VIBRATIONAL SPECTRA OF METHYLAMMONIUM IODIDE AND FORMAMIDINIUM IODIDE IN A WIDE TEMPERATURE RANGE

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Transmission infrared, Attenuated Total Reflectance (ATR) and Raman spectra of crystalline methylammonium iodide (MAI) and formamidinium iodide (FAI) in the temperature interval starting from –170 ºC to 200 ºC were studied. The spectra recorded in the region from 4000 to 500 cm⁻¹ enabled resolving the ambiguities associated with the origin of some bands. For the first time a complete and detailed vibrational investigation and assignment of the IR spectra of these compounds based on the differences in the temperature dependent IR spectra for all phases have been made. The findings support the already established crystal structure of the phases for both compounds. The correlation between the overtones and fundamental modes has been confirmed based on the temperature induced isosbestic point.

Keywords: vibrational spectra; methylammonium iodide; formamidinium iodide; phase transition

1. INTRODUCTION

Even though methylammonium iodide (CH₃NH₂I, MAI) and formamidinium iodide (CH(NH₂)₂I, FAI) have very simple structures, their properties have not been subject to vast investigations. In the last few years, there is considerably an increased interest [1–4] since they have become some of the precursors for synthesis of novel hybrid organic-inorganic perovskites (HOIPs). There are only few known organic cations that can successfully be incorporated in the HOIPs structure. Some of the perovskite properties are a direct consequence of the presence of the organic cation. For example, the improvement of the optoelectronic properties is directly influenced by the bandgap that depends on the type of the organic cation.
A systematic study of the infrared spectra of solid methylammonium halides has been carried out long time ago [5–8]. Even though the work is quite comprehensive, data about the high temperature phase of MAI are missing. As stated by Cabana and Sandorfy [5], the problem for not conducting the analysis above 22 °C is due to signs of decomposition of MAI. Also, the assignation of some of the bands is questionable. By making a detailed investigation about the changes in the spectrum as a function of temperature, one can follow the band evolution and band shift, so an unambiguous conclusion regarding the band assignment can be made.

The situation with formamidinium halides (FAX) is even more problematic. There are no thorough studies done on these compounds. The only information available are those obtained in the investigation of the HOIPs were FAX are used as precursors. Even in these papers, IR analyses are lacking, incomplete [9], or inaccurate [10]. More detailed assignation has been provided recently by Hills-Kimball et al. [11] but in this case only the spectra at two temperatures have been covered (300 K and 350 K), so the phase transitions have not been studied.

Working in the field of synthesis of novel HOIPs, it was decided to examine the vibrational properties of one of the most promising organic cations for that purpose: MA⁺ and FA⁺, in the form of iodides. Even though they seem simple and the assignation of the bands in the IR and Raman spectra should be straightforward, it was shown that the situation is complicated since both of them exist in different phases depending on the temperature. The structural characterization of the different phases has been previously reported [11–15], which can assist the process of assignation.

Three stable phases are known to exist in the temperature range from −170 °C up to the melting point of MAI and FAI. That suggests presence of two phase transitions in each compound. Based on the literature data [8, 11, 13, 15], the space group parameters as well as the temperatures of the transitions of MAI and FAI are given in Scheme 1.

![Scheme 1](image_url)

**Scheme 1.** Distribution of the phases with structural characteristics and phase notation in the entire temperature range from absolute zero to the melting point of the compound

2. EXPERIMENTAL

2.1. Instrumentation

The IR absorption spectra were recorded on a Perkin-Elmer System 2000 FTIR Spectrometer using Liquid Nitrogen Cell (LNC). For the absorption measurements, KBr pellet technique was used. The absorption spectra were recorded with resolution of 2 cm⁻¹, using 32 scans (both for the background and the sample spectra) in the temperature range starting from −170 °C up to 200 °C and again down to room temperature on the same pellet. The CO₂/H₂O software compensation was used in order to reduce the bands intensity originating from the atmospheric moisture and the CO₂.

