**Supplementary Materials**

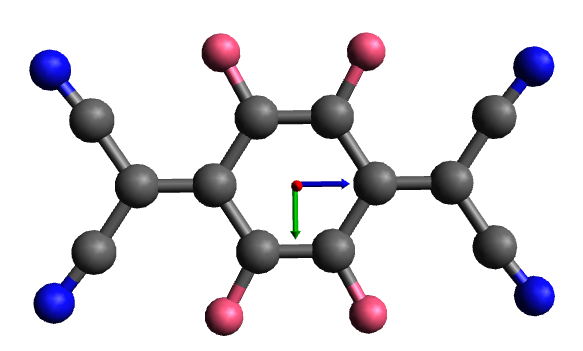
**Probing the charge state and the intermolecular environment by vibrational spectroscopy: the peculiar modulation of frequencies and bands intensities of F4TCNQ and of its anion**

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r1

r2

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r4

**Figure S1.** Sketch of the F4TCNQ molecule with the labelling of the four CN stretching coordinates.

**Figure S2** B3LYP/6-31G\*\* calculated molecular polarizability derivatives with respect to individual bond stretchings.

1. **c.**

**Figure S3** Comparison between the DFT (B3LYP/6-31G\*\*) computed infrared spectra of neutral F4TCNQ in the isolated state and in two different solvents with increasing dielectric constant (PCM method). **a**. spectral region 2500 - 700 cm-1 and zooms in the 1800 – 700 cm-1 region (**b**.) and in the CN stretching region (**c**.)

1. **c.**

**Figure S4** Comparison between the DFT (B3LYP/6-31G\*\*) computed Raman spectra of neutral F4TCNQ in the isolated state and in two different solvents with increasing dielectric constant (PCM method). **a**. spectral region 2400 - 1400 cm-1 and zooms in the 1800 – 1400 cm-1 region (**b**.) and in the CN stretching region (**c**.)

**Figure S5** Comparison between DFT B3LYP/6-31G\*\* computed bond lengths of F4TCNQ in the isolated state and in two different solvents with increasing dielectric constant (PCM method).

**Table S1. a.** Computed wavenumber and Raman Activities (A) of vibrational transitions of F4TCNQ and its singly charged anion, F4TCNQ(-1) for normal modes belonging to the B1g and B2g irreducible representation (DFT B3LYP/6-31G\*\* calculations). Relative Raman Activities (normalized to the strongest Raman transition) are also reported. The last three column report wavenumber shifts and Raman Activity changes from the neutral molecule to the anion. Data concerning very weak transitions are displayed with a grey background. **b.** Computed wavenumber and Infrared Intensities (I) of vibrational transitions of F4TCNQ and its singly charged anion, F4TCNQ(-1) for normal modes belonging to the B3u and Au irreducible representation (DFT B3LYP/6-31G\*\* calculations). Relative Infrared Intensities (normalized to the strongest Infrared transition) are also reported. The last three column report wavenumber shifts and intensity changes from the neutral molecule to the anion. Data concerning very weak transition are displayed with a grey background.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **S1.a** | F4TCNQ | | | F4TCNQ(-1) | | |  |  |  |
| B1G |  (cm-1) | A - Raman Activity | Raman Activity |  (cm-1) | A - Raman Activity | Raman Activity | Δν | Δν% | ΔA% |
| (Å4amu-1/2) | relative | (Å4amu-1/2) | relative | (cm-1) |  |  |
| 1 | 50 | 2 | 0.00 | 31 | 2 | 0.00 | -18 | -37 | 2 |
| 2 | 380 | 0.17 | 0.00 | 394 | 0.54 | 0.00 | 13 | 4 | 213 |
| 3 | 460 | 6 | 0.00 | 477 | 7 | 0.00 | 18 | 4 | 20 |
|  | | | | | | | | | |
| B2G |  (cm-1) | A - Raman Activity | Raman Activity |  (cm-1) | A - Raman Activity | Raman Activity | Δν | Δν% | ΔA% |
| (Å4amu-1/2) | relative | (Å4amu-1/2) | relative | (cm-1) |  |  |
| 1 | 85 | 0.53 | 0.00 | 97 | 0.64 | 0.00 | 12 | 14 | 21 |
| 2 | 218 | 0.09 | 0.00 | 222 | 0.52 | 0.00 | 4 | 2 | 479 |
| 3 | 416 | 0.70 | 0.00 | 386 | 0.02 | 0.00 | -30 | -7 | -97 |
| 4 | 520 | 11 | 0.00 | 507 | 10 | 0.00 | -13 | -7 | -2 |
| 5 | 666 | 64 | 0.00 | 622 | 70 | 0.00 | -44 | -7 | 10 |

