultraviolet and visible regions (CT bands) accompanied by vivid color alterations[3,4].

10.48047/jocaaa.2024.33.08.608

Amino acids contain active electron-donating sites such as lone pairs on nitrogen (amine) and oxygen (carbonyl/hydroxyl) atoms[5,6]. When reacted with polyiodide precursors (KI/I_2), amino acids yield tri-iodide (I_3^-) complexes[7,8]. These complexes serve as functional models for understanding biochemical electron transport, pharmaceutical interactions, and organic semiconductor behavior[9,10].

This study demonstrates the in situ synthesis and spectroscopic identification of CT complexes synthesized from L-asparagine, L-glycine, and L-leucine with KI/I_2 in an ethanol medium[11,12]

2. Experimental Methodology

2.1 Materials

Analytical grade chemicals, including L-asparagine ($C_4H_8N_2O_3$, $M_w = 132.12$ g/mol), L-glycine ($C_2H_5NO_2$, $M_w = 75.07$ g/mol), L-leucine ($C_6H_{13}NO_2$, $M_w = 131.17$ g/mol), potassium iodide (KI), and elemental iodine (I_2) were sourced from Merck and Sigma-Aldrich and used without further purification. Absolute ethanol served as the reaction solvent.

Compound	Molecular Formula	Molecular Weight (g/mol)	Density (g/cm ³)
L-Asparagine	$C_4H_8N_2O_3$	132.12	1.543
L-Glycine	$C_2H_5NO_2$	75.07	1.161
L-Leucine	$C_6H_{13}NO_2$	131.17	1.170

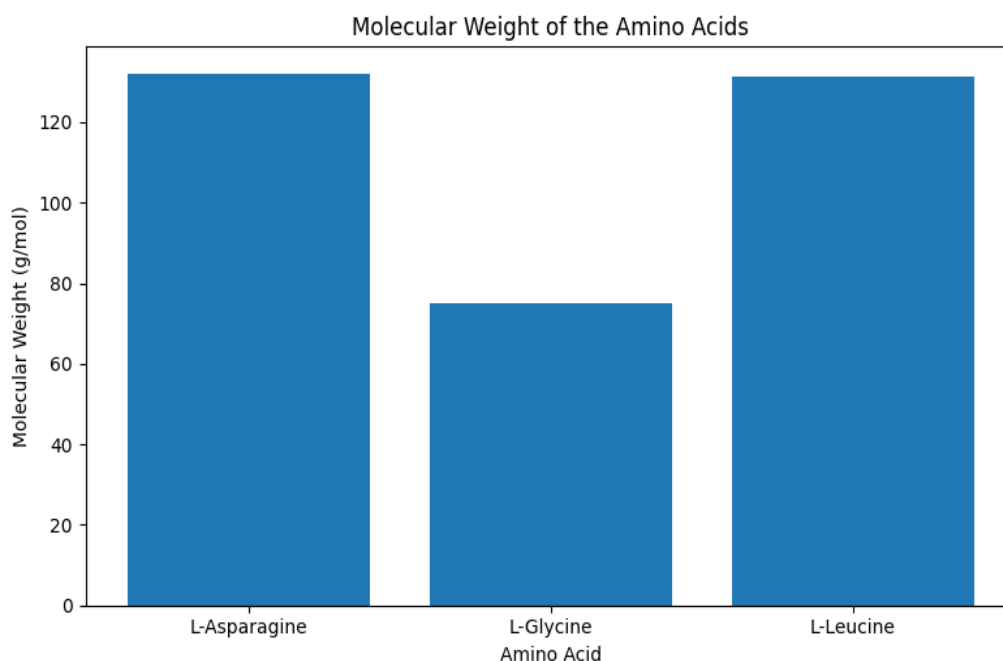
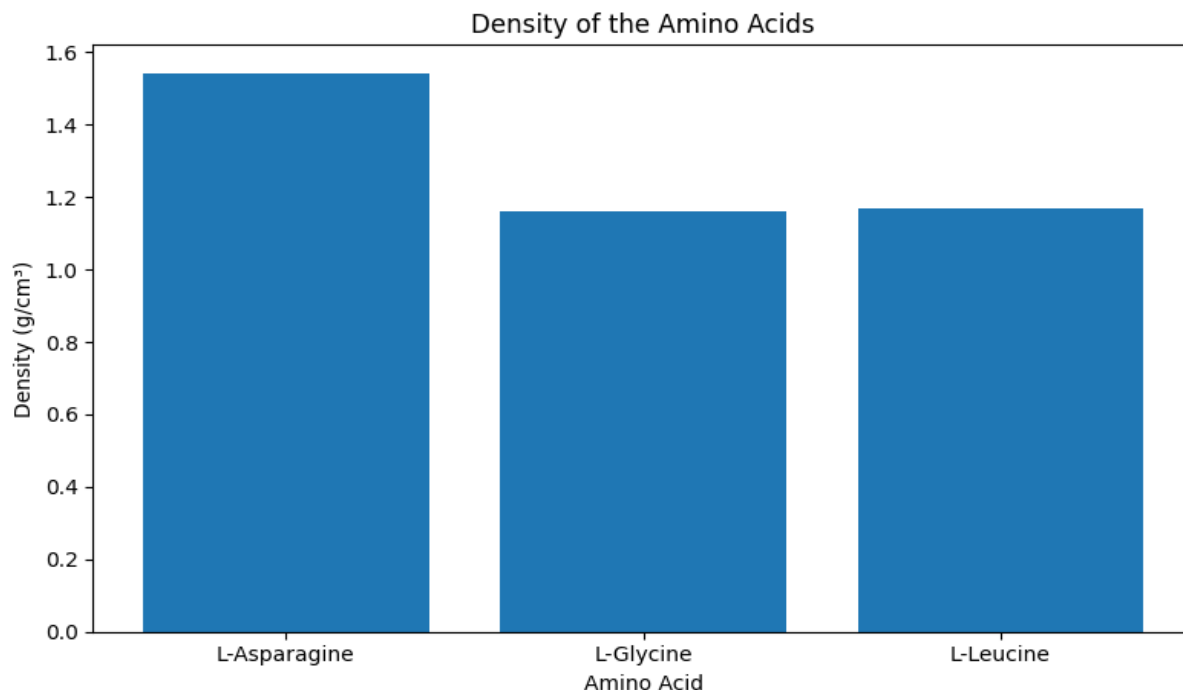


