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SUPPLEMENTARY MATERIAL

Theoretical studies and vibrational spectra of *1H*-Indole-3-Acetic Acid. Exploratory conformational analysis of dimeric species.

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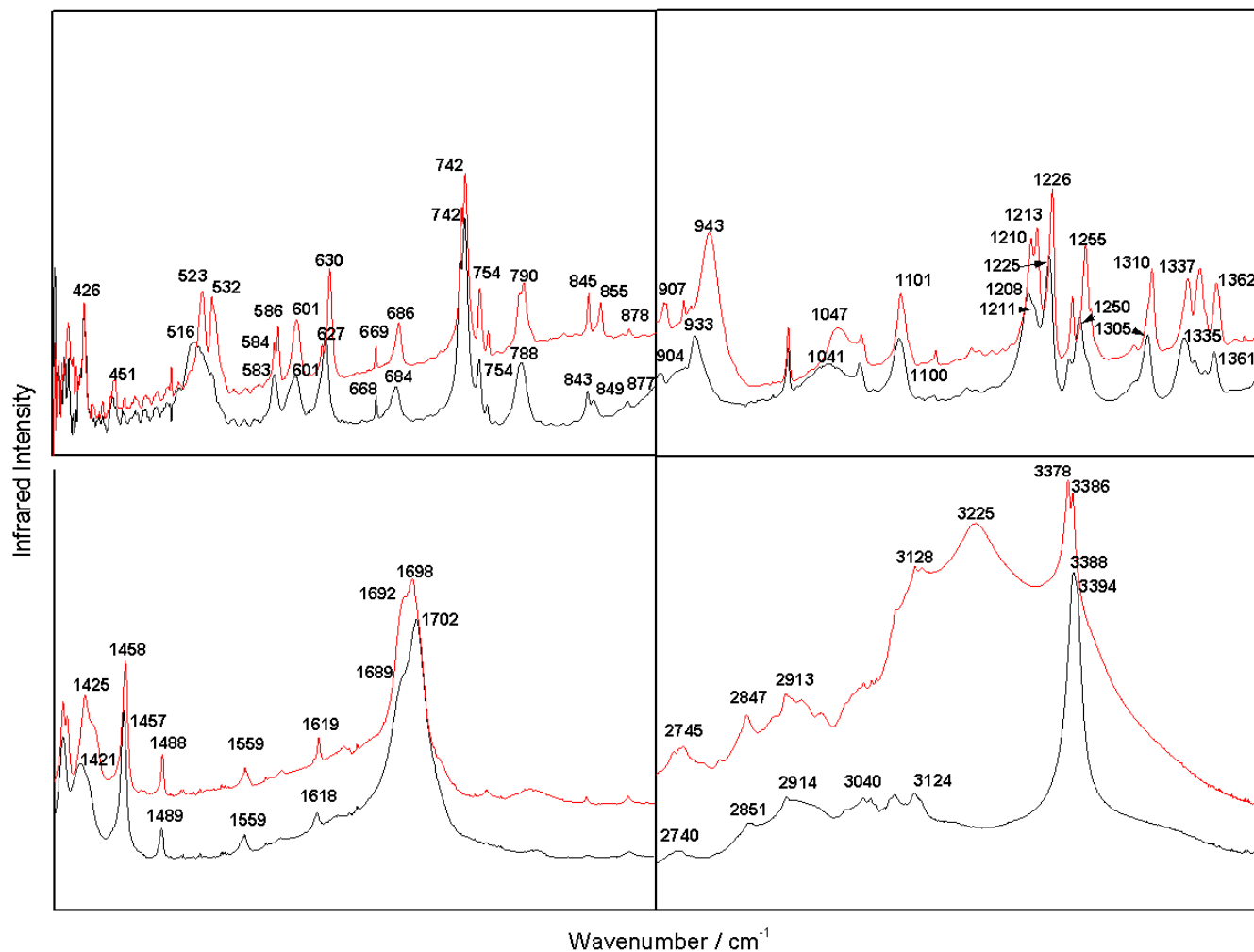
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Figure S1 Infrared spectrum of *1H*-indole-3-acetic acid at 297 K (black line) and 100 K (red line) show softening ($\Delta = -$) and hardening ($\Delta = +$) of several Infrared vibrational modes. Bold wavenumbers correspond to bands that shift at low temperatures.



