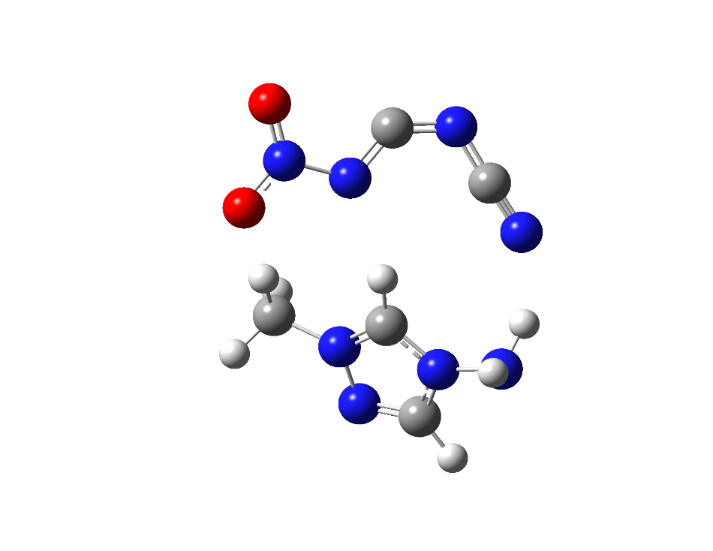
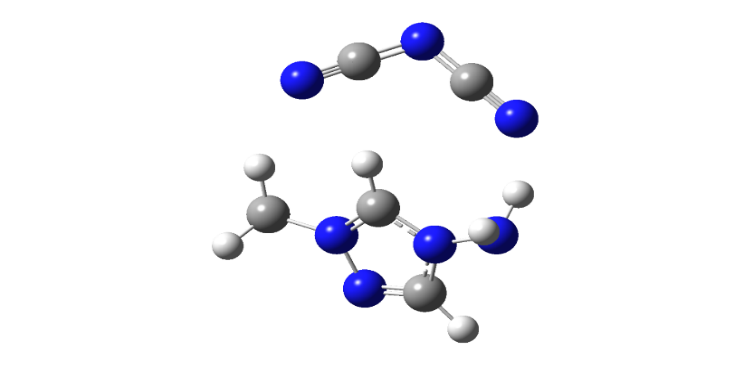
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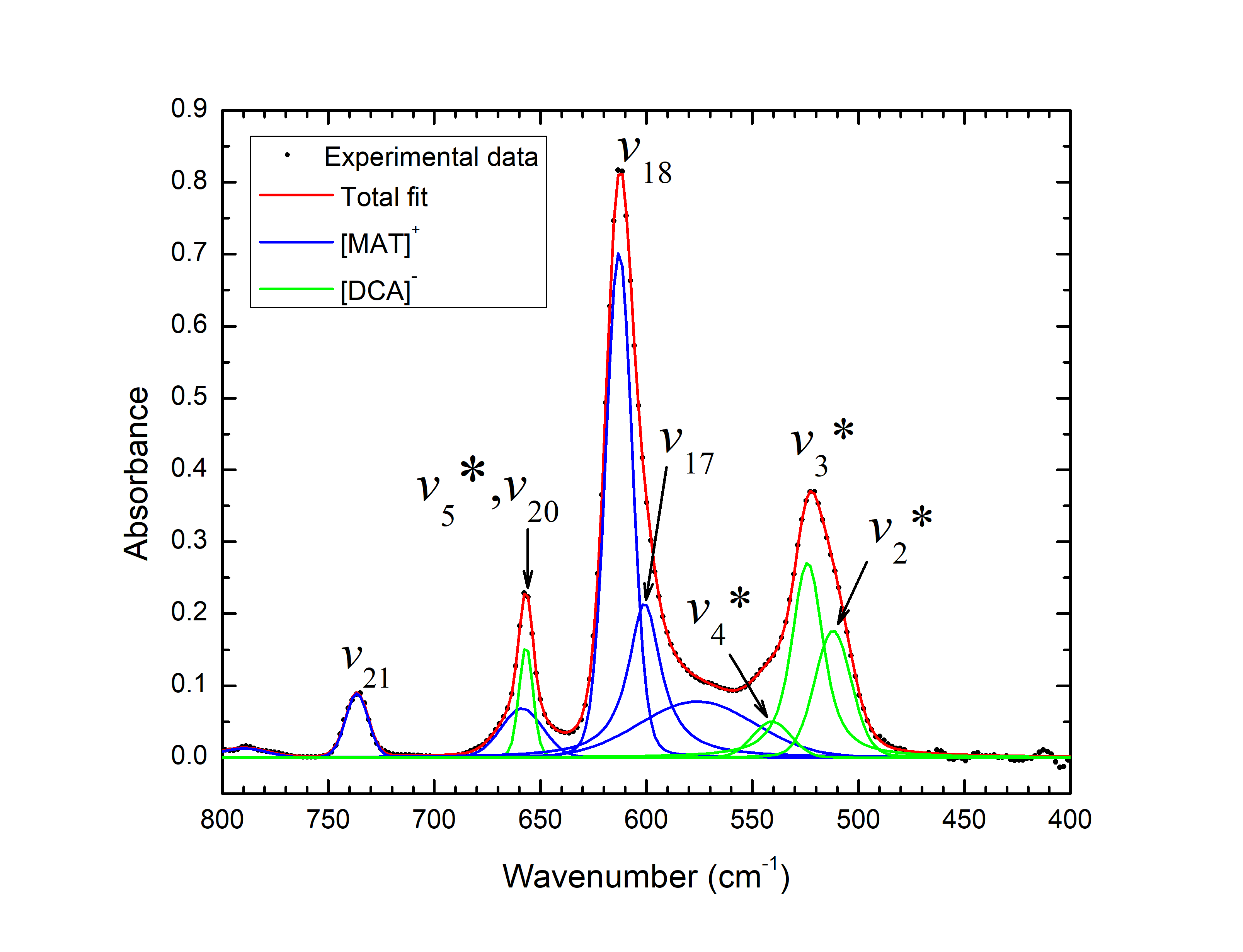
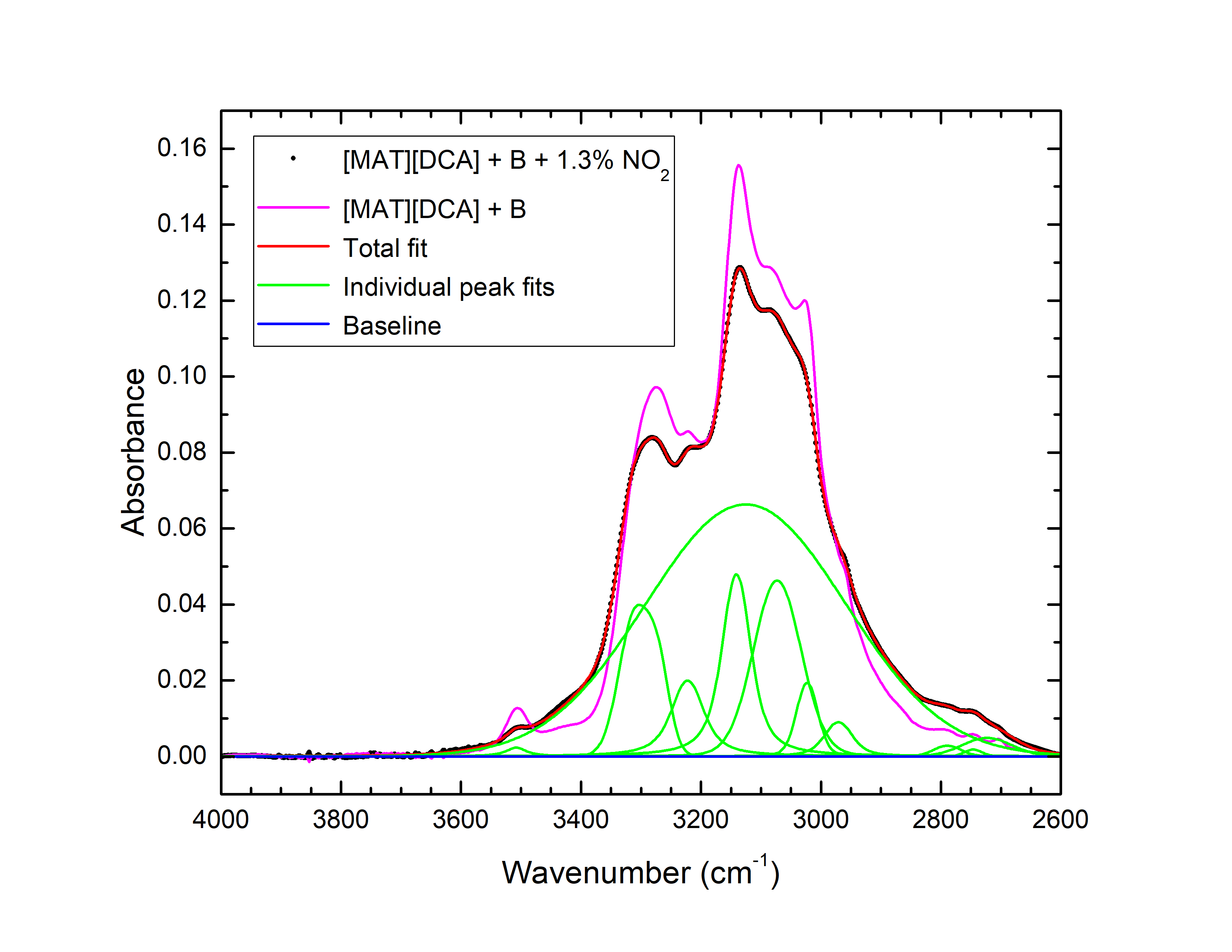
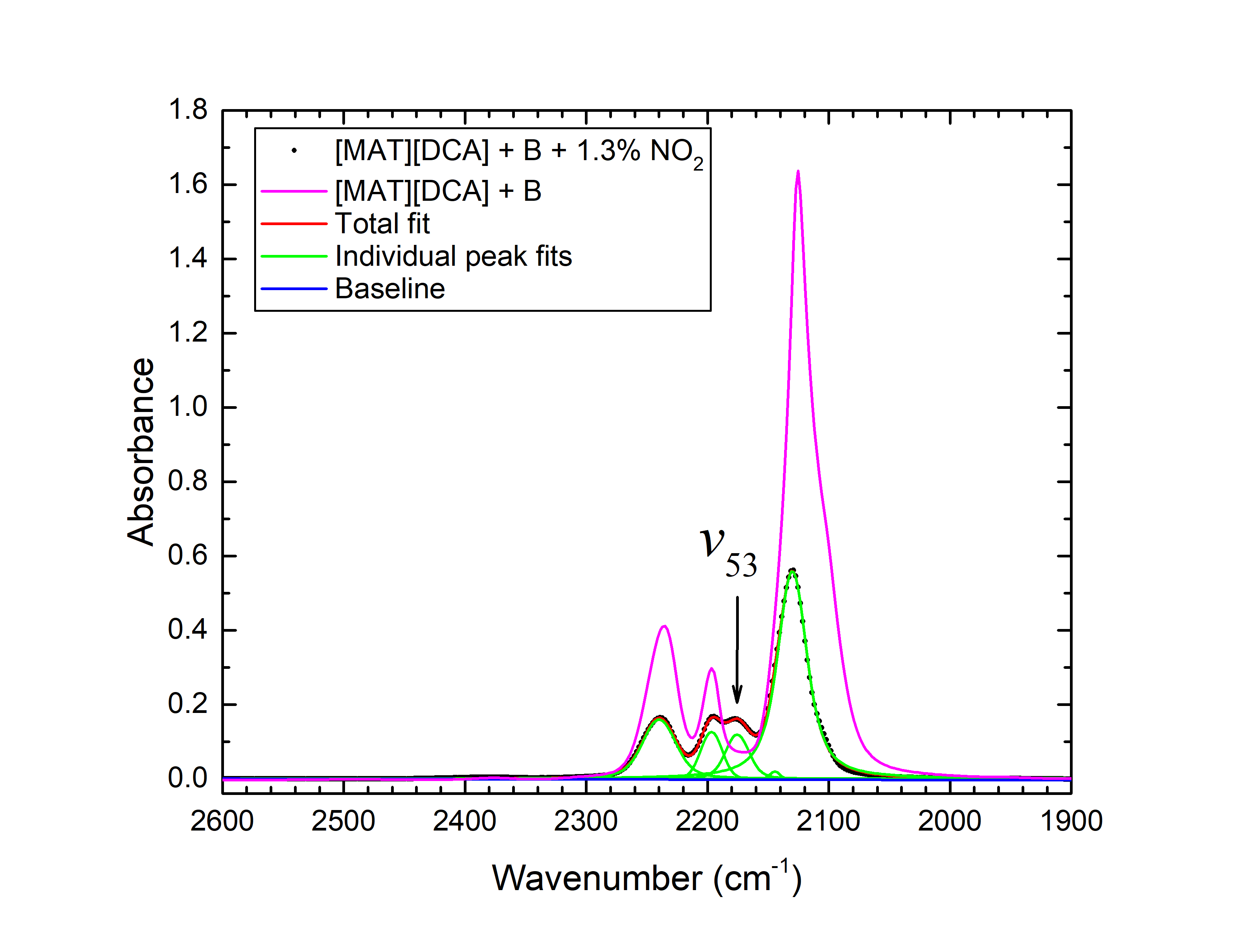
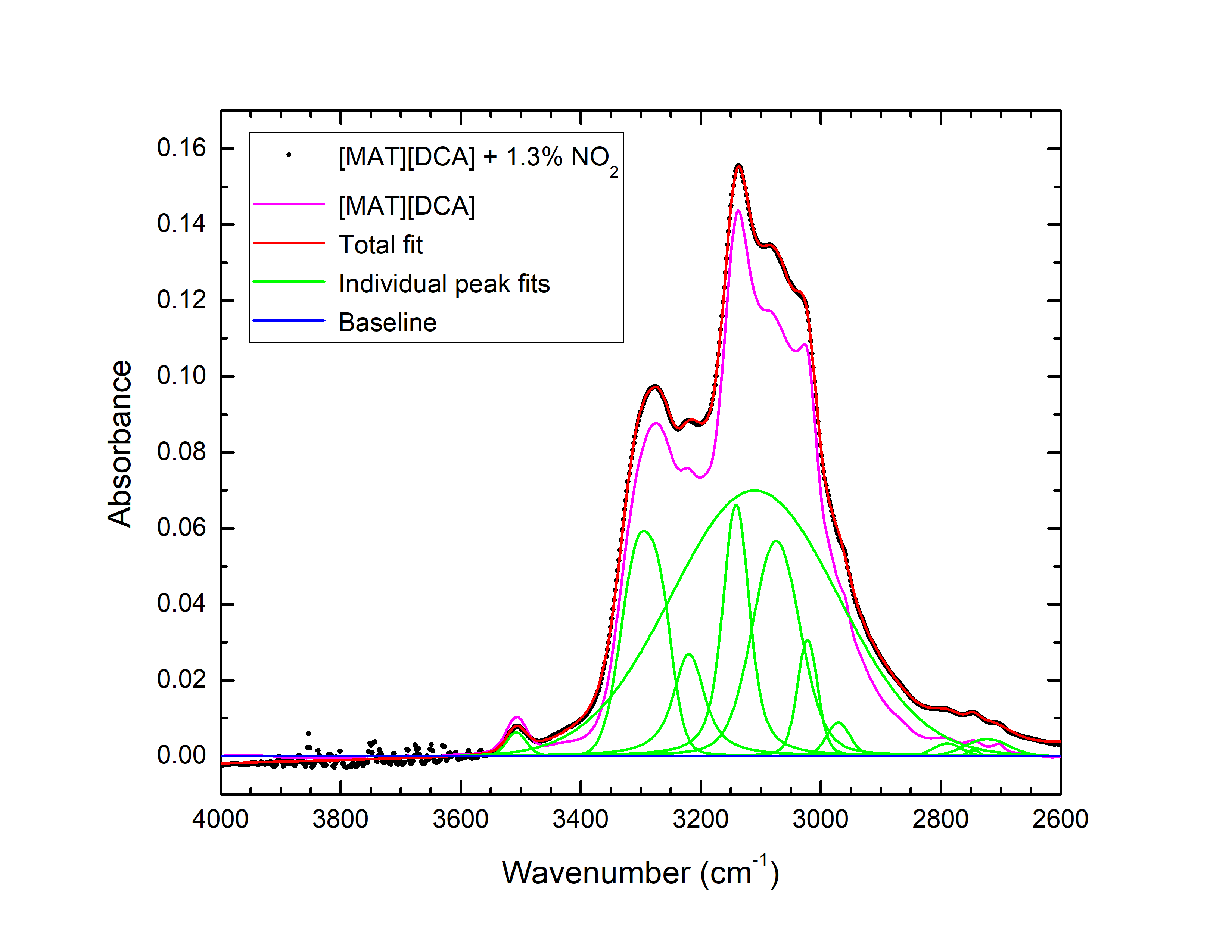
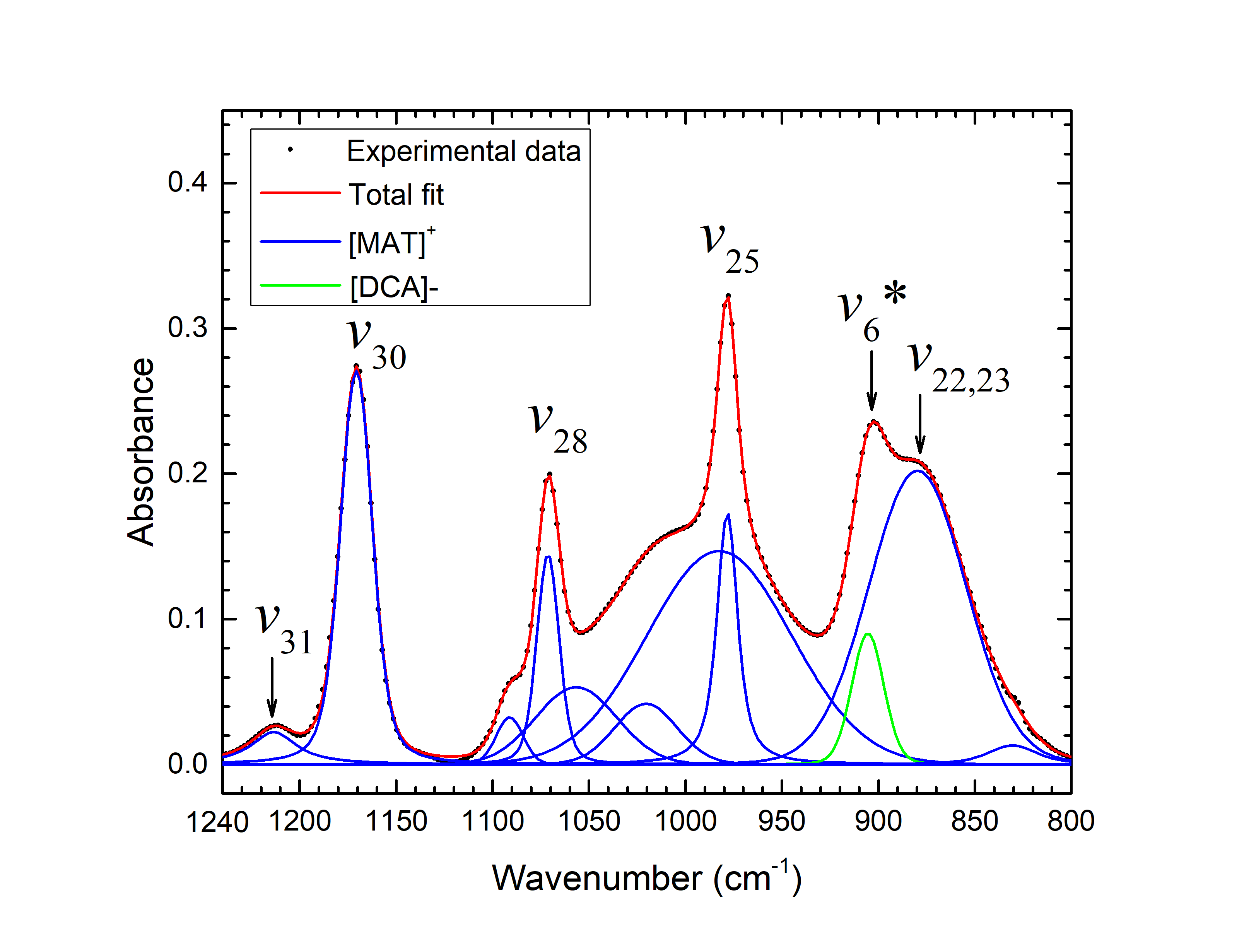
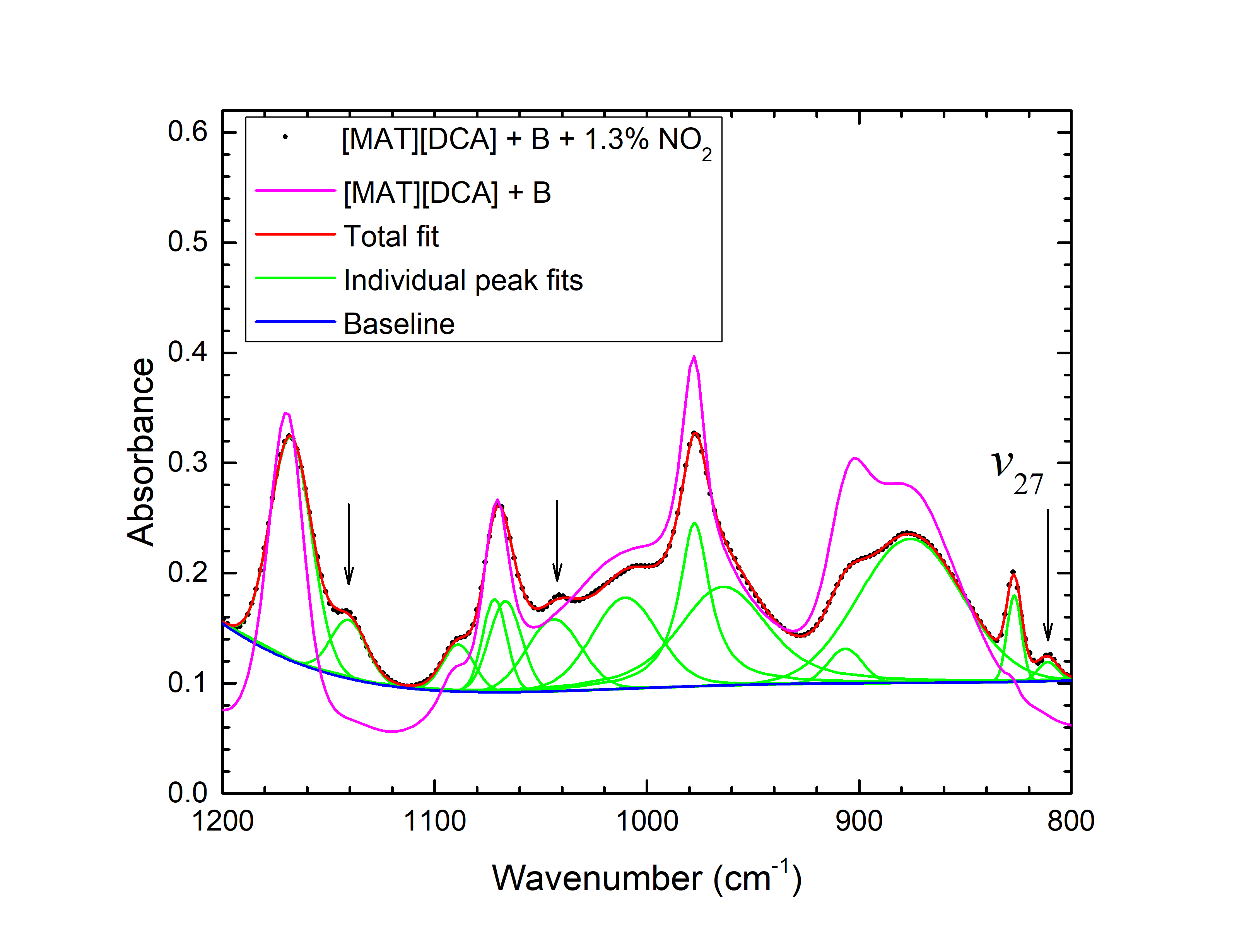
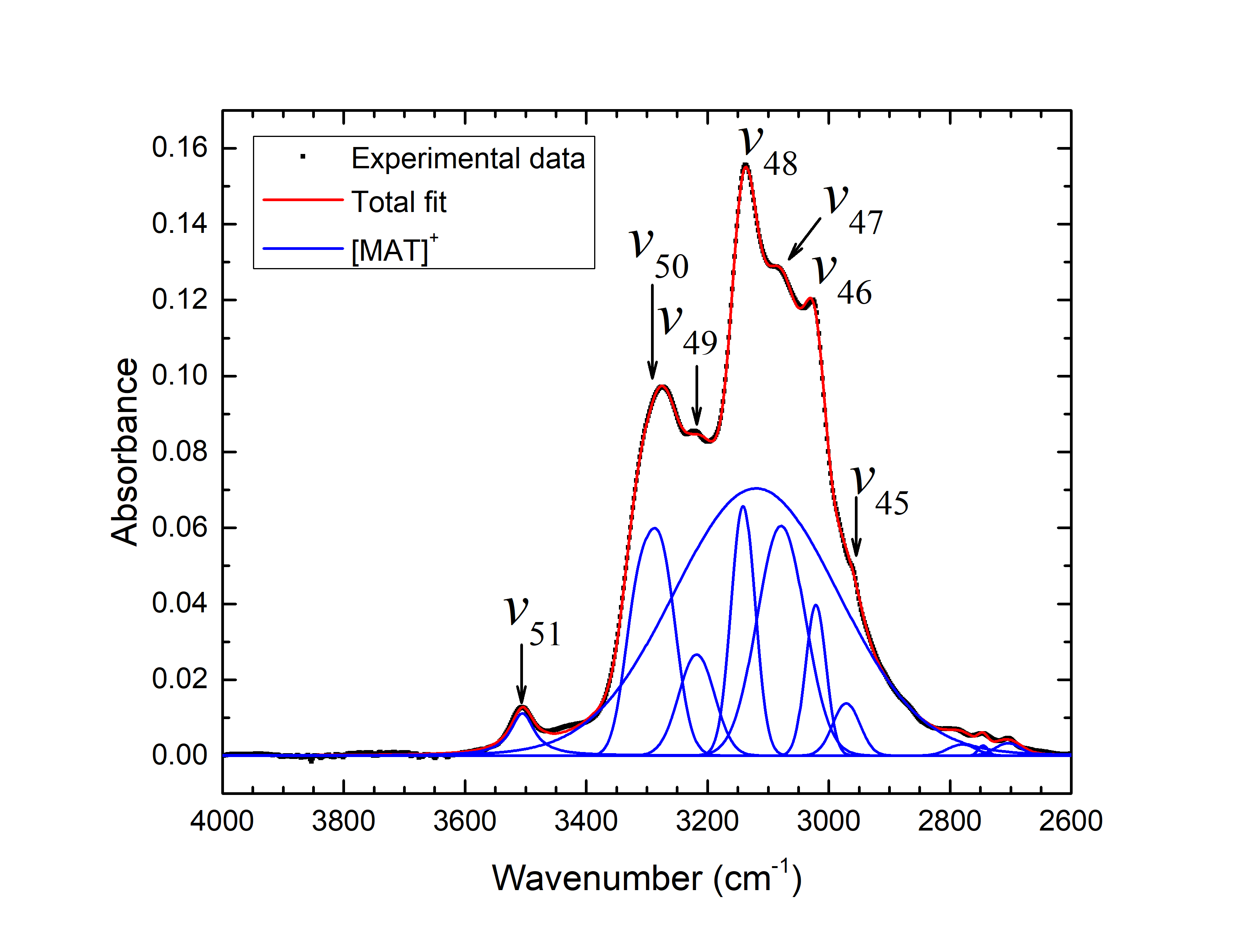
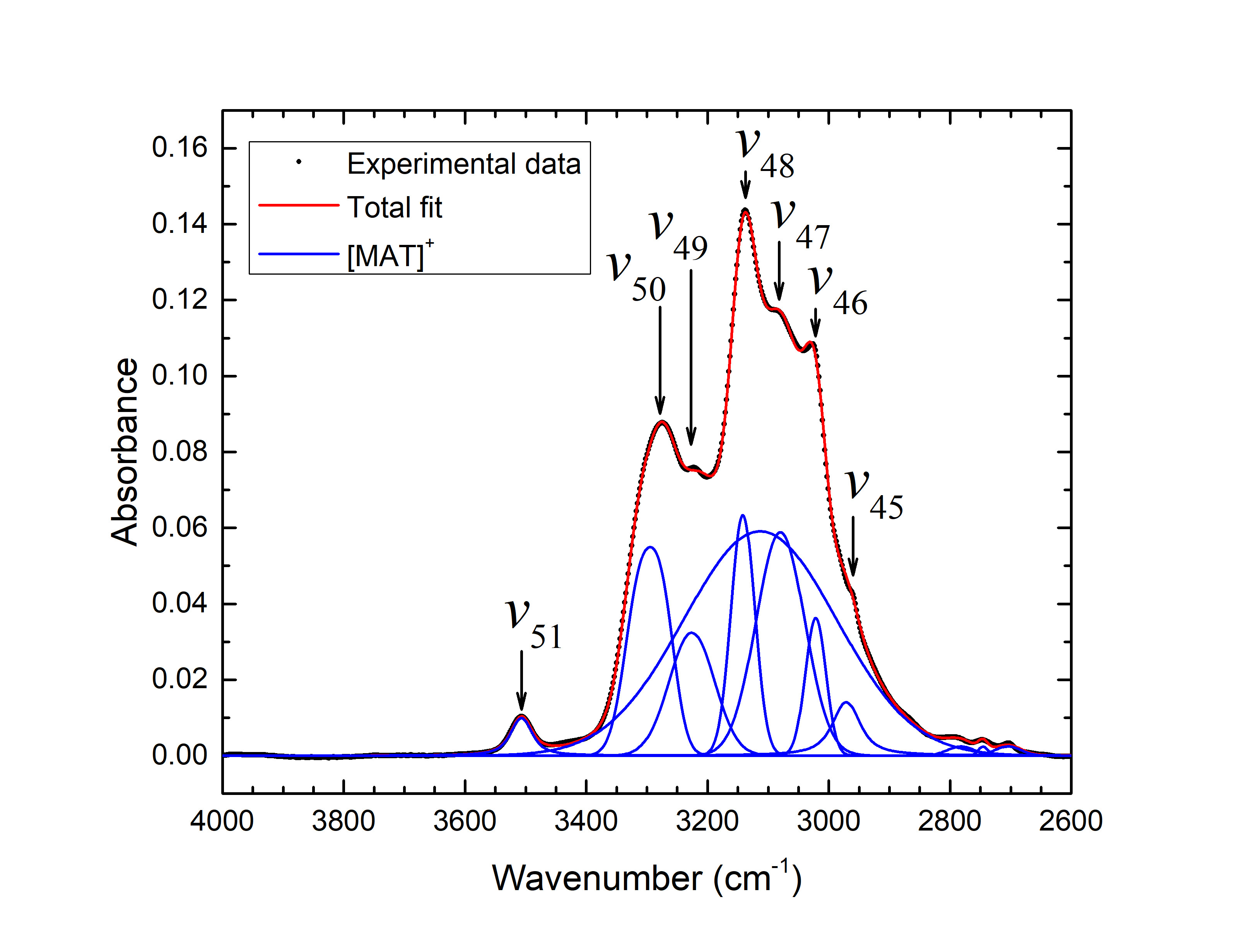
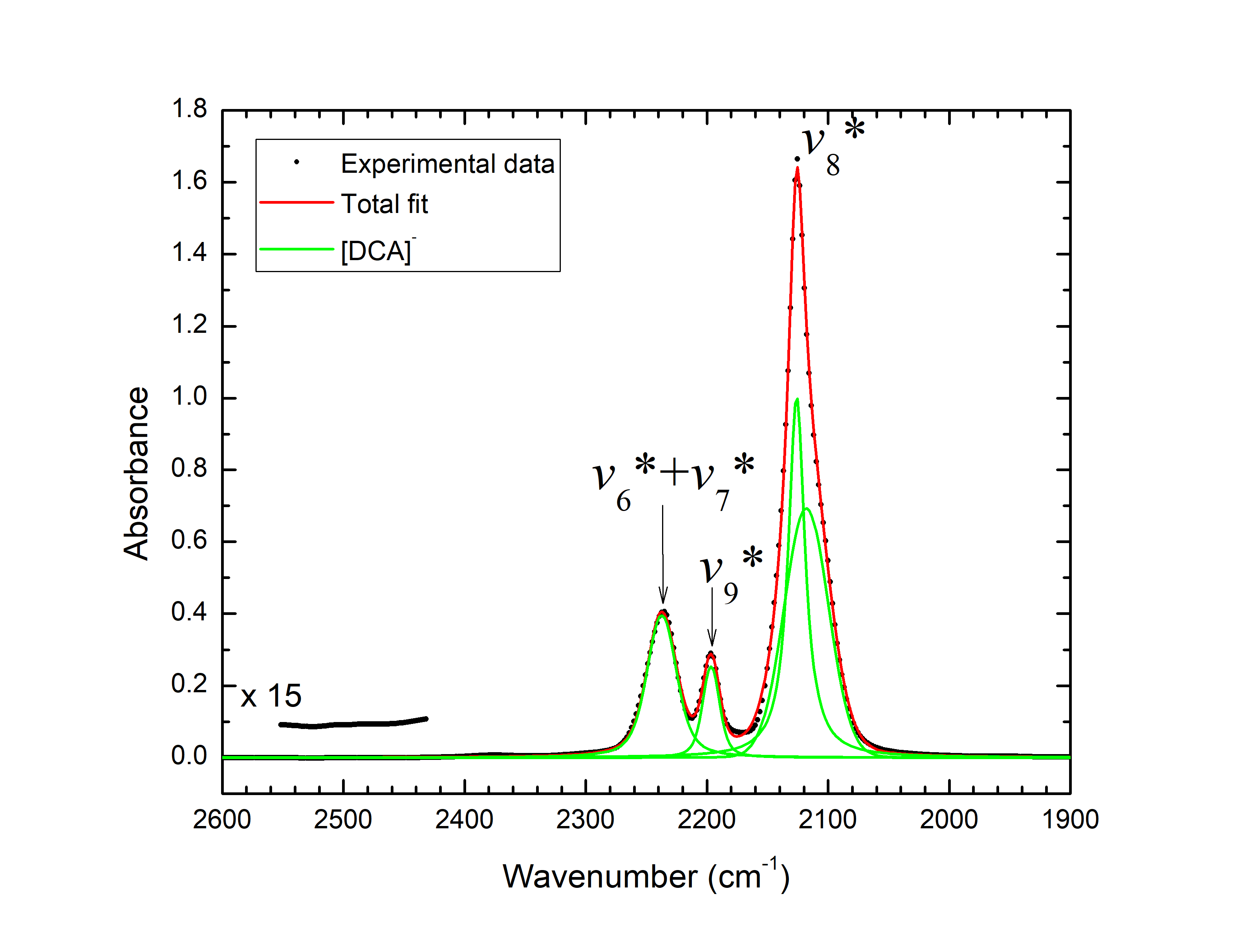
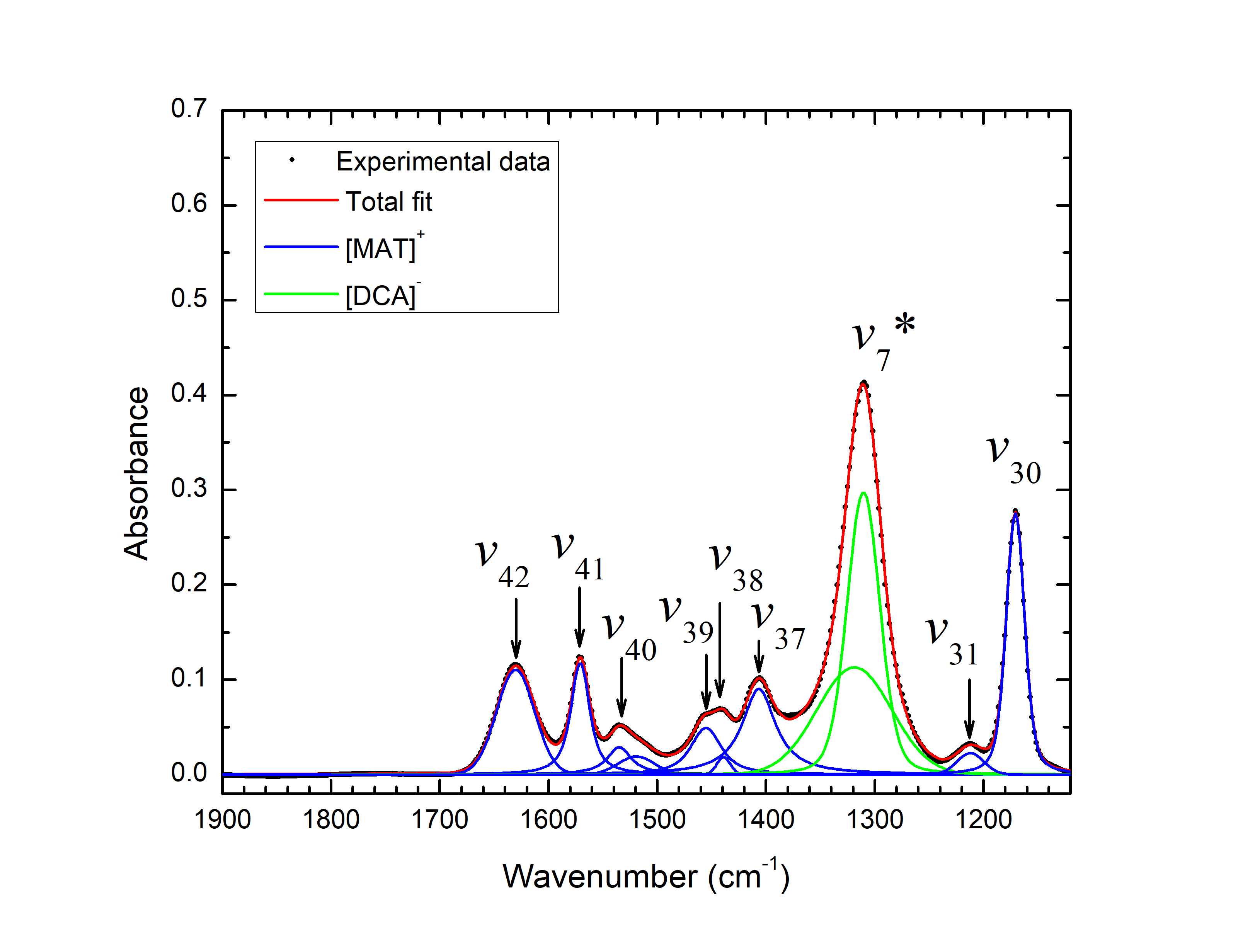
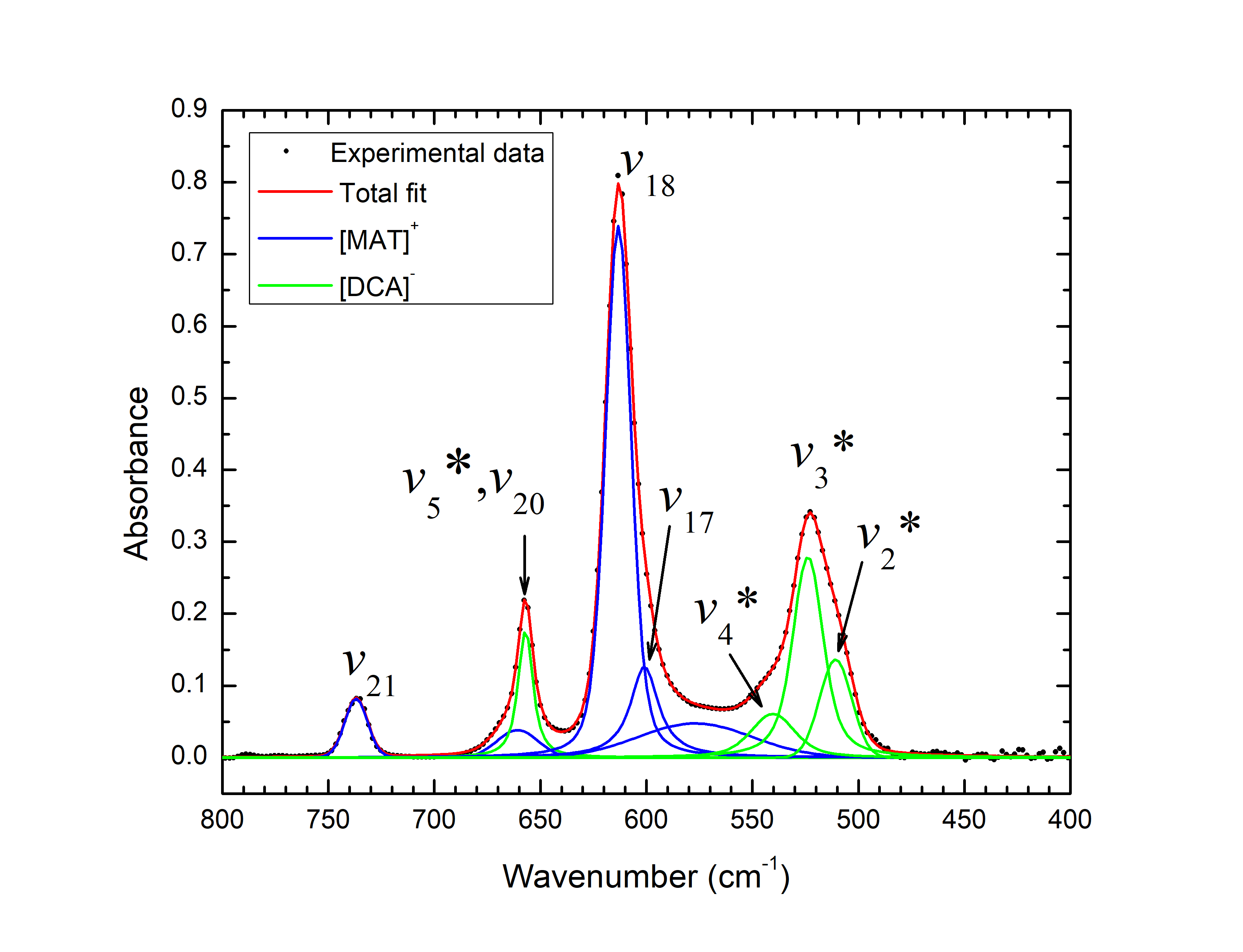
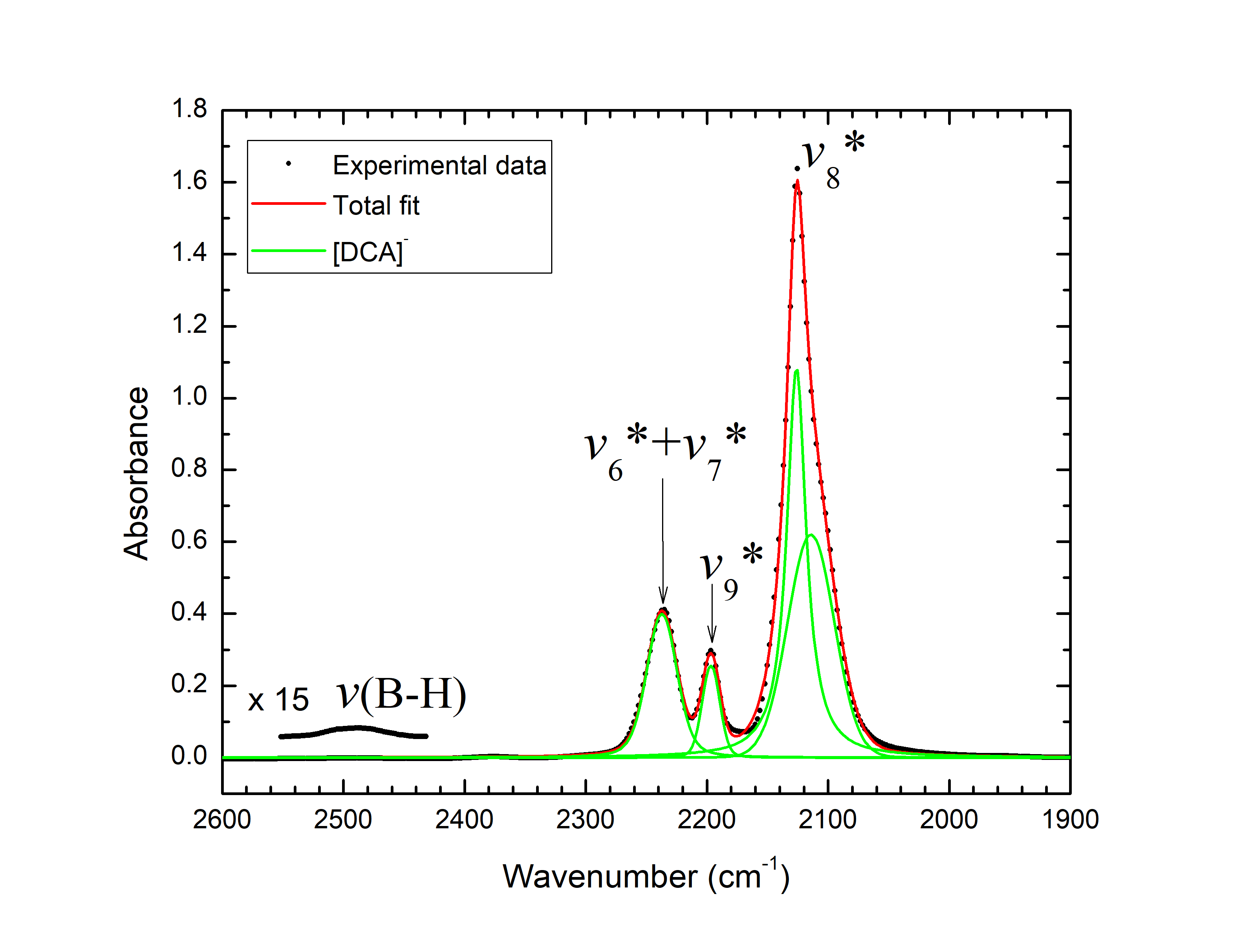
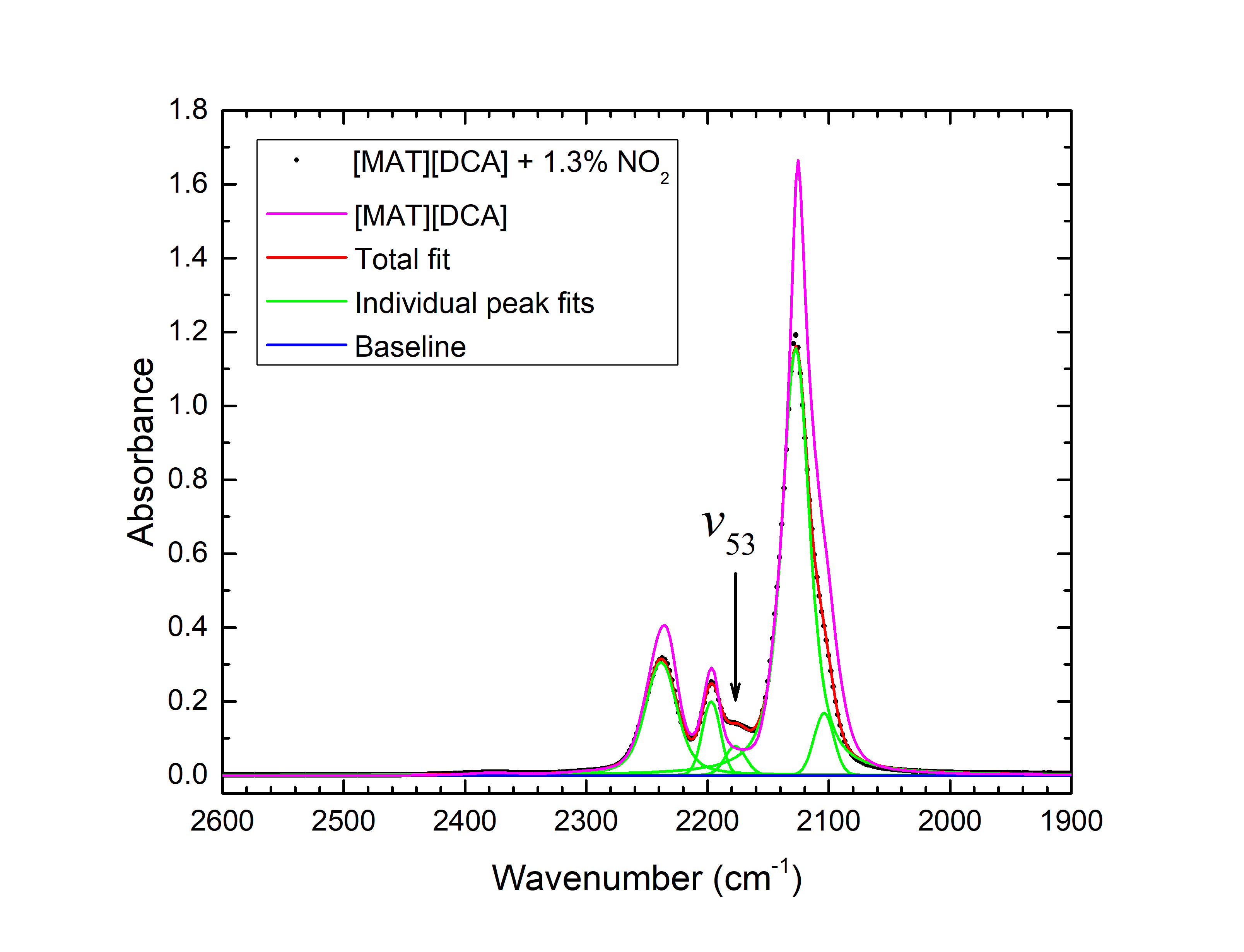
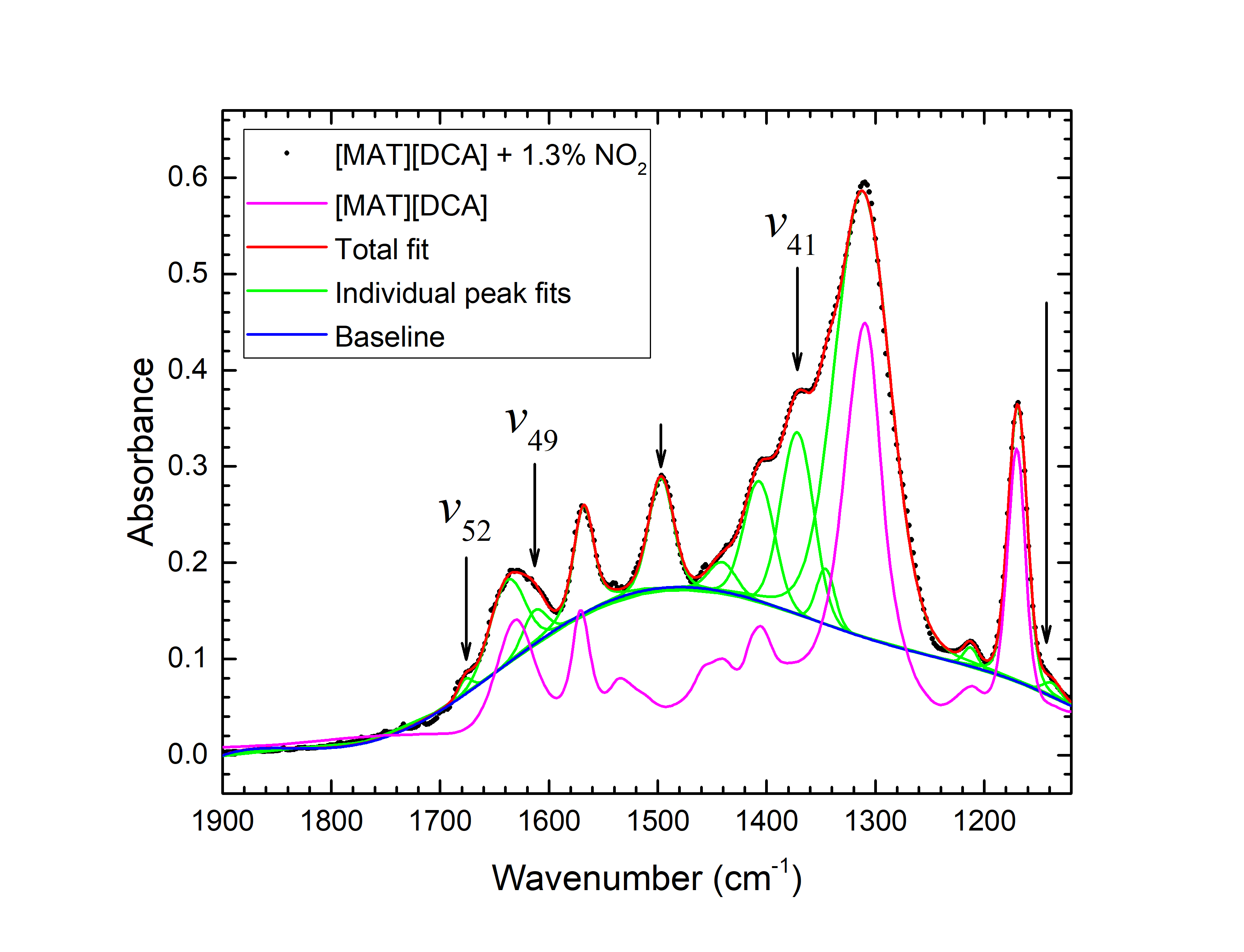
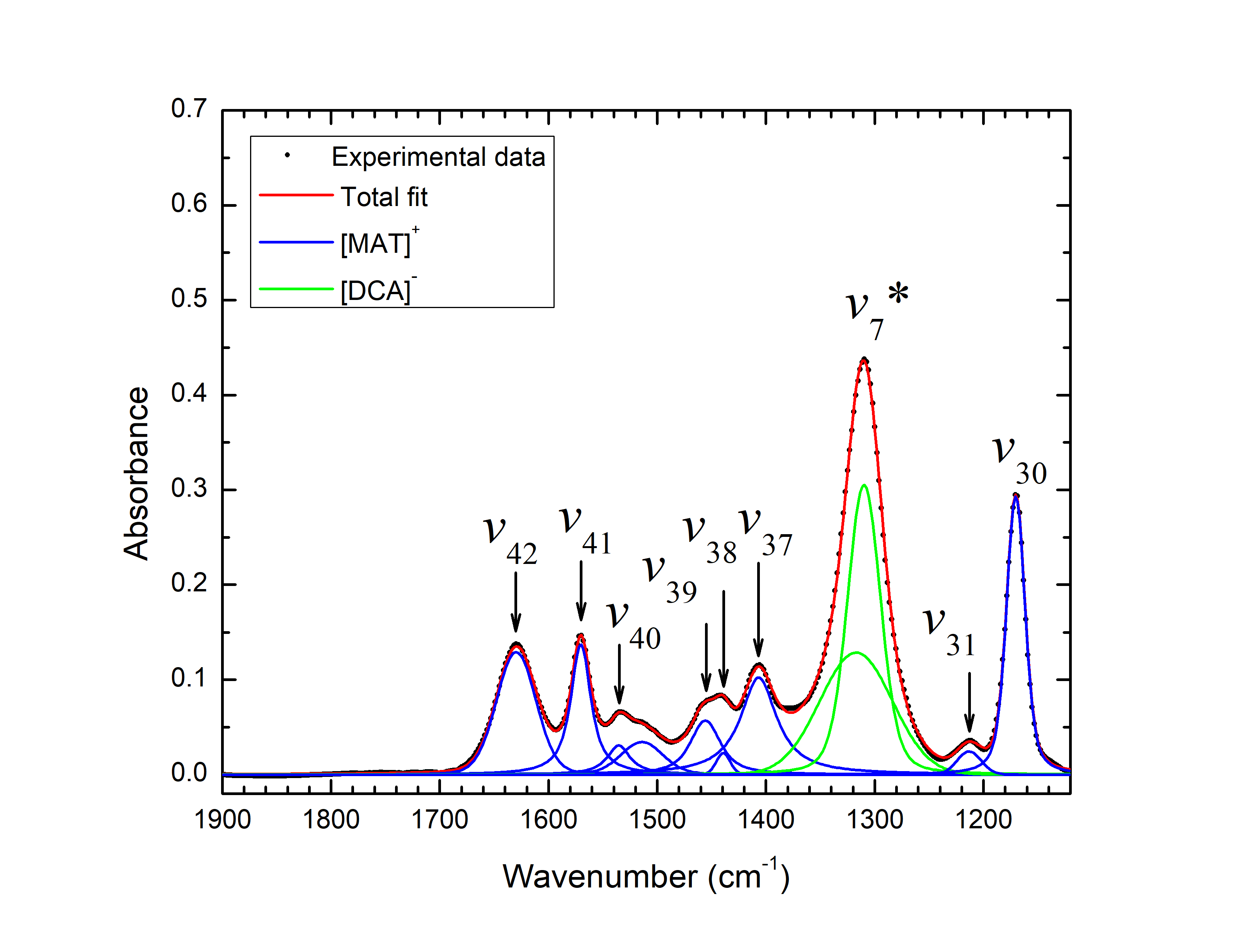