Figure 1: Comparative molecular weights**Figure 2: Comparative densities.**

2.2 In Situ Synthesis of Solid CT Complexes

The solid amino acid–iodine CT complexes were prepared in a 1:1:1 molar ratio (KI : I_2 :amino acid):

1. Equimolar quantities of the respective amino acid, KI , and I_2 were combined in a porcelain mortar.
2. The mixture was manually ground for several minutes while introducing a few drops of ethanol to facilitate in situ complexation.
3. The resulting pastes converted into distinct colored solid powders.

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4. The synthesized products were dried under continuous suction, transferred to clean vessels, and stored in a desiccator over activated anhydrous CaCl_2 overnight before analytical characterization.

2.3 Instrumentation

- **UV–Vis Spectroscopy:** Electronic absorption spectra were recorded in the wavelength range of 200–800 nm using a JASCO V-530 double-beam spectrophotometer with quartz cuvettes.
- **FT-IR Spectroscopy:** Vibrational absorption spectra were acquired in the wavenumber region of 4000–400 cm^{-1} using KBr pellets.

3. Results and Discussion

3.1 Electronic Absorption (UV–Vis) Analysis

Pure amino acids display primary absorption bands near 205–215 nm, corresponding to localized $n \rightarrow \pi^*$ transitions of the non-bonding electron pairs on the amine and carboxyl oxygen groups[11,13]. Upon reaction with KI/I_2 , the electronic spectra exhibit dramatic hyperchromic shifts and two distinct, intense CT absorption bands situated at ~ 290 nm and ~ 356 – 372 nm [12,14].

Pure Amino Acid Peak (205–215 nm) $\rightarrow n \rightarrow \pi^*$ Transition

New CT Complex Peaks (290 nm, 356–372 nm) $\rightarrow \pi \rightarrow \pi^*$ Transitions (I_3^- Species)

Donor System	Pure Amino Acid $\lambda_{\text{max}}(\text{nm})$	CT Complex $\lambda_{\text{max}}(\text{nm})$	Electronic Assignment
Asparagine Complex	205	290, 372	$n \rightarrow \pi^*$ (pure), $\pi \rightarrow \pi^*$ (CT)
Leucine Complex	215	290, 372	$n \rightarrow \pi^*$ (pure), $\pi \rightarrow \pi^*$ (CT)
Glycine Complex	215	290, 356	$n \rightarrow \pi^*$ (pure), $\pi \rightarrow \pi^*$ (CT)