The ATR spectra were recorded on the same Perkin-Elmer System 2000 FTIR Spectrometer using Golden Gate diamond ATR accessory with KRS-5 optics from Specac. The spectra were recorded in the reflectance mode and in the temperature range starting from room temperature (30 °C) up to 200 °C and again down to room temperature on the same sample setting. The recording was conducted with resolution of 2 cm⁻¹, using 32 scans (both for the background and the sample spectra). The entire system (detector, sample compartment, ATR cell) was purged with dry nitrogen (99.999 %).

All IR spectra (both transmission and ATR) were recorded with five degrease interval of the
temperature change between two spectra. Additional, one degree temperature difference was set in order to record the temperature in the vicinity of the phase transition.

Raman spectra of the corresponding samples were recorded on a MicroRaman 300 from Horriba Jobin-Yvon. The spectra were recorded employing the red He-Ne 633 nm laser line, and the green Nd-Yag 532 nm laser line. Long-distance ×50 lens (Olympus) was used as an objective in both cases. The maximum power on the sample for 633 nm was 6.43 mW, while for 532 nm was 2.2 mW. In case of the 633 nm line, a D0.3 filter was used to lower the intensity. The integration time employed was 80 s, 180 s or 240 s, using two or four cycles for the Raman shift from 100 cm⁻¹ to 4000 cm⁻¹. A diffraction grid with 1800 grooves/mm was used.

2.2. Synthesis

All chemicals used for the synthesis were with purity grade “for synthesis” and were used as received. The concentrated hydroiodic acid (57 %, w/w) was purchased by Carlo Erba Reagents with 1.5 % H₃PO₄ as stabilizer, the methylene aqueous solution (40 %, w/w) was purchased by Merck Millipore while the formamidinium acetate (99 %, w/w) was purchased from Sigma-Aldrich Company.

The synthesis of methylammonium iodide is rather straightforward [16]. Minor modifications suggested by the authors contributed to more stable product and have been previously described [17]. The MAI was synthesized using methylamine water solution and concentrated HI. The product was not further purified since both the XRD and IR results showed no impurities except from the H₃PO₄ used as stabilizer of the HI.

The synthesis of the formamidinium iodide and its purification have been previously reported [17, 18]. As described, the synthesis was performed at 0 °C in ethanol solution of formamidinium acetate while adding the concentrated HI drop wise. The obtained product was recrystallized twice from methanol and diethyl ether mixture.

The characterization of both MAI and FAI was done by XRD powder diffraction. The results confirmed the successful synthesis of the compounds and their purity.

3. RESULTS AND DISCUSSION

The recorded IR and Raman spectra of both MAI and FAI at room temperature are in accordance with the already reported literature results [5, 7, 8, 11, 19]. For clarity and systematization of the assignation, parallel comparison of MAI and FAI was applied in every region. The assignation is made for all stable phases. A key moment in the process of the assignment of the vibrational modes are the phase transition points where one can see the drastic changes in the appearance of the spectra. So far in literature the assignation has been made on a temperature at which the existence of a certain phase has already been established by XRD [12] or by other means [8, 13, 20]. In some cases this approach can lead to a wrong assignment of the bands [5, 21]. The reason can be the relatively close values for the wavenumbers of some bands. Additionally, when the evolution of the bands as a function of temperature, is not available improper assignation can be made.

The symmetry of the isolated MA⁺ ions is C₃v (Fig. 1) and if simple group theory considerations of this point group are taken into account than it can be concluded that there are five totally symmetric vibrations A₁, six doubly degenerated vibrations E and one A₂ vibration that is non-degenerated and not totally symmetric. On the other hand, the point group of the isolated FA⁺ ion is C₂ᵥ (Fig. 1), having 18 internal modes. Seven of them are totally symmetric vibrations A₁, two that are not totally symmetric A₂, six of the B₁ type and three that are B₂. All of them are non-degenerate vibrations.

Fig. 1. Structure of the isolated MA⁺ and FA⁺ ions with the designated point group

3.1. IR band analysis

In the absorption spectra of both MAI and FAI, a broad band at 3400 cm⁻¹ can be observed, as well as a band at 1640 cm⁻¹. These bands will not be considered since it is obvious that they arise from the water molecules present in the liquid nitrogen cell at the beginning of the recordings. As the heating of the cell starts, these bands diminished and once they are gone upon cooling they do not reappear.