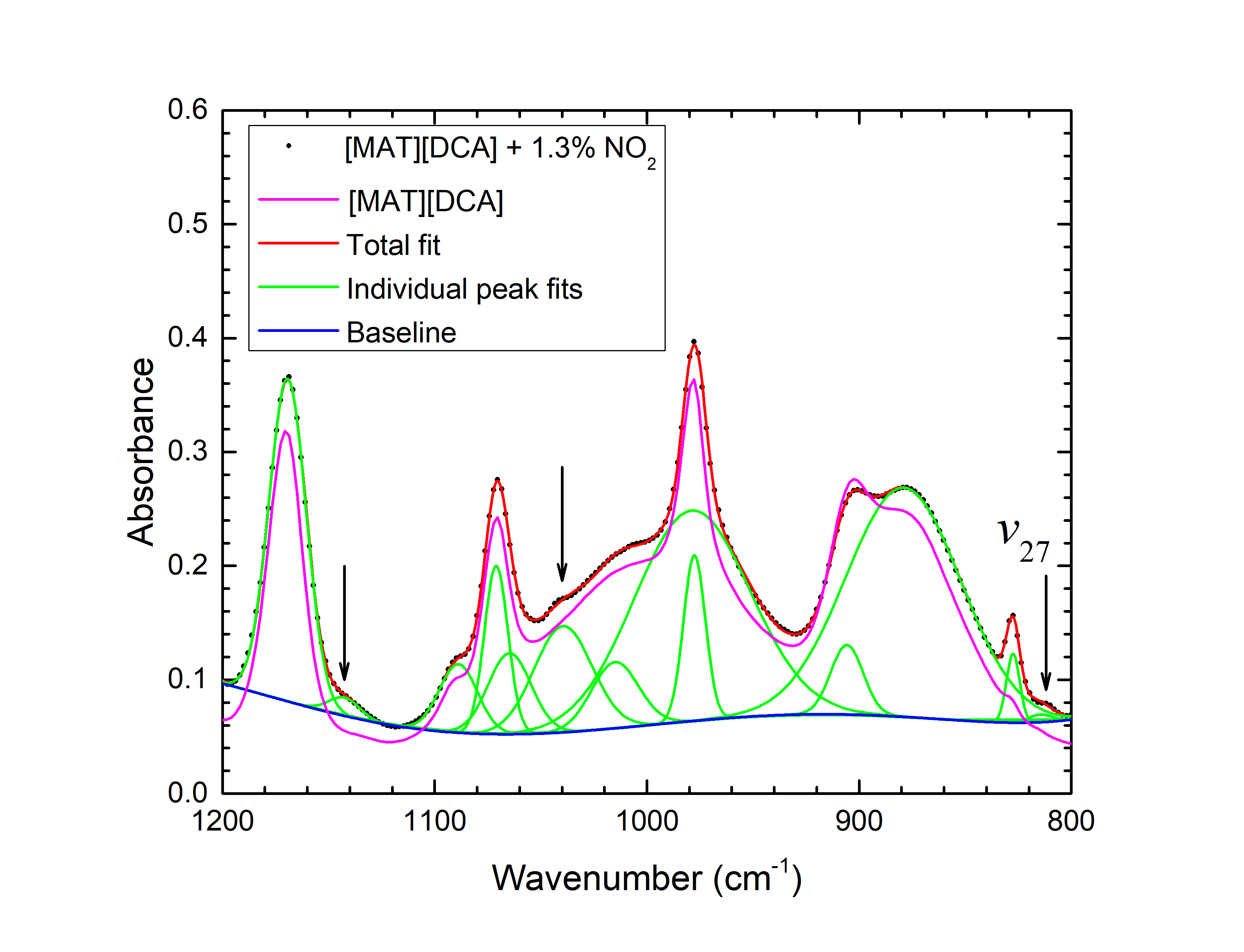
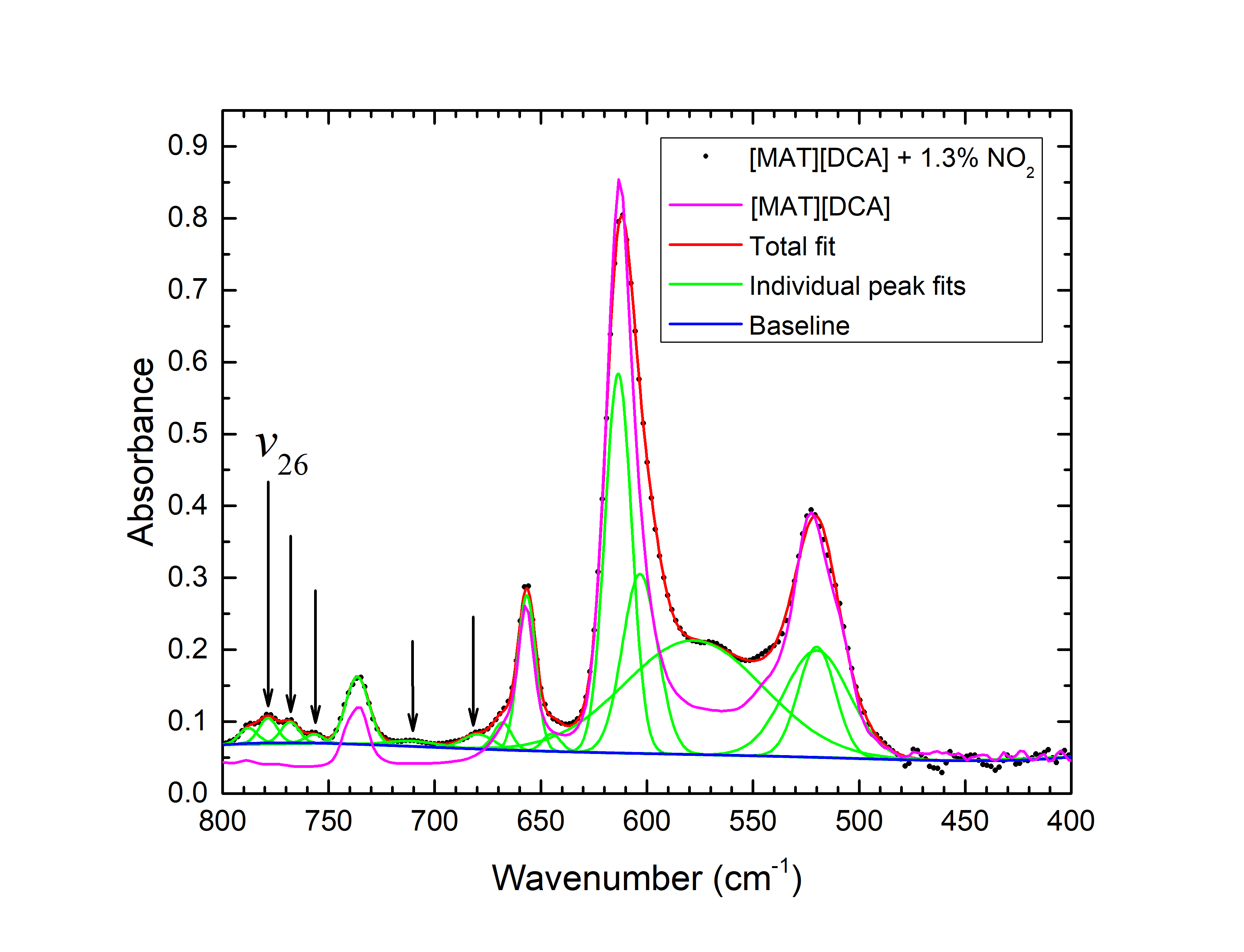
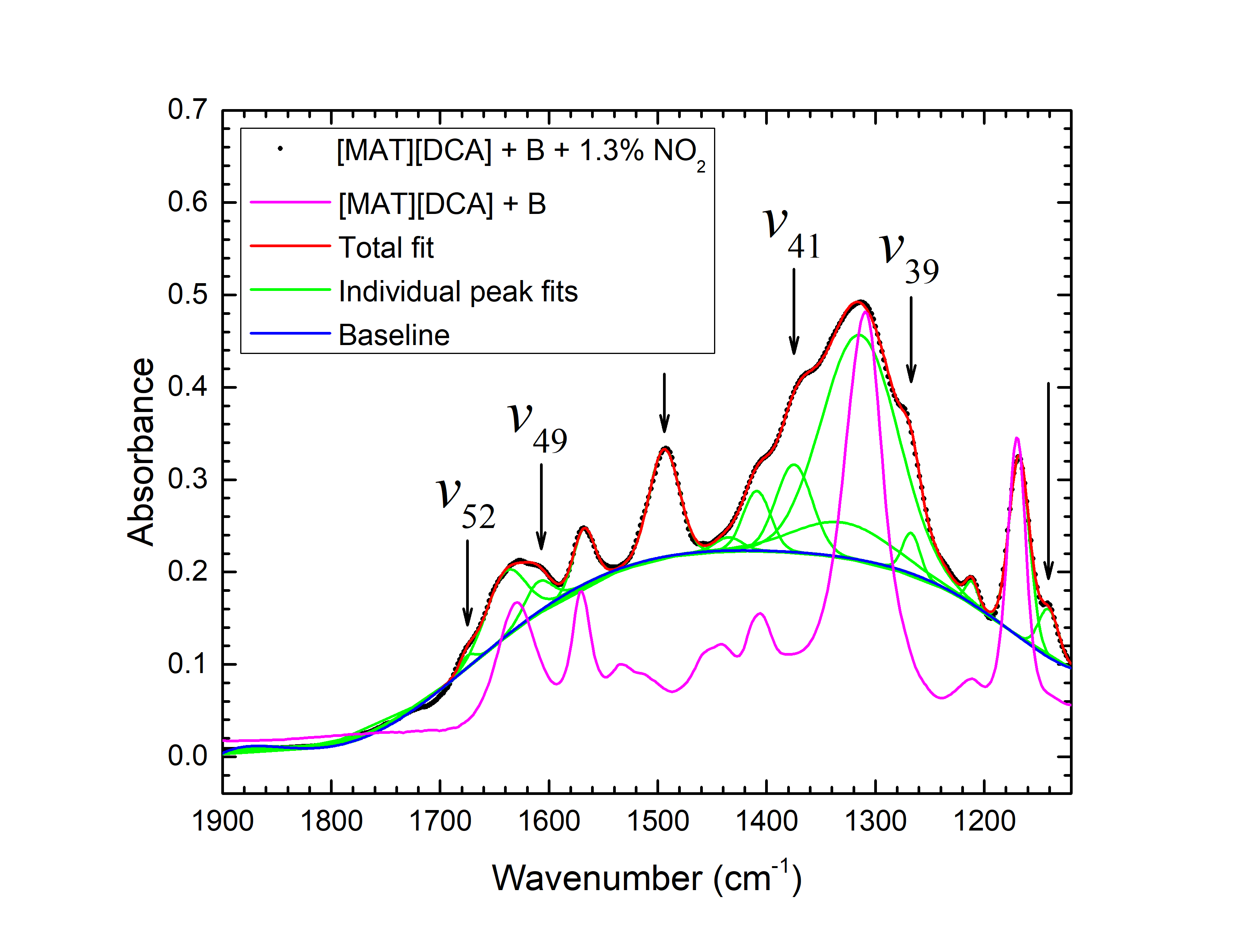
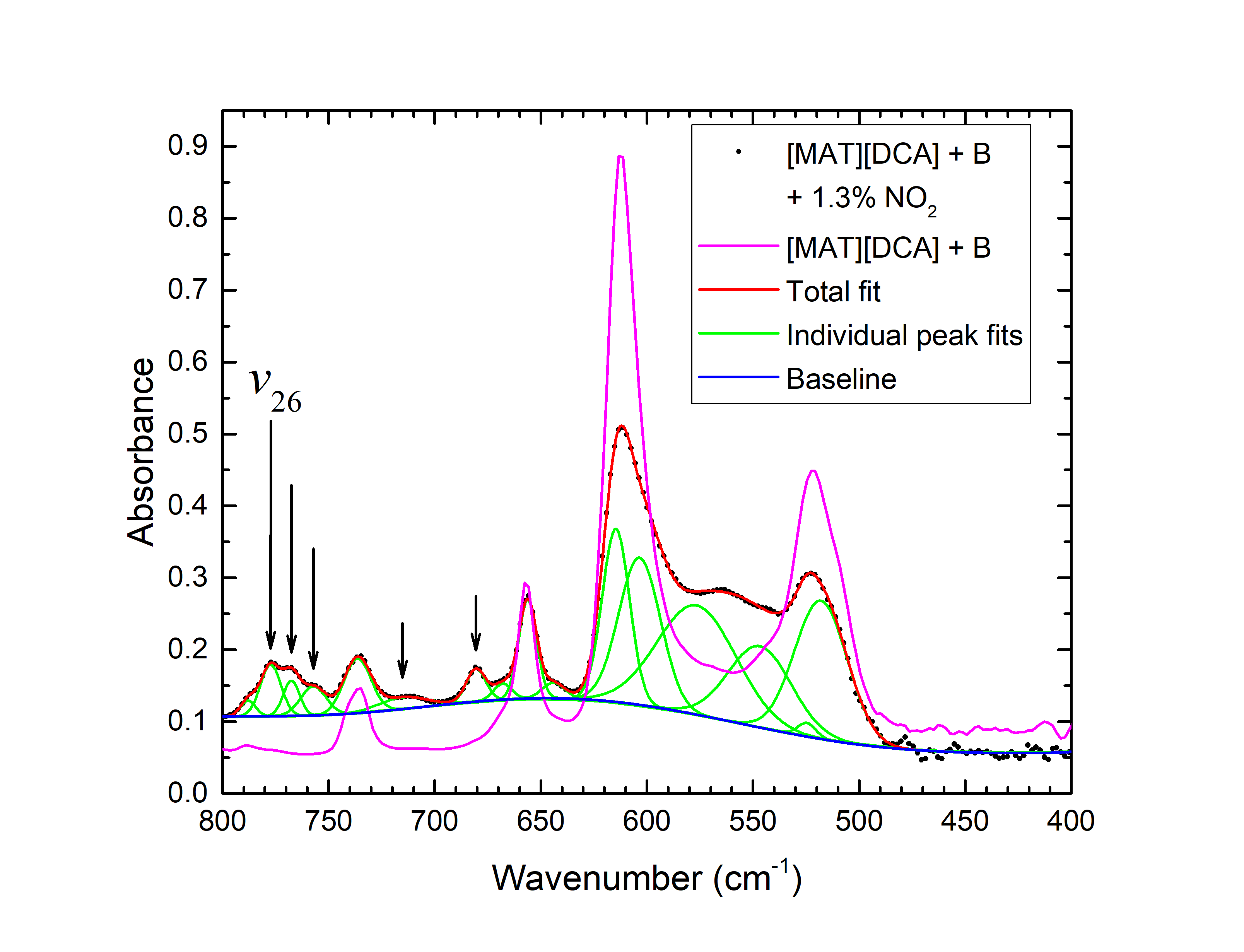
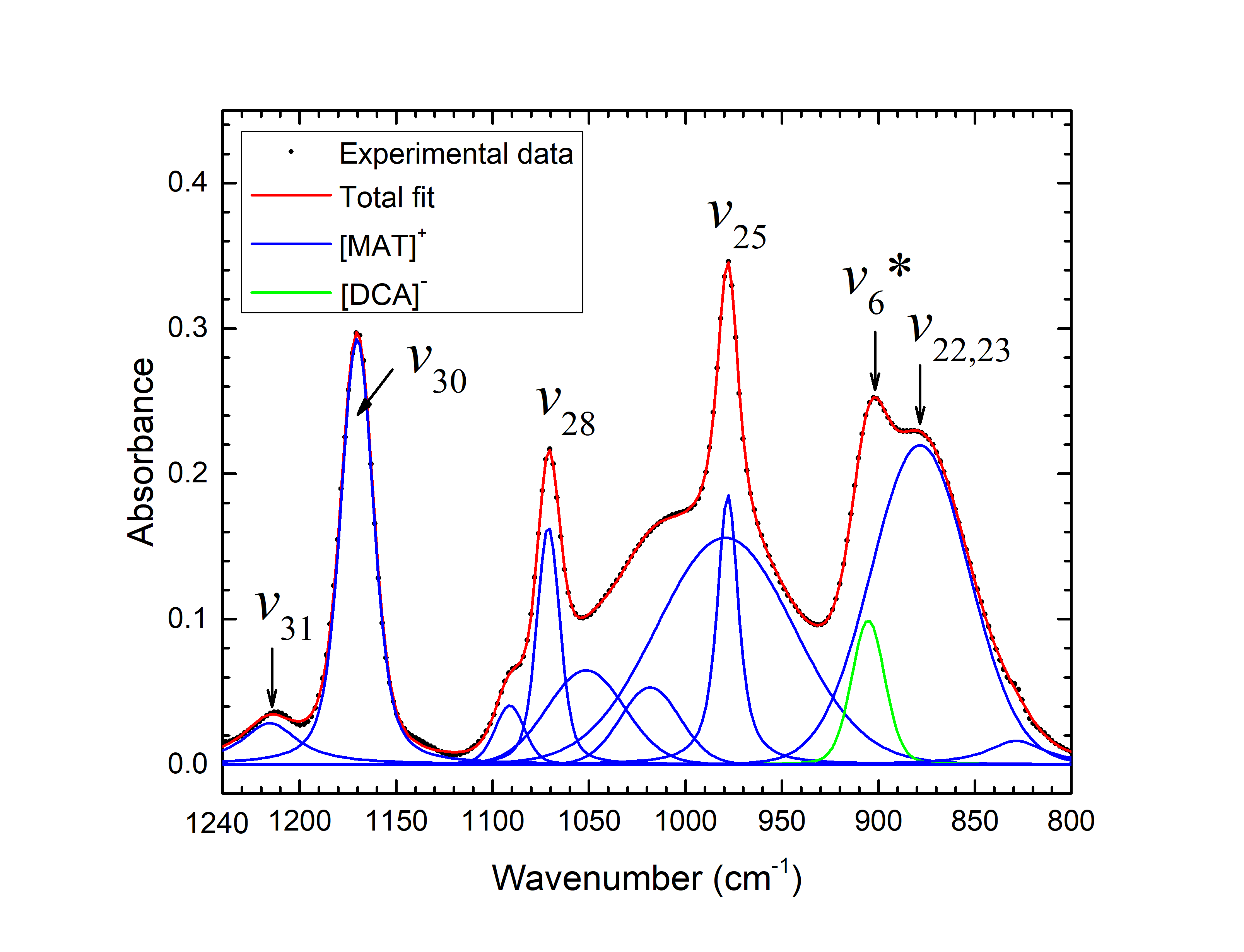
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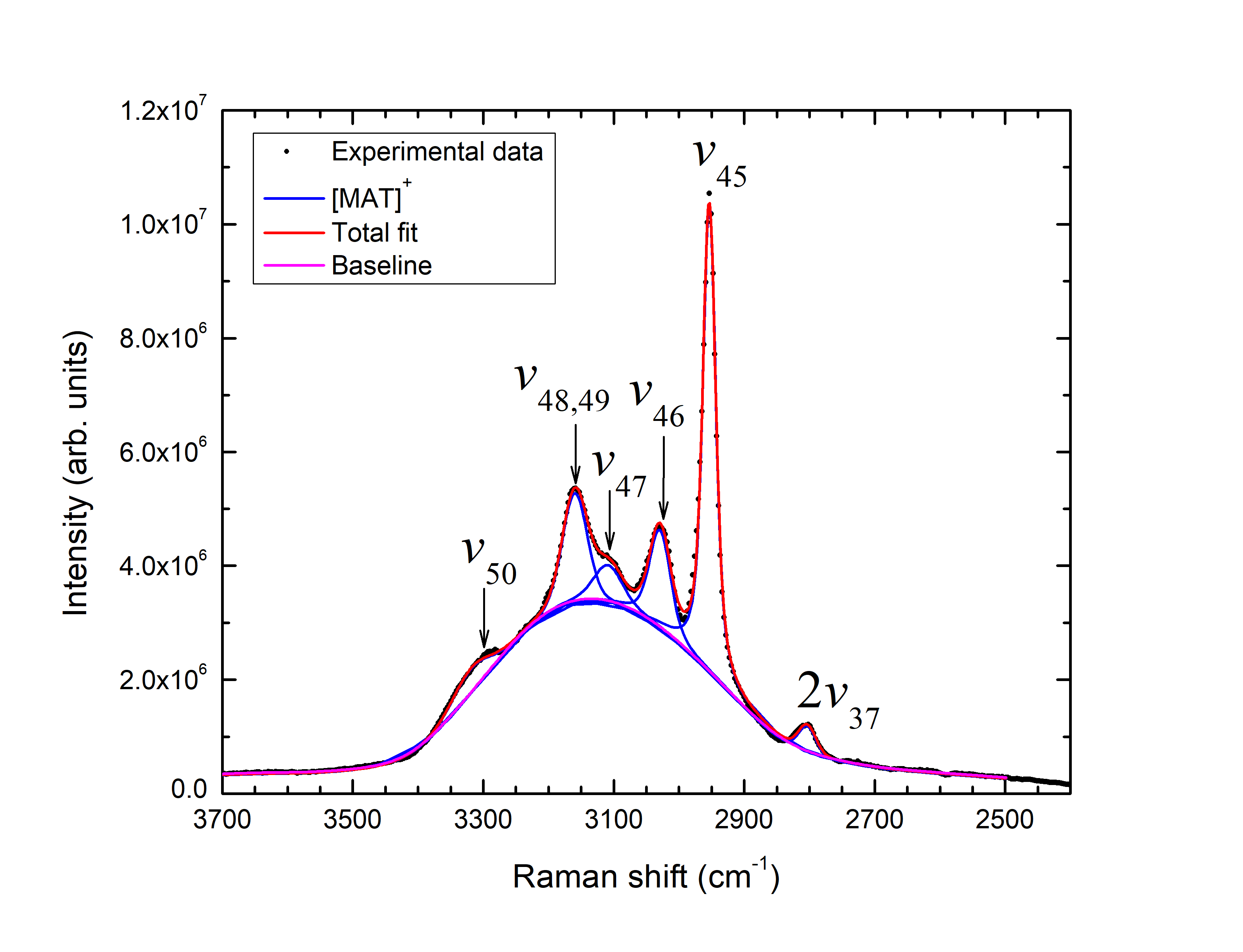
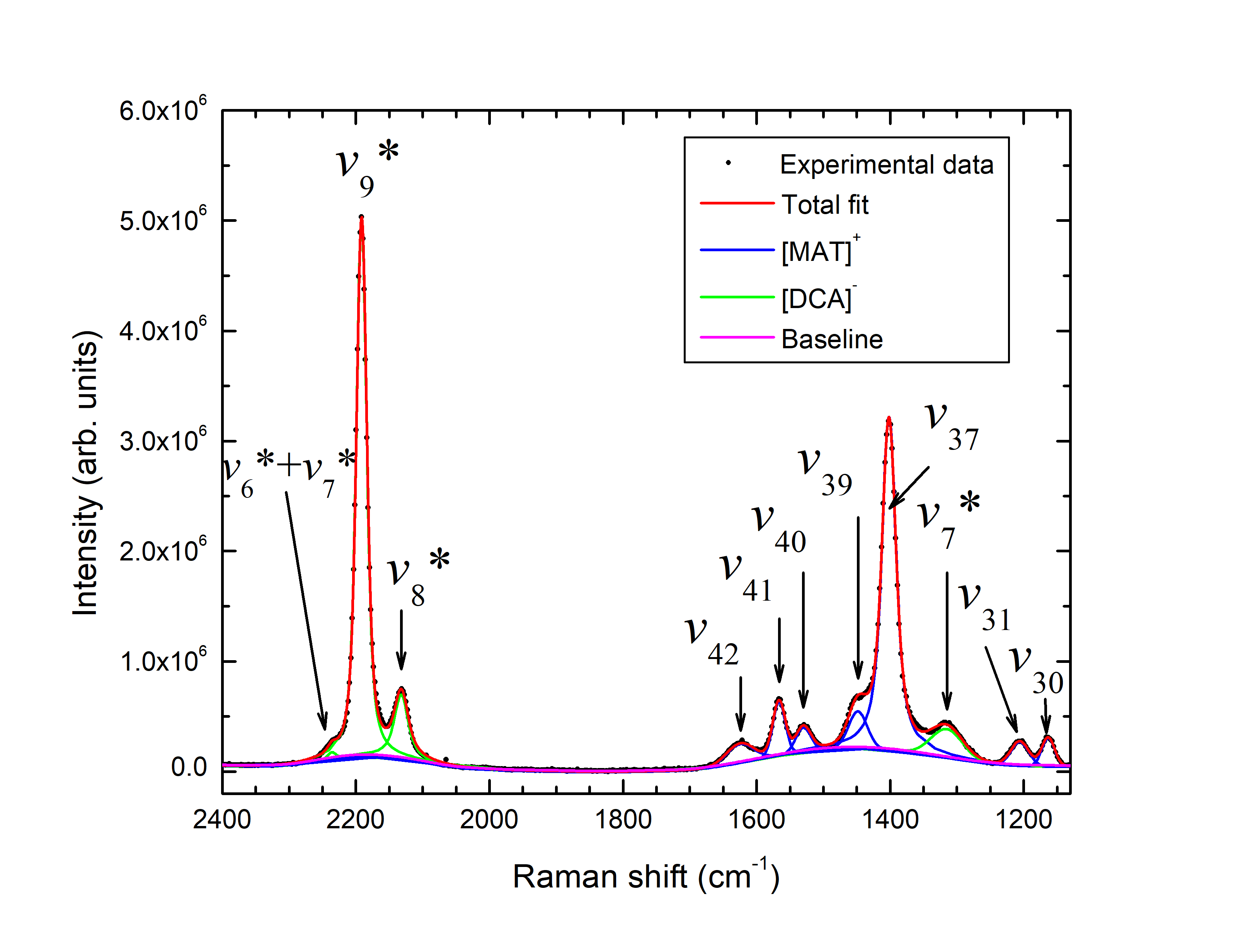
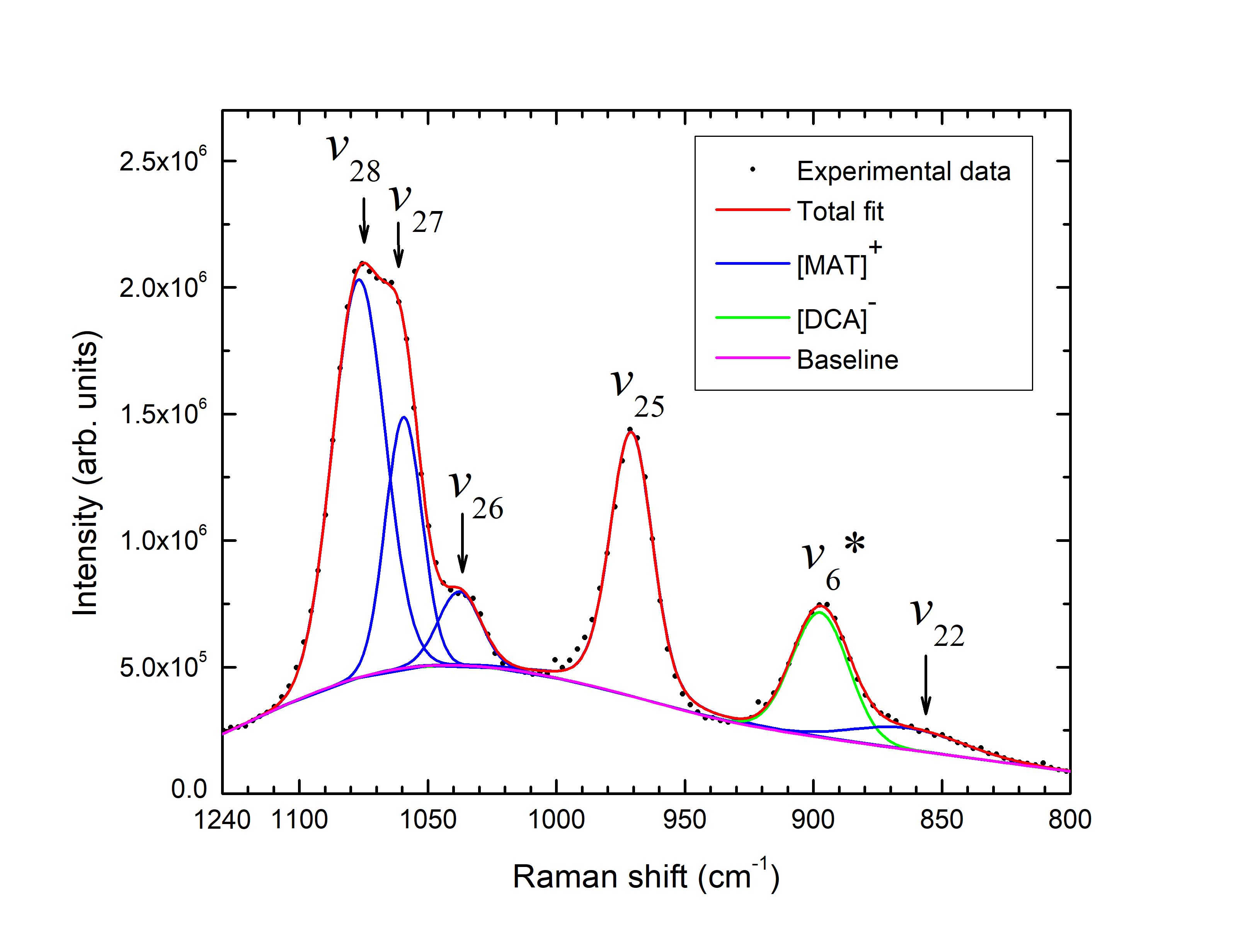
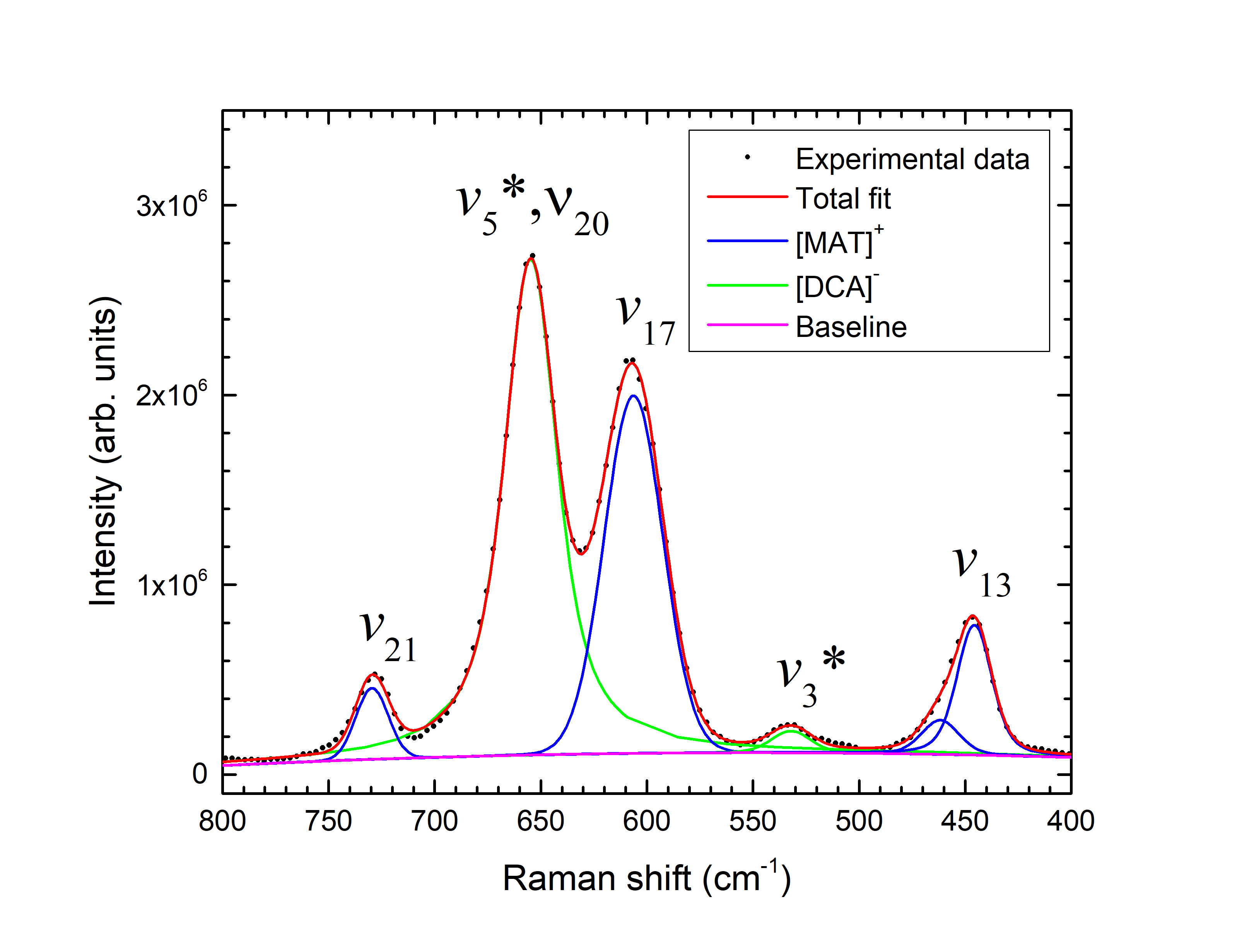
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**Figure 1.** Structure of [MAT][DCA] (left) or [MAT][DCA] after reaction with nitro­gen dioxide (NO2) (right). The numbering con­ven­tion for the positions of the atoms in the triazolium ring is shown. The relative locations of the atoms within each molecule are given in Table S4 (SI).