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **S1.b** | F4TCNQ | | | F4TCNQ(-1) | | | | |  |  |  |
| B3u |  (cm-1) | I - IR Intensity | I - IR Intensity |  (cm-1) | I - IR Intensity | | I - IR Intensity | | Δν | Δν% | ΔI% |
| (km/mol) | relative | (km/mol) | | relative | | (cm-1) |  |  |
| 1 | 34 | 4 | 0.02 | 41 | | 8 | | 0.03 | 7 | 21 | 105 |
| 2 | 168 | 18 | 0.07 | 172 | | 12 | | 0.04 | 4 | 3 | -31 |
| 3 | 260 | 7 | 0.03 | 259 | | 5 | | 0.02 | -1 | 0.004 | -30 |
| 4 | 586 | 5 | 0.02 | 578 | | 15 | | 0.05 | -8 | -1 | 199 |
| 5 | 692 | 3 | 0.01 | 650 | | 13 | | 0.04 | -42 | -6 | 315 |
| Au |  (cm-1) | I - IR Intensity | I - IR Intensity |  (cm-1) | | I - IR Intensity | | I - IR Intensity | Δν | Δν% | ΔI% |
| (km/mol) | relative | (km/mol) | | relative | (cm-1) |  |  |
| 1 | 41 | 0 | 0.00 | 26 | | 0 | | 0.00 | -15 | 0 | 0 |
| 2 | 125 | 0 | 0.00 | 126 | | 0 | | 0.00 | 1 | 0 | 0 |
| 3 | 437 | 0 | 0.00 | 474 | | 0 | | 0.00 | 8 | 0 | 0 |
| 4 | 590 | 0 | 0.00 | 580 | | 0 | | 0.00 | -2 | 0 | 0 |

**Table S2. a.** Computed wavenumber and Raman Activities (A) of all Raman active vibrational transitions of F4TCNQ (DFT B3LYP/6-31G\*\* calculations), in the isolated state and in two different solvents with increasing dielectric constants. Relative Raman Activities (normalized to the strongest Raman transition) are also reported. Data concerning very weak transitions are displayed with a grey background. **b.** Computed wavenumber and Infrared Intensities (I) of all IR active vibrational transitions of F4TCNQ (DFT B3LYP/6-31G\*\* calculations), in the isolated state and in two different solvents with increasing dielectric constants. Relative Infrared Intensities (normalized to the strongest Infrared transition) are also reported. Data concerning very weak transition are displayed with a grey background.