In Figures 2 and 3 the IR spectra of MAI and FAI representing each phase (according to the provided scheme) are given. The assignation is done.
according to the transmittance spectra. The reflectance (ATR) spectra are only used to confirm the assignation in the moderate and high-temperature phases since the ATR spectra are recorded starting from room temperature up to +200 °C.

Fig. 2. (a) Transmission and (b) ATR spectra of MAI showing the low temperature phase – β’, moderate temperature phase – α, and high temperature phase – ε. For clarity, the spectra are separated along the y-axis, so the transmittance and reflectance are given in arbitrary units.

3.1.1. Region of stretching vibrations

In this spectral region bands arising from the symmetric and asymmetric vibrations of the CH₃ and NH₃⁺ groups present in MA⁺ could be found. In the high frequency end of the FAI spectra, where most of the combinational modes are present, the bands from the NH₂ groups are observed. The partial and full deuteration on MAI [7] suggests that the region above 3030 cm⁻¹ does not have bands from the CH₃ group vibrations. This fact led to problematic suggestions in the assignation made in [6].

Fig. 3. (a) Transmission and (b) ATR spectra of FAI showing the lower temperature phase – III, and high temperature phases – II and I, respectively. For clarity, the spectra are separated along the y-axis, so the transmittance and reflectance are given in arbitrary units.
The development of the $v_{as}(NH_3^+)$ and $v_{as}(NH_3^+)$ in the entire temperature range is given in Figure 4. According to the spectra in this figure, it can be concluded that the band at 3050 cm$^{-1}$ from the symmetric NH$_3^+$ stretching vibrations diminish as the temperature increases. On the other hand, the band at 3090 cm$^{-1}$ appears, as the band at 3050 cm$^{-1}$ diminishes. These two bands are inter-connected with an isosbestic point that appears at around 3068 cm$^{-1}$ and indicates the reorientation of the NH$_3^+$ groups in the crystal structure as the temperature rises. It is obvious that these two bands do not disappear but they fuse together with the bands from the combinational vibrations in the vicinity (3030 cm$^{-1}$). So for the $\beta'$ and $\alpha$ phase of MAI the wavenumbers for the $v_{as}(NH_3^+)$ and $v_{s}(NH_3^+)$ are:

\[
\begin{array}{c|c|c|c}
\text{NH}_3^+ & \beta' (-170 \text{ to } -110 \degree C) & \alpha (-110 \text{ to } 146 \degree C) & \epsilon (146 \text{ to } 200 \degree C) \\
\hline
v_{as}/\text{cm}^{-1} & 3161 \text{ to } 3164; \text{at } -150 \degree C \text{ merges with the combinational band } \delta_{as}(\text{NH}_3^+) + \delta(\text{NH}_3^+) & 3134 \text{ to } 3133 (-140 \degree C) & (146 \text{ to } 200 \degree C) \\
& 3128 \text{ to } 3133 (-140 \degree C) & \text{above } -140 \degree C \text{ merges to } 3082 & \\
\hline
v_{s}/\text{cm}^{-1} & 3086 \text{ to } 3082 & 3082 \text{ to } 3066 (-40 \degree C) & 3066 \text{ to } 3083 \\
\end{array}
\]

(The values in the brackets indicate the temperature at which the band disappears in the adequate phase.)

According to the findings in Cabana et al. [5], the band at 3050 cm$^{-1}$ from the low-temperature phase is assigned as $v_s(\text{NH}_3^+)$ mode and for the room temperature phase this band shifts to 3012 cm$^{-1}$. According to Fig. 4a, this assignation can be considered as incorrect since it is obvious that the band shifts to higher values for the wavenumber for the room temperature phase.