The infrared spectrum of IAA (Fig. S1) showed softening ($\Delta = -$) and hardening ($\Delta = +$) of several vibrational modes, thus implying subtle structural changes in the molecule as it cools down. Wavenumber shifting of $+\Delta = 7, 6, 5, 4, 3, 2, 1 \text{ cm}^{-1}$ involves: COO wagging deformation, in-plane ring deformation and out-of-plane CH ring bending modes ($\gamma\text{C}_9\text{O}_{11}\text{O}_{10\text{wag}}$, $\delta 6\text{R}$, $\gamma\text{C}_4\text{H}(-)$, $\gamma\text{C}_5\text{H}(-)$, $\gamma\text{C}_7\text{H}(+)$, and $\gamma\text{C}_6\text{H}(+)$) at 516 and 843 cm^{-1} ; C—C stretching, O—H in-plane bending, N—C ring stretching, in-plane ring deformation, and CH_2 scissoring deformation vibrations ($\nu\text{C}_8\text{C}_9$, $\delta\text{O}_{11}\text{H}$, $\nu\text{N}_1\text{C}_{7a}$, $\nu\text{N}_1\text{C}_2$, $\delta 6\text{R}$, $\delta 5\text{R}$, $\delta\text{C}_8\text{H}_{(2)\text{sciss}}$) at 1250, 1305, 1421 cm^{-1} ; out-of-plane ring deformation, CH_2 wagging deformation, and in-plane C—H ring bending modes ($\tau 6\text{R}$, $\tau 5\text{R}$, $\gamma\text{C}_8\text{H}_{(2)\text{wag}}$, $\delta 6\text{R}$, $\delta 5\text{R}$) at 627 and 1208 cm^{-1} ; COO wagging deformation vibration ($\delta\text{C}_9\text{O}_{11}\text{O}_{10\text{sciss}}$) at 684 cm^{-1} ; out-of-plane ring C—H bending modes ($\gamma\text{C}_4\text{H}(+)$, $\gamma\text{C}_5\text{H}(+)$, $\gamma\text{C}_6\text{H}(+)$, and $\gamma\text{C}_7\text{H}(+)$) at 742 cm^{-1} ; out-of-

plane C—H ring bending mode (γ_{C_2H}) at 788 cm^{-1} ; C—O stretching, and in-plane ring deformation modes ($\nu_{C_9O_{11}}$, δ_{6R} , and δ_{5R}) at 1225 , and 1335 cm^{-1} . Softening of -9 , -6 , -4 cm^{-1} can be seen at 3388 cm^{-1} (ν_{N_1H}) and 1702 cm^{-1} ($\nu_{C_9O_{10}}$).

DETAILED ANALYSIS OF THE VIBRATIONAL MODES ACTIVE IN THE INFRARED AND RAMAN SPECTRA (Table 4, main text)

Amine vibrations

In the experimental infrared spectrum of IAA, a strong band near 3391 cm^{-1} can be assigned to ν_{N-H} mode. This band is splitting in two peaks; the peak at 3388 cm^{-1} corresponds to the N—H stretching in-phase and the peak at 3394 cm^{-1} corresponds to the N—H stretching out-of-phase. In the Raman spectrum of IAA this band is very weak and also appears at 3388 cm^{-1} .

In aromatic secondary amines the N—H bending vibrations are generally expected near 1650 - 1550 cm^{-1} [26]. According to the calculated results this mode contributes to the band at 1576 cm^{-1} in the infrared and Raman spectra of IAA.

All aromatic amines show N—C stretching bands in the 1350 - 1250 cm^{-1} range [22]; in our case these bands appear at 1305 and 1307 cm^{-1} in infrared and Raman spectra, respectively.

Carboxylic vibrations

Carboxylic group vibrations are the best characteristic bands in the vibrational spectra, and hence, such bands have been the subject of extensive studies [19-23].

A intense band should appear between 3600 and 2500 cm^{-1} corresponding to ν_{O-H} mode in the infrared and Raman spectra [20, 21]. For IAA dimers this band appears clearly in Raman spectrum at 2915 cm^{-1} .

In the infrared spectrum the intense band at 1702 cm^{-1} is assigned to $\nu_{C=O}$ vibration. The wavenumber of this vibration is slightly lower than the wavenumber of the non-associated carboxylic C=O group 1800 - 1740 cm^{-1} [19-21]. Therefore, this finding indicates that in IAA the C=O group is involved in an intermolecular hydrogen bonding, as was analyzed in the main text. As was also mentioned in the main text when the dimeric molecule is considered as a whole, two carbonyl stretching wavenumbers (symmetric and asymmetric) are expected. The dimeric molecule has a center of symmetry, so the symmetric carbonyl stretching should be Raman active only, and the asymmetric stretching should be infrared active only [19]. In the infrared spectrum wavenumbers from 1720 to 1680 cm^{-1} correspond to the asymmetric C=O stretching [19-22], in our case this band shows a splitting with peaks at 1689 and 1702 cm^{-1} . In Raman spectrum a band should appears at 1680 –

1640 cm^{-1} corresponding to the symmetric C=O stretching [19, 23], in our case, this band appears at 1641 cm^{-1} . When the carbonyl is hydrogen bonded, but not dimerized, a band should appear at 1730-1705 cm^{-1} in both infrared and Raman spectra [19, 21].

The mentioned infrared wavenumber of the $\nu\text{C=O}$ mode is slightly lower than the wavenumber of the non-associated carboxylic C=O group 1800 - 1740 cm^{-1} [19-21]. This finding also indicates that in IAA the C=O group is involved in an intermolecular hydrogen bonding, as was suggested by geometrical analysis and was confirmed through our AIM characterizations.