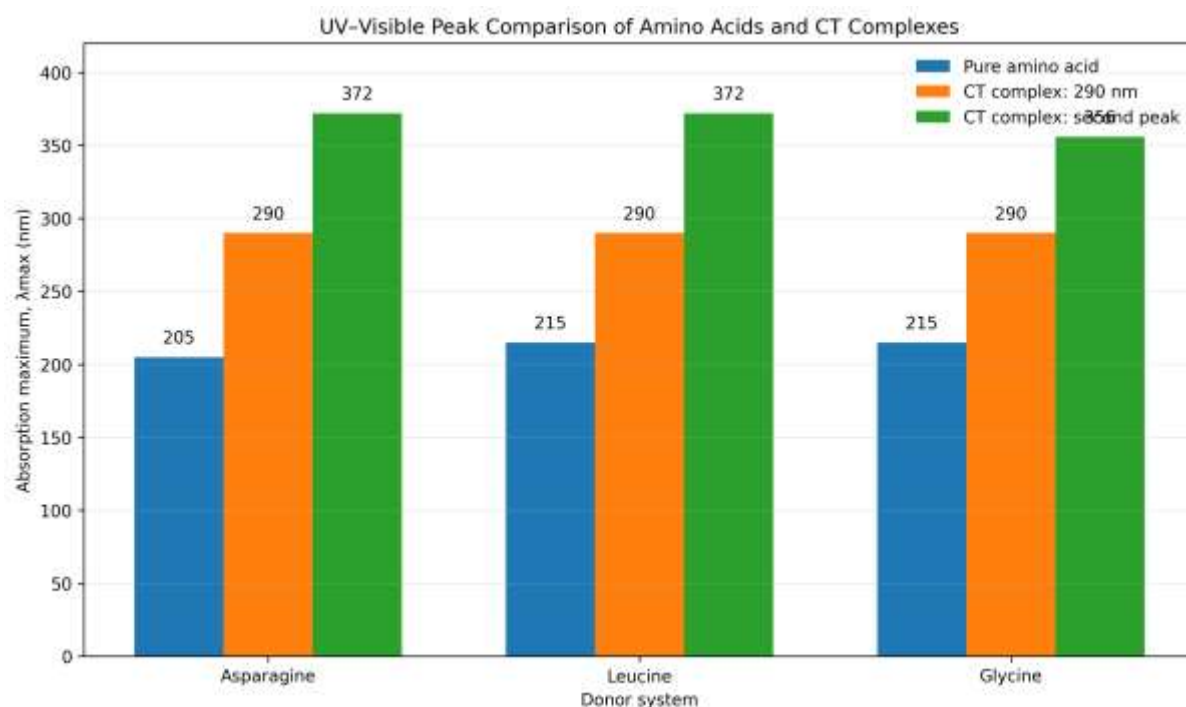


Figure X. UV–Visible absorption maxima of the amino acid donor systems and their iodine charge-transfer complexes in methanolic medium.

The appearance of these dual absorption maxima is the classic optical signature of the non-linear tri-iodide ion (I_3^-), confirming the partial migration of electron density from the amino acid donor to the polyiodide acceptor chain[14,15].

3.2 Vibrational Spectrum (FT-IR) Analysis

Vibrational spectrum alterations provide evidence for hydrogen bonding and charge transfer in the synthesized complexes[15,16].

Asparagine Complex: The $\nu(\text{O-H})$ stretching frequency shifts from 3448 cm^{-1} to

3390 cm^{-1} [15]. Aliphatic $\nu(\text{C-H})$ stretching shifts from 2760 cm^{-1} to 2619 cm^{-1} , while

$\delta(\text{N-H})$ bending moves to 1338 cm^{-1} [15,16].