The stretching vibrations of the CH$_3$ groups give bands at 2962 and 2919 cm$^{-1}$ for the asymmetric and symmetric mode, respectively. Even though the band at 2962 cm$^{-1}$ diminishes drastically, its presence in the spectra at 200 °C can still be observed. Unlike the asymmetric vibration, the band from the symmetric vibration disappears at around −65 °C. The wavenumbers of these bands are:

\[
\begin{array}{c|c|c|c}
\text{CH}_3 & \beta' (-170 \text{ to } -110 \degree C) & \alpha (-110 \text{ to } 146 \degree C) & \epsilon (146 \text{ to } 200 \degree C) \\
\hline
v_{as}/\text{cm}^{-1} & 2962 & 2962 & 2962 \text{ to } 2967 \\
v_{s}/\text{cm}^{-1} & 2920 & 2920 (-65 \degree C) & \\
\end{array}
\]
The stretching vibrations of the NH$_2$ groups in the FAI are located in the frequency region from 3400 to 3000 cm$^{-1}$. The origin of these bands can be additionally confirmed by the IR spectra obtained from the chloroformamidinium chloride [ClC(NH$_2$)$_2$]Cl [22]. In the low-temperature region, the number of bands is higher, but as the temperature increases, the bands shifts and they merge into one band (Fig. 5). The wavenumbers of these bands, corresponding to the certain phase are:

|       | III (–170 to 73 ºC) | II (73 to 115 ºC) | I (115 to 200 ºC) |
|-------|---------------------|-------------------|-------------------|
| $\nu_{as}$/cm$^{-1}$ | 3377 to 3373 (35 ºC) | 3347 to 3345 | merged to very broad band 3500 – 2800 cm$^{-1}$ |
| $\nu_{s}$/cm$^{-1}$ | 3281 3208 | 3180 3140 | 3118 |

Fig. 5. Temperature dependent spectra of FAI in the region of stretching vibrations recorded in the temperature interval from (a) –170 to 45 ºC and (b) from 50 to 200 ºC. The arrows indicate the direction of the temperature increase.

In FAI, the carbon atom is bonded to a single hydrogen atom, and the C–H stretching vibrations of this group will give band in the region from 3000 to 2750 cm$^{-1}$. In the recorded spectra, these bands diminish as the temperature increases. At high temperatures, they have very weak intensity, and the band at 3000 cm$^{-1}$ merges with the one from the NH$_2$ vibrations forming a wider band. The assignation in the entire temperature range is given:

|       | III (–170 to 73 ºC) | II (73 to 115 ºC) | I (115 to 200 ºC) |
|-------|---------------------|-------------------|-------------------|
| $\nu$/cm$^{-1}$ | 3024 to 3016 2915 | 3016 to 3015 | 3015 to 3010 (sh) vw |
|       | 2806 to 2807 | 2807 to 2813 | 2813 to 2795 vw |

3.1.2. Deformation vibrations

In this section, the in-plane bending vibrations of the NH$_3^+$, NH$_2$ and CH$_3$ groups will be considered followed by the analysis of the rocking, wagging and twisting modes. The out-of-plane CH vibrations of the FAI will also be considered here even though they are with combinational origin at higher temperatures.

In-plane bending vibrations

The asymmetric (Fig. 6a) and symmetric (Fig. 6b) bending vibrations of NH$_3^+$ groups in MAI give bands in the region from 1580 to 1470 cm$^{-1}$. In Figure 6 all spectra in the temperature range from –170 to 200 ºC are shown. The temperature difference between the spectra in the low-
The vibrational spectra of methylammonium iodide and formamidinium iodide in a wide temperature range are 5 degrees and in the region between −30 and 200 °C, the differences are 10 degrees. Additionally, the spectra recorded in the vicinity of the transition temperature (146 °C) are also given. It is obvious that as the temperature increases, the bands originating from the asymmetric bending deformation merge into one broad band. On the other hand, the band assigned to the symmetric bending vibrations vanishes when MAI undergoes the α → ε phase transition.