Wavenumbers of the modes showing the largest wavenumber shift are highlighted in boldface.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **S2.a** | | isolated molecule | | | | | | PCM (ε=4.7113) | | | | | | PCM (ε=35.6880) | | | | | |
| AG | |  (cm-1) | | Raman Activity | | Raman Activity | |  (cm-1) | | Raman Activity | | Raman Activity | |  (cm-1) | | Raman Activity | | Raman Activity | |
| (Å4amu-1/2) | | relative | | (Å4amu-1/2) | | relative | | (Å4amu-1/2) | | relative | |
| 1 | | 138 | | 40 | | 0.01 | | 139 | | 93 | | 0.00 | | 139 | | 128 | | 0.00 | |
| 2 | | 297 | | 40 | | 0.01 | | 296 | | 107 | | 0.00 | | 295 | | 162 | | 0.00 | |
| 3 | | 342 | | 40 | | 0.01 | | 342 | | 140 | | 0.00 | | 342 | | 211 | | 0.00 | |
| 4 | | 489 | | 27 | | 0.00 | | 489 | | 123 | | 0.00 | | 490 | | 219 | | 0.00 | |
| 5 | | 631 | | 18 | | 0.00 | | 636 | | 165 | | 0.00 | | 637 | | 312 | | 0.01 | |
| 6 | | 902 | | 9 | | 0.00 | | 902 | | 45 | | 0.00 | | 901 | | 74 | | 0.00 | |
| 7 | | 1323 | | 116 | | 0.02 | | 1318 | | 452 | | 0.01 | | 1317 | | 768 | | 0.01 | |
| 8 | | **1510** | | 7712 | | 1.00 | | **1517** | | 34470 | | 1.00 | | **1521** | | 58620 | | 1.00 | |
| 9 | | 1711 | | 2654 | | 0.34 | | 1715 | | 12830 | | 0.37 | | 1718 | | 22890 | | 0.39 | |
| 10 | | 2338 | | 4343 | | 0.56 | | 2340 | | 16140 | | 0.47 | | 2340 | | 25320 | | 0.43 | |
| B3G | |  (cm-1) | | Raman Activity | | Raman Activity | |  (cm-1) | | Raman Activity | | Raman Activity | |  (cm-1) | | Raman Activity | | Raman Activity | |
| (Å4amu-1/2) | | relative | | (Å4amu-1/2) | | relative | | (Å4amu-1/2) | | relative | |
| 1 | | 156 | | 2 | | 0.00 | | 157 | | 2 | | 0.00 | | 158 | | 2 | | 0.00 | |
| 2 | | 247 | | 10 | | 0.00 | | 248 | | 20 | | 0.00 | | 248 | | 25 | | 0.00 | |
| 3 | | 425 | | 2 | | 0.00 | | 423 | | 12 | | 0.00 | | 422 | | 24 | | 0.00 | |
| 4 | | 460 | | 0.27 | | 0.00 | | 465 | | 0.16 | | 0.00 | | 465 | | 0.01 | | 0.00 | |
| 5 | | 783 | | 9 | | 0.00 | | 783 | | 33 | | 0.00 | | 783 | | 52 | | 0.00 | |
| 6 | | 1167 | | 0.12 | | 0.00 | | 1164 | | 0.11 | | 0.00 | | 1162 | | 0.29 | | 0.00 | |
| 7 | | 1218 | | 187 | | 0.02 | | 1217 | | 680 | | 0.02 | | 1216 | | 1055 | | 0.02 | |
| 8 | | **1490** | | 145 | | 0.02 | | **1480** | | 618 | | 0.02 | | **1476** | | 1046 | | 0.02 | |
| 9 | | 2322 | | 2263 | | 0.29 | | 2323 | | 6601 | | 0.19 | | 2323 | | 9527 | | 0.16 | |
| B2G | |  (cm-1) | | Raman Activity | | Raman Activity | |  (cm-1) | | Raman Activity | | Raman Activity | |  (cm-1) | | Raman Activity | | Raman Activity | |
| (Å4amu-1/2) | | relative | | (Å4amu-1/2) | | relative | | (Å4amu-1/2) | | relative | |
| 1 | | 85 | | 0.53 | | 0.00 | | 80 | | 0.38 | | 0.00 | | 83 | | 0.21 | | 0.00 | |
| 2 | | 218 | | 0.09 | | 0.00 | | 218 | | 0.03 | | 0.00 | | 219 | | 0.20 | | 0.00 | |
| 3 | | 416 | | 0.70 | | 0.00 | | 415 | | 2 | | 0.00 | | 418 | | 4 | | 0.00 | |
| 4 | | **520** | | 11 | | 0.00 | | **530** | | 32 | | 0.00 | | **546** | | 46 | | 0.00 | |
| 5 | | 666 | | 64 | | 0.01 | | 666 | | 173 | | 0.01 | | 670 | | 267 | | 0.00 | |
| B1G | |  (cm-1) | | Raman Activity | | Raman Activity | |  (cm-1) | | Raman Activity | | Raman Activity | |  (cm-1) | | Raman Activity | | Raman Activity | |
| (Å4amu-1/2) | | relative | | (Å4amu-1/2) | | relative | | (Å4amu-1/2) | | relative | |