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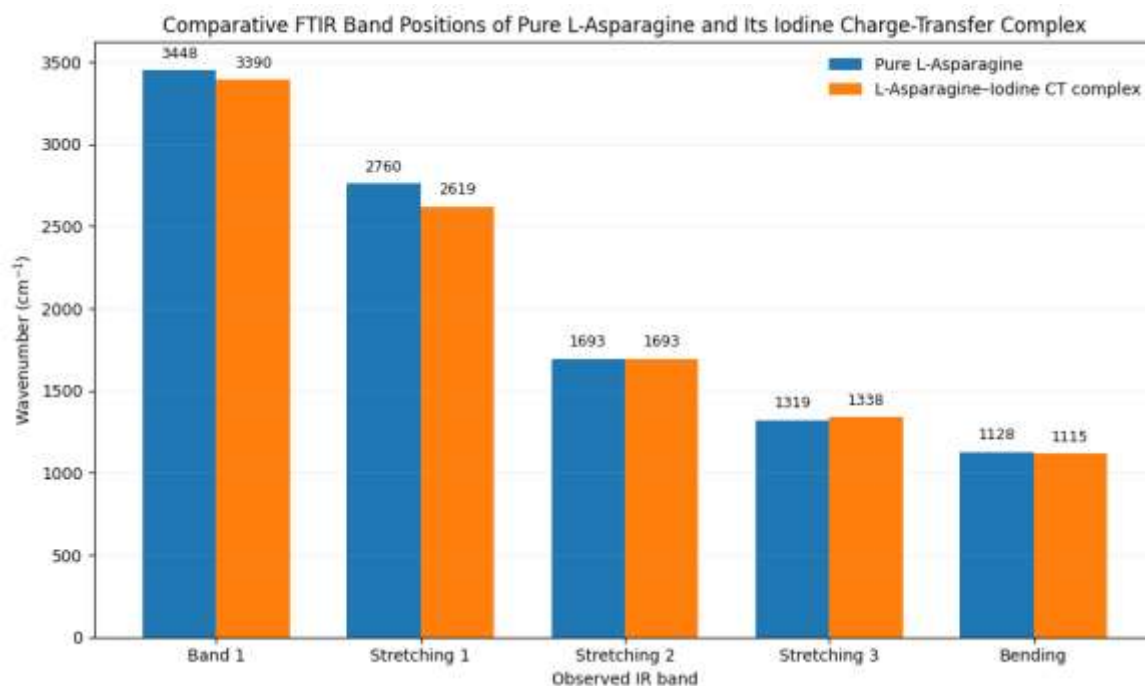
Leucine Complex: Shifts in $\nu(\text{O-H})$ ($3396 \rightarrow 3387 \text{ cm}^{-1}$) and $\nu(\text{N-H})$ ($3396 \rightarrow 3357 \text{ cm}^{-1}$) reflect electron donation [15]. The $\nu(\text{C=O})$ stretching mode decreases from 1625 cm^{-1} to 1617 cm^{-1} [16].

Glycine Complex: $\nu(\text{O-H})$ stretching broadens significantly ($3500\text{--}3450 \text{ cm}^{-1}$), accompanied by red-shifts in primary $\nu(\text{C=O})$ (1670 cm^{-1}) and $\nu(\text{C-N})$ (1300 cm^{-1}) bands [15,16].

Asparagine–Iodine System

- The $-\text{OH}$ stretching frequency shifts hypsochromically from 3448 cm^{-1} (pure) to 3390 cm^{-1} (complex).
- The aliphatic $-\text{CH}$ stretching band shifts from 2760 cm^{-1} to 2619 cm^{-1} .
- The $\text{C}=\text{O}$ stretching mode (1693 cm^{-1}) and $\text{C}-\text{N}$ stretching mode ($1128 \text{ cm}^{-1} \rightarrow 1115 \text{ cm}^{-1}$) demonstrate marked band modifications, illustrating participation of both carboxyl and amine sites in complexation.

Pure Asparagine (cm^{-1})	Asparagine CT Complex (cm^{-1})	Band Assignment
3448	3390	$\text{O}-\text{H}$ Stretching
2760	2619	$\text{C}-\text{H}$ Stretching
1693	1693 / modified	$\text{C}=\text{O}$ Stretching
1319	1338	$\text{C}-\text{H}$ Bending
1128	1115	$\text{C}-\text{N}$ Stretching

