**Supplementary material**

**Vibrational spectra of methylammonium iodide and formamidinium iodide in wide temperature range**

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The representative spectra for the assignation are selected in a way so they represent each and corresponding phase for both compounds.

Table S1

*Assignation of the IR bands appearing in the spectrum of MAI for the three phases*

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Wavenumber / cm–1 | | | Assignation | According to ref. |
| –170 ºC | +80 ºC | +160 ºC |
| 3218 vw |  |  | 2δas(NH3+) | [5,6] |
| 3187 sh | 3167 s | 3178 sh | δas(NH3+) + δs(NH3+) | [5] |
| 3161 sh | νas(NH3+) | [5,6] |
| 3134 s | 3099 vs | 3077 vs |
| 3127 s |
| 3089 s |  | [6,7] |
| 3051 vs | νs(NH3+) | [5,6] |
| 3030 vs | 3035 vw | 3036 | δas(NH3+) + δas(CH3) | [5,6] |
| 2995 sh |  |  | δs(NH3+) + δas(CH3) | [5,6] |
| 2961 m | 2962 m | 2965 vw | νas(CH3) | [6,7] |
| 2920 vw |  |  | νs(CH3) | [5–7] |
| 2890 m |  |  | 2δas(CH3) | [5,6] |
| 2875 w | 2886 vw |  |
| 2850 vw | 2856 vw |  | δs(CH3) + δas(CH3) | [5,6] |
| 2827 w |  |  |
| 2789 vw |  |  | 2δs(CH3) | [5,6] |
| 2776 vw | 2787 vw | 2832 m |
| 2701 m | 2706 m | 2730 b | δas(CH3) + ρ(NH3+) | [5,6] |
| 2486 w | 2503 b | 2509 b | δas(NH3+) + ρ(CH3) | [5] |
| 2447 vw | 2446 vw | 2442 b | δs(NH3+) + ν(C–N) | [5] |
| 2391 w |  |  | δas(CH3) + ρ(CH3) | [5,6] |
| 2377 w | 2380 w | 2381 vw | [5] |
| 2364 w | 2367 vw |  | [5] |
| 2353 w | 2350 vw | 2353 vw | [5] |
| 2347 w | 2344 vw |  | this work |
| 2167 vw |  |  | ρ(NH3+) + ρ(CH3) | this work |
| 2152 vw |  |  | [5,6] |
| 2132 vw |  |  | this work |
| 1868 vw |  | 1951 b | ν(CN) + ρ(CH3) | [5] |
| 1858 w | this work |
| 1833 vw | 1830 vw | 1885 b | 2ρ(CH3) | this work |
| 1830 vw |
| 1823 w | [5] |
| 1577 m |  |  | δas(NH3+) | [5,7,25] |
| 1566 m | 1567 m | 1572 m |
| 1487 s | 1488 s | 1485 sh | δs(NH3+) | [5–7] |
| 1457 vw | 1461 | 1459 m | δas(CH3) | [5–7,25] |
| 1453 | 1454 m |
| 1447 w |  |  |
| 1440 m |  |
| 1402 s | 1407 s | 1417 m | δs(CH3) | [5–7] |
| 1394 sh |  |  |
| 1386 sh | 1385 vw |  | this work |
| 1251 s | 1259 m | 1260 m | ρ(NH3+) | [5,6] |
| 994 m | 990 m | 975 w | ν(C–N) | [5–7] |
| 918 sh |  |  | ρ(CH3) | [5,7] |
| 910 s | 917 s | 928 m |

Table S2

*Assignation of the IR bands appearing in the spectrum of FAI for the three phases*

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Wavenumber / cm–1 | | | Assignation | According to ref. | |
| –170 ºC | +80 ºC | +160 ºC |
| 3376 s | 3354 vs | 3500 - 2800 |  |  | |
| 3355 vs | νas(NH2) | [9,11] | |
| 3305 s |  |  | |
| 3281 w | 3290 - 2900 | νs(NH2) | [9,11,20] | |
| 3208 s |
| 3180 s |
| 3140 s |
| 3118 s |
| 3024 s | 3015 sh | 3010 sh | ν(CH) | [9,11,20] | |
| 2915 vw |  |  |
| 2806 vw | 2807 vw | 2795 vw |
| 1704 sh | 1708 s | 1710 s | νas(NCN) + δ(NH2) + δ(CH) | [11] | |
| 1699 vs | 1700 s | 1702 s |
| 1686 sh | 1687 sh | 1686 sh | this work | |
| 1676 sh | 1677 sh | 1679 sh |
| 1637 m | 1634 m |  | δ(NH2) | [11,20] | |
| 1602 m | 1606 m | 1617 w |
| 1400 s | 1400 s | 1400 s | νs(NCN) |  | |
| 1364 sh |  |  | [11,20] | |
| 1337 m | 1334 m | 1332 m |  | |
| 1273 sh |  |  | ρ(NH2) | [11,20] | |
| 1249 s | 1254 w |  |
| 1159 vw |  |  | ? | [11] | |
| 1113 w | 1110 w | 1116 vw | τ(NH2) | [11] | |
| 1045 m | 1044 sh |  | ρ(NH2) | [11] | |
| 1034 m | 1035 m | 1049 m | δ(CH) | this work | |
| 1018 m | 1019 m | 1023 vw | γ(CH) | this work | |
| 754 m |  | 727 w | γ(CH) + τ(NH2) | [20] | |
| 693 m | 683 m | 630 m | γ(CH) | [20] |
| 686 m | τ(NH2) | [11] |
| 631 vs | 620 m | [20] | |
| 612 s | ω(NH2) | [11] | |
| 586 vs | 595 s |
| 514 w | 516 w | 521 w | τ(NH2) | [11] | |



**Fig. S1.** Room temperature Raman spectra of MAI and FAI