The band shape of the δs(NH₃⁺) vibrations in the low-temperature range (at 1487 cm⁻¹ for −170 °C), suggests presence of two bands as found for the MACl [12]. In the case of MAI this splitting at low temperatures (−170 °C) is not as pronounced as in the case of MACl, although the temperature of the recorded MACl spectra is stated to be −185 °C. The change in the position and the disappearance of the bands from the bending NH₃⁺ groups is summarized:

| NH₃⁺ | β (−170 to −110 °C) | α (−110 to 146 °C) | ε (146 to 200 °C) |
|------|---------------------|---------------------|---------------------|
| δas/cm⁻¹ | 1577 to 1573 (sh) | 1573 to 1572 (−70 °C) | 1569 to 1575 |
| δs/cm⁻¹ | 1487 to 1488 | 1488 to 1486 | 1486 to 1484 (sh) |

The important band assembly is the one formed by the asymmetric bending CH₃ vibrations. Its importance is in the fact that these bands are part of an isosbestic point formation that can reveal the exact temperature at which the phase transition occurs [17]. Additionally, they show the appearance/disappearance of the bands so their evolution and assignation can be followed only by investigating the temperature dependent spectra. The entire temperature region of this spectral range is presented in Figure 7, so the assignation can be made with high degree of certainty:

| CH₃ | β (−170 to −110 °C) | α (−110 to 146 °C) | ε (146 to 200 °C) |
|-----|---------------------|---------------------|---------------------|
| δas/cm⁻¹ | 1457 | 1461 to 1460 | 1460 to 1459 |
| δs/cm⁻¹ | 1402 | 1402 to 1407 | 1407 to 1418 (w) |
|       | 1394 (−125 °C) |                      |                     |
|       | 1385 |                      |                     |

Fig. 6. IR spectra of MAI. (a) Asymmetric NH₃⁺ bending vibrations in the range between −165 and −90 °C (upper set) and between −30 and 200 °C (lower set of spectra). (b) Symmetric NH₃⁺ bending vibrations in the entire temperature interval (−165 to 200 °C).
The bands arising from the NH$_2$ bending vibrations in FAI are not as clearly distinguished as the ones from the NH$_3^+$ groups in MAI. Most of these bands are with combinational origin. A proof for that can be found in the DFT calculations [19].

According to the spectra shown in Figure 8, the shape of the band appearing at 1602 cm$^{-1}$ suggests presence of a doublet. The wavenumbers of the bending vibrations of NH$_2$ groups for all three phases are assigned as:

| NH$_2$     | Phase I (–170 to 73 °C) | Phase II (73 to 115 °C) | Phase III (115 to 200 °C) |
|------------|-------------------------|--------------------------|---------------------------|
| $\delta$/cm$^{-1}$ | 1637 to 1635            | 1635 to 1634             | 1634 to 1638 (140 °C)      |
|            | 1616 to 1618 (v)        | 1616 to 1618             |                           |

**Fig. 8.** Region of bending NH$_2$ group vibrations in FAI. Spectra recorded (a) between –170 and 110 °C and (b) up to 200 °C. The arrows indicate the direction of the temperature increase.
Rocking, wagging and twisting vibrations

The bands originating from these vibrations are below 1350 cm\(^{-1}\) and are present in both MAI and FAI spectra for the NH\(_3^+\), CH\(_3\) and NH\(_2\) groups. They are usually combinations (between each other), but at a certain extent, they can be present as pure rocking, wagging and twisting vibrations especially in the low-temperature region.

In the case of MAI, only the rocking mode of NH\(_3^+\) and CH\(_3\) can be observed in the IR spectra. According to the presented spectra in Figure 9, one can conclude that there is not only a band shift, but there is also a change in the intensity of the bands. It is interesting to mention that the band from the rocking NH\(_3^+\) vibrations has a change in the intensity right at the phase transition temperature [17,23], as can be observed in the spectra in Figure 9b. It is important to study the changes that occur in narrower temperature intervals in order not to be misled. If one analyzes Figure 9a only, it might look like that there are two bands that form while increasing the temperature. However, if the analysis includes the spectra given in Figure 9b (one degree temperature difference of recorded spectra), a more precise conclusion can be made. Namely, it is clearly visible that only a band shift occurs (Fig. 9b). The band positions are given as:

| NH\(_3^+\); CH\(_3\) | ρ(NH\(_3^+\))/cm\(^{-1}\) | ρ(CH\(_3\))/cm\(^{-1}\) |
|----------------------|--------------------------|----------------------|
| β (–170 to –110 °C)  | 1251 to 1250             | 918 to 920           |
| α (–110 to 146 °C)   | 1250 to 1259             | 920 to 920 (–90 °C)  |
| ε (146 to 200 °C)    | 1259 to 1261             | 911 to 923           |