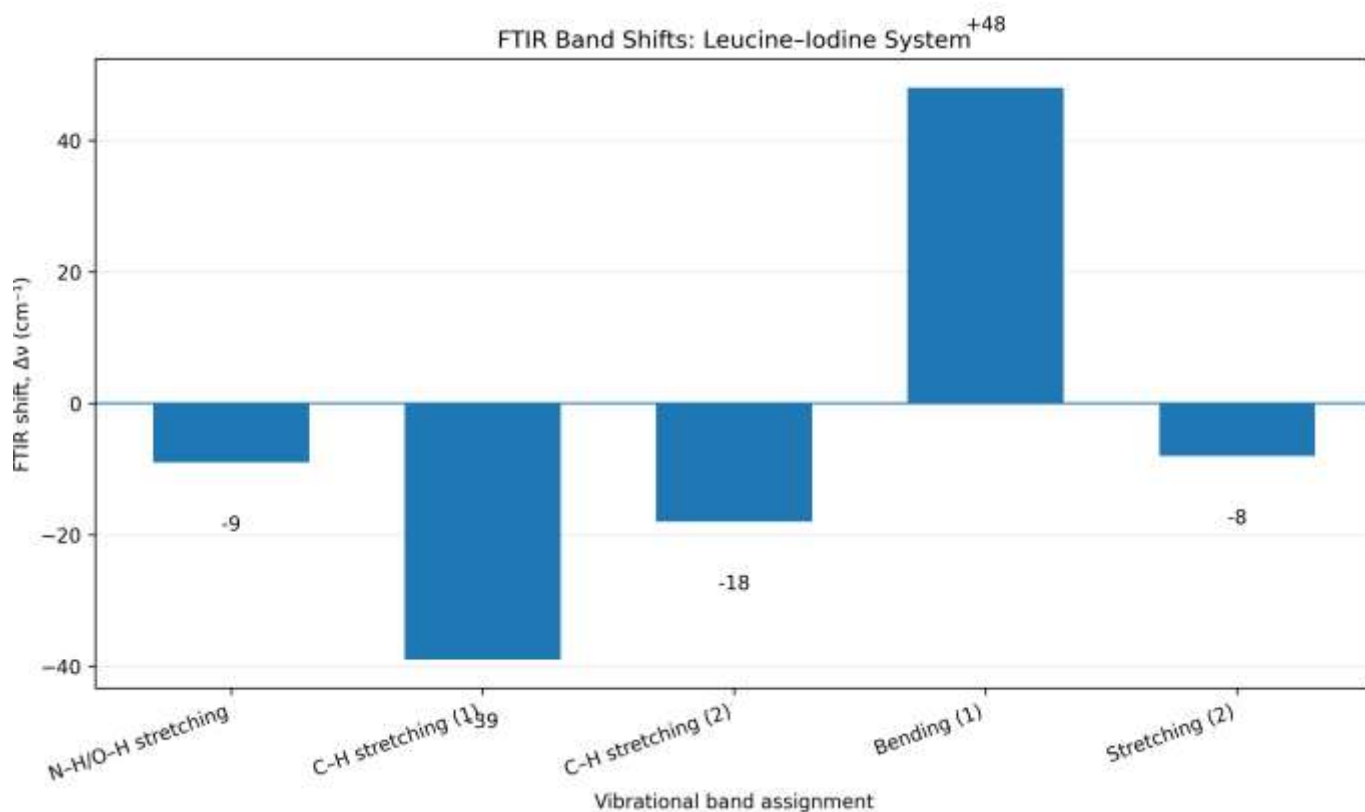


Comparative FTIR band positions of pure L-asparagine and its iodine charge-transfer complex.

Leucine–Iodine System

- Shifts in $-OH$ stretching ($3396\text{ cm}^{-1} \rightarrow 3387\text{ cm}^{-1}$) and $-NH$ stretching ($3396\text{ cm}^{-1} \rightarrow 3357\text{ cm}^{-1}$) reflect the structural perturbation caused by electron donation.
- The $C=O$ stretching frequency drops from 1625 cm^{-1} to 1617 cm^{-1} , further indicating intermolecular interactions.