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**Figure 2**. The top and second rows show, respectively, fits to the FTIR spectra of pure and boron-doped [MAT][DCA] before reaction with nitrogen dioxide. The assignments of the vibrational modes for [DCA]- are based on measured values[34,36,37](#_ENREF_31)and distinguished by an asterisk. The remainder of the assignments were performed utilizing our theoretical GIL calculations. The third and bottom rows display fits to the FTIR spectra of pure and boron-doped [MAT][DCA], respectively, previously levitated in nitrogen dioxide and argon. The spectra of the non-reacted ionic liquids are presented for comparison purposes (purple). The newly formed vibrational peaks are identified by arrows and the assignments given where available.



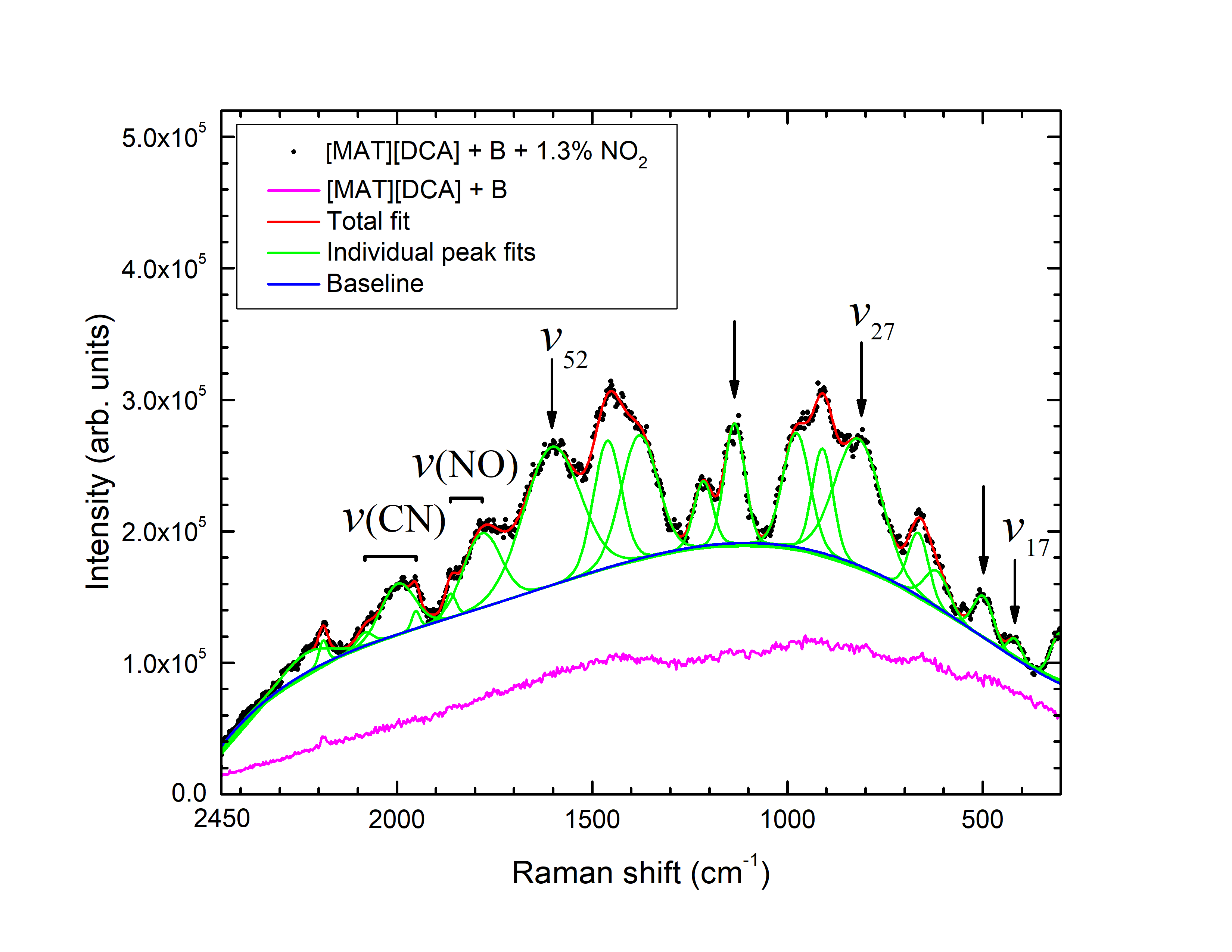
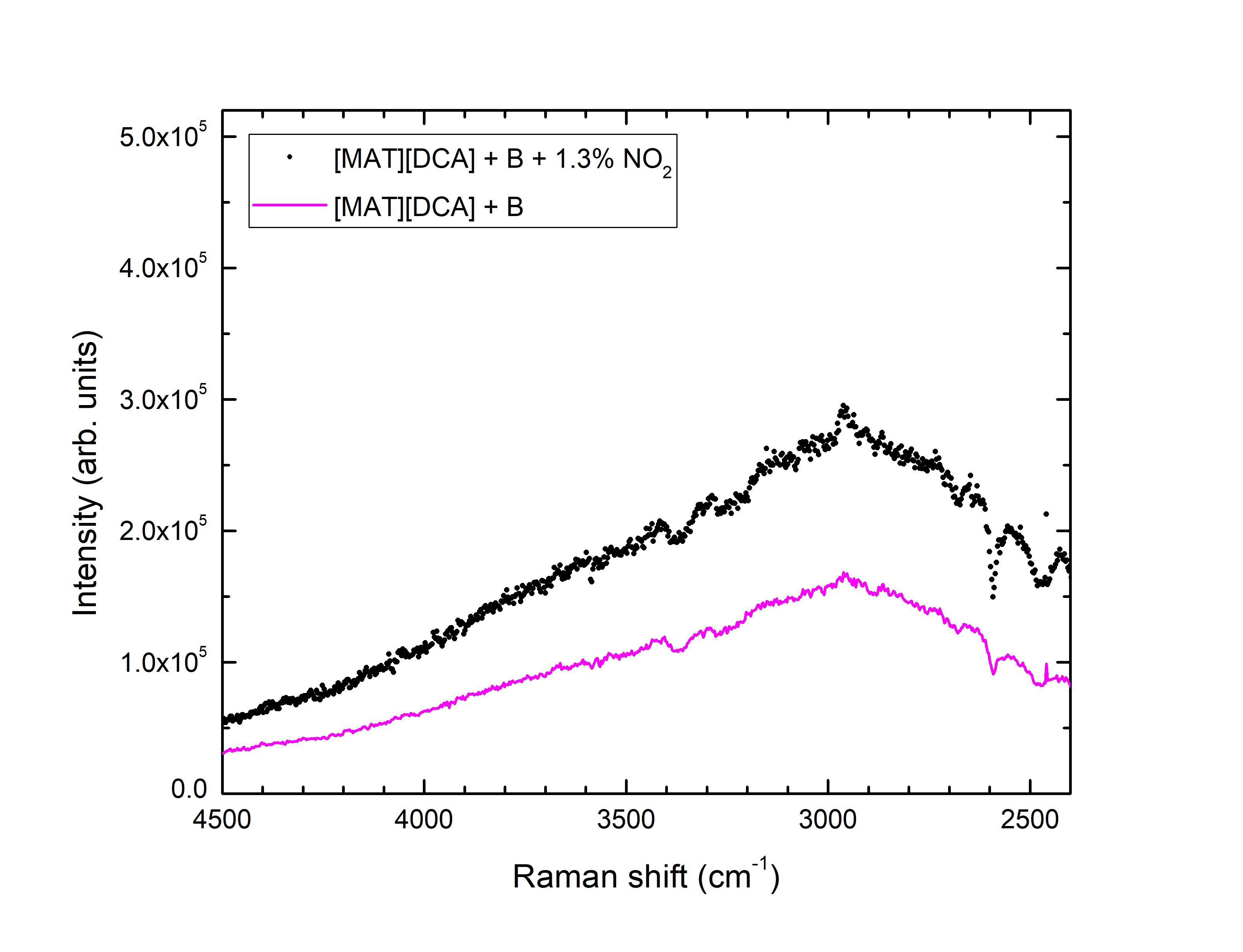
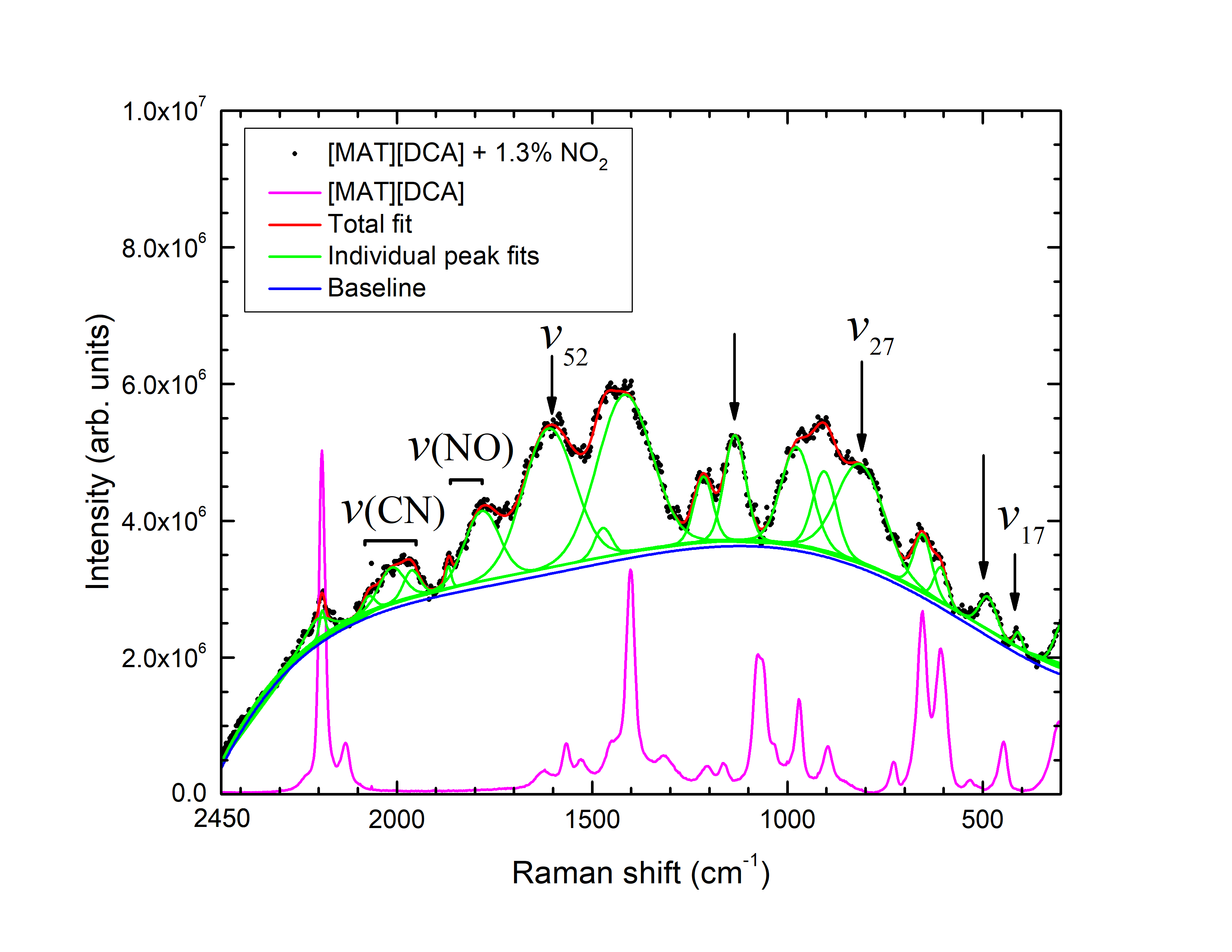
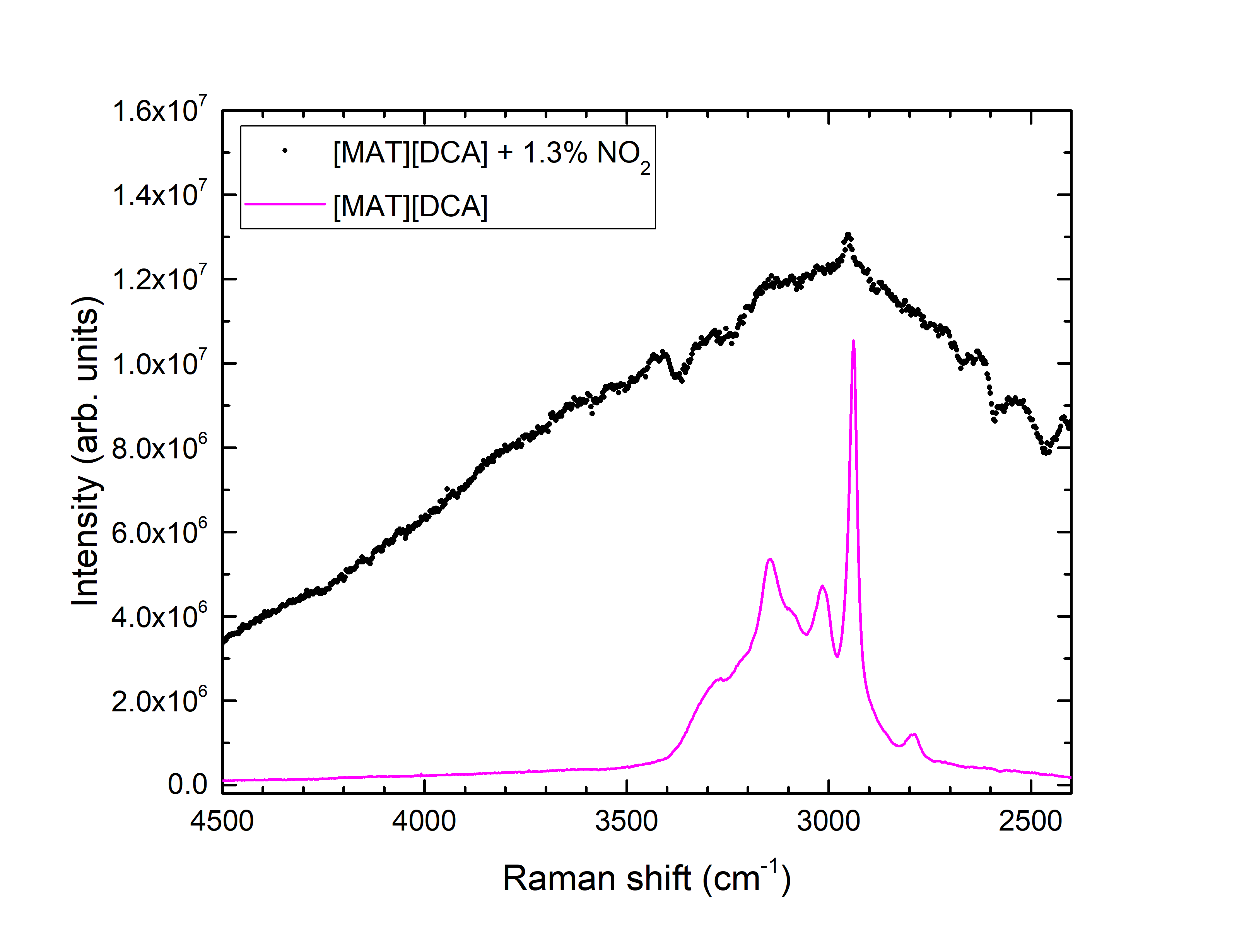
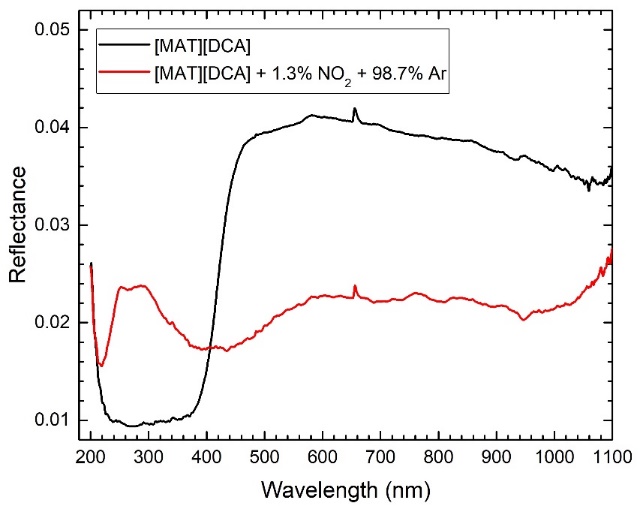
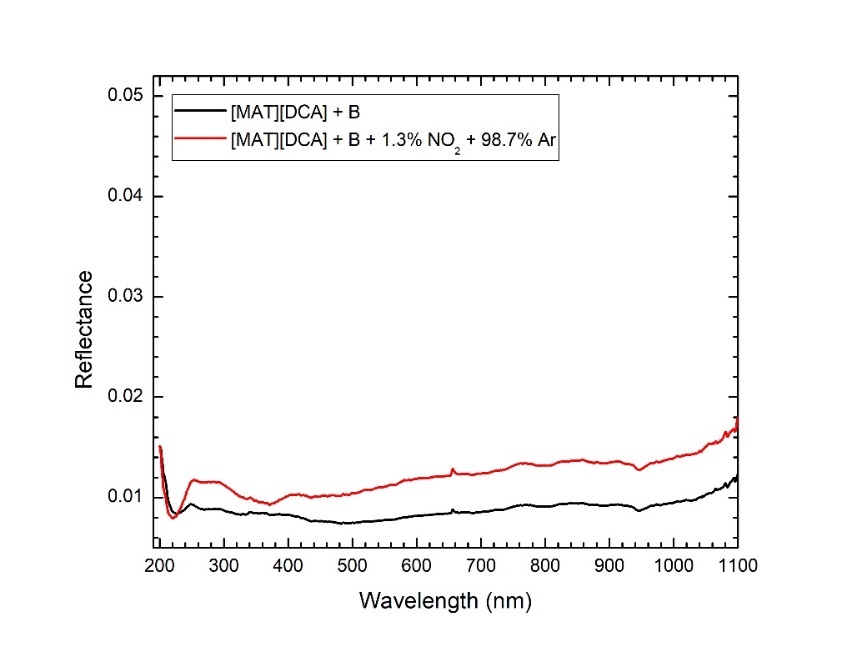
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Figure 3. The top row shows fits to the Raman spectra of an [MAT][DCA] droplet levitated in argon. The assignments of the vibrational modes for [DCA]- are based on measured values[34,36,37](#_ENREF_31)and distinguished by an asterisk. The bottom row displays Raman spectra for a droplet of pure or boron-doped [MAT][DCA] levitated in nitrogen dioxide and argon. In the low Raman-shift spectra (2450-300 cm-1), the individual peak fits are shown (green) and the spectra of the non-reacted [MAT][DCA] are displayed for comparison purposes (purple). The newly formed vibrational modes are identified by arrows and the assignments given where available.



**Figure 4**. UV-visible spectra for a droplet of [MAT][DCA] (left) or [MAT][DCA] doped with hydrogen-capped boron nanoparticles (right). The reference spectra (black lines) were collected prior to the reaction; the spectra in red were collected after reaction with the nitrogen dioxide.

**Table 1a**. Wavenumbers of the new peaks formed in the ATR-FTIR spectra of [MAT][DCA] or [MAT][DCA] doped with hydrogen-capped boron nanoparticles after reaction with nitrogen dioxide assigned by comparison with GIL theoretical values.\*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| number | vibrational mode | theoretical wavenumbers  [MAT][DCA]  (cm-1) | measured wavenumbers [MAT][DCA]  (cm-1) | measured wavenumbers  boron-doped [MAT][DCA]  (cm-1) |
|  |  |  | 680 ± 8 | 681 ± 1 |
|  |  |  | 712 ± 2 | 711 ± 1 |
|  |  |  | 757 ± 1 | 756 ± 1 |
|  |  |  | 768 ± 1 | 768 ± 1 |
| ν26 | N-NO2 umbrella | 779 | 778 ± 1 | 778 ± 1 |
| ν27 | N=C=NNO2 bend + N-NO2 umbrella | 784 | 815 ± 1 | 811 ± 1 |
|  |  |  | 827 ± 1 | 827 ± 1 |
|  |  |  | 1040 ± 3 | 1044 ± 3 |
|  |  |  | 1143 ± 1 | 1141 ± 1 |
| ν39 | C=NNO2 stretch | 1271 | - | 1267 ± 1 |