![Fig. 9. Spectra representing the regions of rocking vibrations of NH\(_3^+\) and CH\(_3\) groups in MAI. The recorded spectra are with (a) ten degree difference in the region from –170 to 200 °C and (b) one degree difference in the region from 138 to 150 °C.](image)

In the case of FAI, there are three bands originating from the rocking NH\(_2\) vibration and the other deformation vibrations are assigned to the wagging and twisting modes. One of the rocking modes tends to merge with the other bands originating from the CH deformation vibrations, so it will be considered in the section “combinational bands” (Fig. 14). The other ρ(NH\(_2\)) vibrational modes are relatively simple and with predictable behavior so they will not be considered in more details.

By the spectra presented in Figure 10, it is obvious that at higher temperatures the bands from the twisting and wagging modes fuse into a single broad band. This is observed in the low-frequency region (Fig. 10b). The changes in band positions regarding the values for the wavenumbers are:

| NH\(_2\) | III (–170 to 73 °C) | II (73 to 115 °C) | I (115 to 200 °C) |
|---------|---------------------|-------------------|-------------------|
| ρ/cm\(^{-1}\) | 1273 to 1269 (–80 °C) | 1249 to 1254 | 1045 to 1044 |
| τ/cm\(^{-1}\) | 1113 to 1110 | 1110 to 1112 | 1112 to 1119 (170 °C) |
| ω/cm\(^{-1}\) | 612 | 592 | merged to 622 |

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Out-of-plane vibrations

The assignation of the out-of-plane CH vibration in FAI has been previously reported [11, 19] but has not been addressed properly since it is more difficult to distinguish the band origin at room temperature rather than at the liquid N2 temperatures. From our detailed analysis of the bands given in Figure 11, several conclusions can be drawn. First, the band at 693 cm\(^{-1}\) fuses together with the one at 687 cm\(^{-1}\) at ~80 °C, forming a new band at 686 cm\(^{-1}\). The obtained new band behaves similarly as the one at 754 cm\(^{-1}\) assigned as \(\gamma(CH) + \tau(NH_2)\) [11]. This result leads to the conclusion regarding the assignation of the starting bands (693 cm\(^{-1}\) and 687 cm\(^{-1}\)). More precisely, the band at 693 cm\(^{-1}\) is assigned as \(\gamma(CH)\) and the one at 687 cm\(^{-1}\) as \(\tau(NH_2)\). Above ~80 °C the combined band (now at 680 cm\(^{-1}\)) shifts towards lower values for the wavenumber until it merges with another combinational band \(\tau(NH_2) + \omega(NH_2)\). The formation of the later band is shown in Figure 11b. It is interesting that both bands (680 and 754 cm\(^{-1}\)) disappear above 75 °C, and then reappear at 115 °C when the phase transition takes place [17].

These new findings enable more precise assignation of the bands appearing in the low-frequency region.

\[
\begin{array}{|c|c|c|c|}
\hline
& \text{III} (-170 to 75 °C) & \text{II} (73 to 115 °C) & \text{I} (115 to 200 °C) \\
\hline
\tau(NH_2) + \gamma(CH)/cm^{-1} & 754 to 750 & \text{disappears} & 727 to 728 \\
\gamma(CH)/cm^{-1} & 693 merges with \tau(NH_2) at ~80 °C, to 684 & & \text{reappears at 115 °C, 680} \\
\hline
\end{array}
\]

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**Fig. 10.** Region of the rocking, wagging and twisting vibrations in FAI for the (a) low-temperature range and (b) high-temperature range. The bands tend to fuse together as the temperature increases.