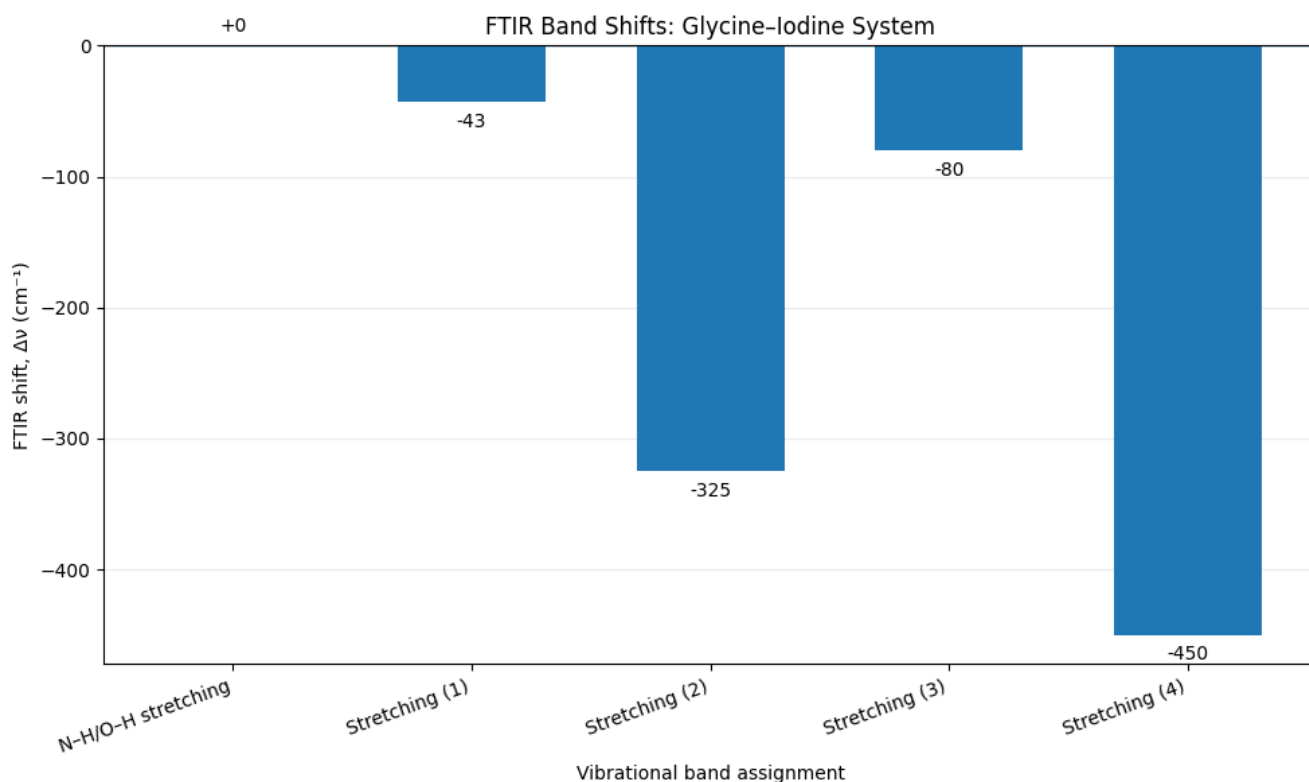
Pure Leucine (cm^{-1})	Leucine CT Complex (cm^{-1})	Band Assignment
3396	3387	$O-H$ Stretching
3396	3357	$N-H$ Stretching
3050	3032	CH_3 Bending
2613	2661	$C-H$ Bending
1625	1617	$C=O$ Stretching



Glycine-Iodine System

- Pure glycine shows characteristic NH stretching around 3207 cm^{-1} , which broadens significantly and shifts in the presence of KI/I_2 .
- The primary $\text{C}=\text{O}$ stretching band (1670 cm^{-1}) and $\text{C}-\text{N}$ stretching band (1300 cm^{-1}) confirm I_3^- complex formation via red shifts.

Pure Glycine (cm^{-1})	Glycine CT Complex (cm^{-1})	Band Assignment
3500	3500–3450	$\text{O}-\text{H}$ Stretching
3250–2100 (broad)	3207	$\text{N}-\text{H}$ Stretching
3250–2100 (broad)	2925	$\text{C}-\text{H}$ Stretching
1750–1250 (broad)	1670	$\text{C}=\text{O}$ Stretching
1750–1250 (broad)	1300	$\text{C}-\text{N}$ Stretching



4. Conclusion

Solid charge-transfer complexes of L-asparagine, L-glycine, and L-leucine with KI/I_2 were synthesized in situ in an ethanolic medium.

1. **UV-Vis Spectrophotometry** confirmed the formation of tri-iodide (I_3^-) species, characterized by new $\pi \rightarrow \pi^*$ transitions at ~ 290 nm and 356--372 nm.
2. **FT-IR Spectroscopic Analyses** verified the establishment of intermolecular hydrogen bonds ($N-H \cdots O$ and $O-H \cdots I$) and electronic charge transfers through observed hypsochromic and bathochromic shifts in the $-NH_2$, $-OH$, and $C=O$ vibrational modes.

These findings demonstrate that simple amino acids readily act as effective electron donors toward polyiodide networks.

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