| 1 | | 50 | | 2 | | 0.00 | | 47 | | 3 | | 0.00 | | 49 | | 4 | | 0.00 | |
| 2 | | 380 | | 0.17 | | 0.00 | | 375 | | 0.02 | | 0.00 | | 383 | | 0.04 | | 0.00 | |
| 3 | | 460 | | 6 | | 0.00 | | 461 | | 12 | | 0.00 | | 464 | | 15 | | 0.00 | |
| B1u | |  (cm-1) | | IR Intensity | | IR Intensity | |  (cm-1) | | IR Intensity | | IR Intensity | |  (cm-1) | | IR Intensity | | IR Intensity | |
| (km/mol) | | relative | | (km/mol) | | relative | | (km/mol) | | relative | |
| 1 | | 155 | | 9 | | 0.04 | | 156 | | 17 | | 0.04 | | 156 | | 22 | | 0.03 | |
| 2 | | 318 | | 3 | | 0.01 | | 317 | | 7 | | 0.02 | | 317 | | 11 | | 0.02 | |
| 3 | | 500 | | 0.02 | | 0.00 | | 502 | | 0.13 | | 0.00 | | 501 | | 0.15 | | 0.00 | |
| 4 | | 631 | | 1 | | 0.01 | | 636 | | 1 | | 0.00 | | 637 | | 1 | | 0.00 | |
| 5 | | 813 | | 41 | | 0.17 | | 813 | | 90 | | 0.20 | | 812 | | 119 | | 0.18 | |
| 6 | | 1162 | | 6 | | 0.03 | | 1162 | | 31 | | 0.07 | | 1161 | | 54 | | 0.08 | |
| 7 | | **1388** | | 177 | | 0.73 | | **1377** | | 460 | | 1.00 | | **1374** | | 653 | | 1.00 | |
| 8 | | 1583 | | 29 | | 0.12 | | 1583 | | 184 | | 0.40 | | 1583 | | 342 | | 0.52 | |
| 9 | | 2342 | | 0.53 | | 0.00 | | 2343 | | 80 | | 0.17 | | 2342 | | 205 | | 0.31 | |
| B2u | |  (cm-1) | | IR Intensity | | IR Intensity | |  (cm-1) | | IR Intensity | | IR Intensity | |  (cm-1) | | IR Intensity | | IR Intensity | |
| (km/mol) | | relative | | (km/mol) | | relative | | (km/mol) | | relative | |
| 1 | | 105 | | 4.039 | | 0.02 | | 105 | | 7 | | 0.01 | | 105 | | 8 | | 0.01 | |
| 2 | | 257 | | 2.137 | | 0.01 | | 259 | | 4 | | 0.01 | | 260 | | 5 | | 0.01 | |
| 3 | | 328 | | 0.62 | | 0.00 | | 327 | | 1 | | 0.00 | | 327 | | 1 | | 0.00 | |
| 4 | | 475 | | 0.16 | | 0.00 | | 479 | | 0.34 | | 0.00 | | 479 | | 0.47 | | 0.00 | |
| 5 | | 1000 | | 109 | | 0.45 | | 996 | | 176 | | 0.38 | | 994 | | 212 | | 0.32 | |
| 6 | | 1218 | | 5 | | 0.02 | | 1216 | | 10 | | 0.02 | | 1215 | | 15 | | 0.02 | |
| 7 | | 1415 | | 82 | | 0.34 | | 1417 | | 111 | | 0.24 | | 1419 | | 122 | | 0.19 | |
| 8 | | 1639 | | 241 | | 1.00 | | 1638 | | 372 | | 0.81 | | 1639 | | 435 | | 0.67 | |
| 9 | | 2322 | | 6 | | 0.02 | | 2323 | | 0.25 | | 0.00 | | 2323 | | 5 | | 0.01 | |
| B3u | |  (cm-1) | | IR Intensity | | IR Intensity | |  (cm-1) | | IR Intensity | | IR Intensity | |  (cm-1) | | IR Intensity | | IR Intensity | |
| (km/mol) | | relative | | (km/mol) | | relative | | (km/mol) | | relative | |
| 1 | | **34** | | 4 | | 0.02 | | **30** | | 6 | | 0.01 | | **22** | | 7 | | 0.01 | |
| 2 | | 168 | | 18 | | 0.07 | | 168 | | 25 | | 0.05 | | 170 | | 28 | | 0.04 | |
| 3 | | 260 | | 7 | | 0.03 | | 259 | | 9 | | 0.02 | | 258 | | 11 | | 0.02 | |
| 4 | | 586 | | 5 | | 0.02 | | 586 | | 7 | | 0.02 | | 594 | | 10 | | 0.01 | |
| 5 | | 692 | | 3 | | 0.01 | | 692 | | 6 | | 0.01 | | 697 | | 8 | | 0.01 | |
| Au | |  (cm-1) | | IR Intensity | | IR Intensity | |  (cm-1) | | IR Intensity | | IR Intensity | |  (cm-1) | | IR Intensity | | IR Intensity | |
| (km/mol) | | relative | | (km/mol) | | relative | | (km/mol) | | relative | |
| 1 | | 41 | | 0 | | 0.00 | | 36 | | 0 | | 0.00 | | 37 | | 0 | | 0.00 | |
| 2 | | 125 | | 0 | | 0.00 | | 122 | | 0 | | 0.00 | | 125 | | 0 | | 0.00 | |
| 3 | | 437 | | 0 | | 0.00 | | 483 | | 0 | | 0.00 | | 447 | | 0 | | 0.00 | |
| 4 | | 590 | | 0 | | 0.00 | | 585 | | 0 | | 0.00 | | 592 | | 0 | | 0.00 | |