**Fig. 11.** Region of the out-of-plane CH vibrations and NH\(_2\) twisting vibrations as a function of temperature in FAI. Both insets depict the behavior of the higher frequency \(\gamma(CH)\) band. The spectra are recorded (a) from ~170 to 75 °C and (b) up to 200 °C.
3.1.3. Skeletal vibration

Characteristic feature in the IR spectra of both MAI and FAI are the bands arising from the C–N stretching vibrations. The phase transition in MAI is due to the changes of the CH$_3$ and NH$_3^+$ rotations against the C$_3$ axis over the C–N bond, which is observed in the spectra. In the MAl spectra, the $\nu$(C–N) appears at around 990 cm$^{-1}$:

| MAI     | $\beta'$ (–170 to –110 °C) | $\alpha$ (–110 to 146 °C) | $\varepsilon$ (146 to 200 °C) |
|---------|-----------------------------|-----------------------------|-----------------------------|
| $\nu$/cm$^{-1}$ | 994 to 993                  | 993 to 988                  | 988 to 974                  |

The "purity" of the bands assigned to the C–N vibrations in the FAI is questionable. It is apparent that the band at 1700 cm$^{-1}$ consists of several bands and at low temperatures two maxima can be distinguished (Fig. 12a). This enables to understand the bands' nature. Accordingly, this complex band can be assigned as combinational band, even though the highest contribution is by N–C–N vibration [11, 19]. The assignation of this complex band is possible because of the opportunity to follow its evolution as a function of temperature. In the low-temperature region, the assignation can be made as shown in Figure 12a. Unexpectedly, the bands at higher temperatures are more pronounced and more distinguishable (Fig. 12b). This could be a consequence of the symmetry of the FA$^+$. At low-temperatures the rigidity of the NH$_2$ groups is higher. Because of that the NH$_2$ motion is more restricted. On the other hand, the increase in temperature results in more pronounced NH$_2$ activity that disturbs the symmetry. The wavenumber of the peaks could be summarized as:

| FAI | III (–170 to 73 °C) | II (73 to 115 °C) | I (115 to 200 °C) |
|-----|---------------------|------------------|------------------|
| $\nu$(NCN)/cm$^{-1}$ | 1704 to 1708        | 1708 to 1711     | 1711 to 1710     |
| $\delta$(CH)/cm$^{-1}$ | 1698 to 1699        | 1699 to 1703     | 1703 to 1701     |
| $\delta$(NH$_2$)/cm$^{-1}$ | 1687 to 1687       | 1687 to 1686     | 1686 to 1685     |
| $\nu$(NCN)/cm$^{-1}$ | 1400                | 1400             | 1400             |
| $\delta$(NH$_2$)/cm$^{-1}$ | 1337 to 1335        | 1334 to 1332     | 1332 to 1333 vdw |

Fig. 12. Combinational band $\nu$(NCN) + $\delta$(CH) + $\delta$(NH$_2$) in FAI for the temperature range (a) from –170 to –70 °C, (b) from 100 to 160 °C and (c) the transition between the two clearly distinguished states.

Even though the entire band assembly is a complex combinational band, as a result of the fact that the major contribution to the band intensity is by the stretching C–N vibration, it is considered in this section.
3.1.4. Overtones and combinations

In this section, the overtones and the combination vibrations of MAI will be considered. In the case of FAI, no overtones were observed in the vibrational spectra. Part of the combination vibrations in FAI were studied in the section regarding the bands arising from the deformation vibrations (γ(CH) + τ(NH$_2$)). This is a consequence of their origin and the fact that they consist of pure vibrational modes in the low-temperature range. The rest of the combinational modes are considered at the end of this section.

Four bands in the spectra of MAI are assigned as overtones. Some are present only in the low-temperature range and understandably, all of them are with low intensity. For the ε phase most of the bands disappear except the overtone from the δ$_s$(CH$_3$). The assignation is as follows:

| NH$_3^+$; CH$_3$ | β' (–170 to –110 ºC) | α (–110 to 146 ºC) | ε (146 to 200 ºC) |
|-----------------|----------------------|-------------------|------------------|
| 2δ$_{as}$(NH$_3^+$)cm$^{-1}$ | 3218 vw | | |
| 2δ$_{as}$(CH$_3$)cm$^{-1}$ | 2890 to 2896 | 2896 to 2901 (65 ºC) | |
| 2δ$_{as}$(CH$_3$)cm$^{-1}$ | 2875 to 2882 | 2882 to 2887 (120 ºC) | |
| 2δ$_s$(CH$_3$)cm$^{-1}$ | 2789 to 2791 | 2779 to 2830 | 2830 to 2837 |
| 2ρ(CH$_3$)cm$^{-1}$ | 1833 to 1829 | 1829 (merged at –70 ºC) | 1845 to 1887 |