The C—O stretching and C—O—H in-plane deformation modes are strongly coupled and can be assigned to two characteristic bands that appear in the ranges 1320-1210 cm^{-1} and 1440-1395 cm^{-1} [21]. The C—O stretching mode appears at 1225 cm^{-1} and 1218 cm^{-1} in the infrared and Raman spectra of IAA, respectively. The C—O—H in-plane deformation mode appears at 1407 cm^{-1} and 1404 cm^{-1} in the infrared and Raman spectra, respectively.

The characteristic infrared band for the carboxylic dimer is a broad and medium intensity band at 960-875 cm^{-1} due to C—O—H out-of-plane deformation mode [19]. This band is present at that range only for the dimer and is usually noticeably broader than other bands in this region. The absence of a band here would be fairly good evidence for the lack of the dimer form [19]. This vibration appears at 933 cm^{-1} and 928 cm^{-1} in the infrared and Raman spectra of IAA, respectively.

The $\delta\text{COO}_{\text{sciss}}$ is not predicted to be a “pure” vibration and contributes to the other modes that appear at 425, 684, and 904 cm^{-1} in infrared spectrum, and at 423, 675 and 905 cm^{-1} in Raman spectrum.

Methylene vibrations

The asymmetric CH_2 stretching mode is expected in the region near 2925 cm^{-1} and the symmetric mode around 2850 cm^{-1} [23, 26]. The asymmetric stretching mode appears as medium infrared band at 2914 cm^{-1} , while the symmetric stretching vibration is observed at 2851 and 2938 cm^{-1} in infrared and Raman spectra, respectively.

The CH_2 group gives rise to a band near 1465 cm^{-1} due to the scissoring vibration [26]. This band position does not vary greatly unless very strongly electronegative elements or unsaturated groupings are present in the vicinity. When CH_2 group is in the α -position to a carbonyl group their deformation frequency lower to about 1425 cm^{-1} and is intensified [19, 26]. In IAA this mode appears as a strong band at 1421 cm^{-1} and as very strong band at 1427 cm^{-1} in infrared and Raman spectra, respectively.

The wagging vibration of CH_2 group is expected in the region between 1347-1182 cm^{-1} [19]. The frequencies show the same sensitivity to electronegative substituents that the scissoring mode. In IAA, this vibration gives rise to a strong band at 1208 cm^{-1} and a very weak peak at 1205 cm^{-1} in infrared and Raman spectra, respectively.

The CH₂ twisting vibrations usually are quite weak and appear at a little lower frequency than the CH₂ wagging frequencies [19]. This mode is correlated to the medium band observed at 1189 cm⁻¹ in Raman spectrum of IAA.

Ring vibrations

Aromatic compounds show the C—H stretching vibrations in the region 3200 – 3000 cm⁻¹[23]. According to our calculations, the C—H stretching vibrations can be assigned to bands at 3040 and 3053 cm⁻¹ in the infrared spectrum. In the Raman spectrum these vibrations can be correlated to the very strong band at 3060 cm⁻¹. Moreover, the C₂H stretching mode appears not mixed with mentioned modes by the DFT calculation. This mode has been identified at 3123 cm⁻¹ in the infrared spectrum of IAA.

According with bibliography in the region between 1618 and 1457 cm⁻¹ there are bands associated with C—C ring stretching modes [23]. Four bands of strong, medium and weak intensity appear at 1457, 1489, 1559, and 1618 cm⁻¹ in the infrared spectrum. The first band accounts for $\nu_{C_{3a}C_{7a}}$, $\nu_{C_4C_5}$, and $\nu_{C_6C_7}$ modes; the second band can be assigned to the $\nu_{C_4C_5}$ and $\nu_{C_6C_7}$ modes; the third band can be attributed to the $\nu_{C_2C_3}$, $\nu_{C_5C_6}$, and $\nu_{C_7C_{7a}}$ modes; the fourth band can be assigned to the $\nu_{C_4C_5}$, $\nu_{C_{7a}C_7}$, and $\nu_{C_2C_3}$. In the Raman spectrum corresponding peaks appear at 1457, 1493, 1558, and 1618 cm⁻¹, respectively.

In aromatic compounds there is an in-plane ring deformation which involves displacing alternate carbon atoms around the ring. It always occurs near 1010 cm⁻¹ and is always one of the strongest bands in the Raman spectrum [23]. This mode has been identified at 1007 cm⁻¹ in both spectra.

The C—H in-plane ring deformation modes appear in the region 1275-1000 cm⁻¹ [21]. These modes are correlated to the bands at 1100 and 1125 cm⁻¹ in infrared spectrum. In the Raman spectrum corresponding bands appears at 1105 and 1127 cm⁻¹.

The coupled modes of C—H out-of-plane ring deformation in which all adjacent hydrogen are deformed together develop strong dipole moment changes and give rise to the very strong band in the infrared spectrum. In Raman spectrum the corresponding band is weak. The coupled modes appear in the region of 770-735 cm⁻¹ [23]. These vibrations give rise to a very strong band at 742 cm⁻¹ in infrared spectrum of IAA and a weak peak at 740 cm⁻¹ in Raman spectrum.