| ν41 | N=C=N-NO2 symmetric stretch + NH2 rock | 1351 | 1373 ± 2 | 1375 ± 1 |
|  |  |  | 1497 ± 1 | 1494 ± 1 |
| ν49 | O=N=O antisymmetric stretch | 1568 | 1613 ± 7 | 1610 ± 1 |
| ν52 | O2NNC=NCN stretch | 1632 | 1677 ± 2 | 1677 ± 1 |
| ν53 | N=C=N antisymmetric stretch | 2256 | 2177 ± 2 | 2176 ± 1 |

**Table 1b**. Wavenumbers of the new peaks formed in the Raman spectra of [MAT][DCA] or [MAT][DCA] doped with hydrogen-capped boron nanoparticles after reaction with nitrogen dioxide assigned by comparison with GIL theoretical values and a Ref. [40].\*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| number | vibrational mode | theoretical wavenumber  [MAT][DCA]  (cm-1) | measured wavenumber  [MAT][DCA]  (cm-1) | measured wavenumber  boron-doped [MAT][DCA]  (cm-1) |
| ν17 | O2NN=C=N in plane bend | 432 | 409 ± 2 | 418 ± 2 |
|  |  |  | 487 ± 2 | 498 ± 2 |
| ν27 | N=C=NNO2 bend + N-NO2 umbrella | 784 | 813 ± 4 | 818 ± 2 |
|  |  |  | 1135 ± 1 | 1136 ± 1 |
| ν52 | O2NNC=NCN stretch | 1632 | 1611 ± 2 | 1603 ± 1 |
| *v*(NO) | NO stretch | 1798a | 1782 ± 2 | 1782 ± 2 |
| *v*(NO) | NO stretch | 1837a | 1868 ± 1 | 1863 ± 2 |
| *v*(CN) | CN stretch | 1967a | 1960 ± 10 | 1951 ± 2 |
| *v*(CN) | CN stretch | 1998a | 2010 ± 20 | 1998 ± 3 |
| *v*(CN) | CN stretch | 2086a | 2071 ± 5 | 2082 ± 4 |

\*The quoted errors combine the uncertainties from determining the peak wavenumbers in the fitting procedure and calibrating the wavenumber scale.