The overtones worth mentioning are the ones from the CH$_3$ bending vibrations δ(CH$_3$). Both the asymmetric and symmetric fundamental stretching vibrations are part of an isosbestic point (Fig. 7). If the bands from the overtones of these vibrations are considered (Fig. 13), another set of isosbestic points can be observed. This finding supports the assignation of the overtones.

The most complex band assembly is the one in the region of stretching NH$_3^+$ vibrations. These bands are in their pure state only at very low temperatures. As the temperature is increased, the complexity is even more pronounced and is harder to assign them unambiguously. The proposed assignation is as follows:

Fig. 13. Overtones of the CH$_3$ bending vibrations in MAI are part of an isosbestic point formation, finding that confirms the proper assignation not only of the overtones, but also of the fundamental vibrational modes. The presented spectra are recorded in the temperature range from –170 to –110 ºC.
Vibrational spectra of methylammonium iodide and formamidinium iodide in a wide temperature range

The last combinational band to be considered is the one originating from the deformation vibrations in FAI. In the low temperature region a distinct band shapes could be observed, so the assignment is relatively simple. On the other hand, as the temperature increases, the band structure becomes more complex. In Figure 14a the spectra in the temperature range corresponding to the phase III (from –170 to 65 °C) are shown. It is obvious that the bands assigned as ρ(NH₂) and δ(CH) start to fuse together, but at the point of the phase transition (Fig. 14b), the fused band continues to “develop” independently. At the next phase transition, this band starts to shift towards higher wavenumber values. At higher temperatures (Fig. 14c) all three bands in question fuse together. The changes in the wavenumber are:

| Wavenumber/cm⁻¹ | Phase I (–170 to –110 °C) | Phase II (–110 to 146 °C) | Phase III (146 to 200 °C) |
|-----------------|--------------------------|---------------------------|--------------------------|
| ρ(NH₂)          | 1045 to 1044             | 1037 to 1048              | 1048 to 1056             |
| δ(CH)           | 1034 to 1037             | 1017.4 to 1023            | 1023 to 1046             |
| γ(CH)           | 1018 to 1017             | 1017.4 to 1023            | 1023 to 1046             |

Fig. 14. Combinational band ρ(NH₂) + δ(CH) + γ(CH) in FAI that is obtained by the increase in temperature. Behavior of the bands in the temperature range (a) before the first phase transition (from –170 to 65 °C), (b) around the first and second transition, (c) after the second transition (above 125 °C).
The results obtained by the analysis of the temperature dependent IR and ATR spectra for all stable phases of MAI and FAI are summarized in Table S1 and S2 given in the Supplementary material.

3.2. Raman spectra

Raman spectra (Fig. S1) reveal the characteristic features of MAI α phase and phase I of FAI. The Raman shift for the bands of MAI and FAI are given in Table 1. These spectra are relatively simpler compared to the infrared spectra of the same compounds.

The assignation of the bands in the Raman spectra is made according to the available literature data [6, 9, 19, 24–27]. These results assisted the assignation of the bands in the IR spectra, the once involved in the phase transition as well as the characterization of the change during the phase transition.

| Table 1 |
|------------------|------------------|
| Raman shift for the room temperature phases of MAI and FAI |
| | MAI | FAI |
| | ν(cm⁻¹) | Assignment | Acc. to ref. | ν(cm⁻¹) | Assignment | Acc. to ref. |
| 3360 s | ν(NH₂) | [24] |
| 3254 m | | |
| 3192 s | | |
| 3142 m | | |
| 3127 | ν(As(NH₃)+) | [25] |
| 3079 s | ν(NH₃) | [25] |
| 2958 m | υ(CH₃) | [25] |
| 2899 m | υ(CH₃) | [25] |
| 2883 m | | |
| | | |
| 1608 b | δ(As(NH₃)+) | [6, 25, 26] |
| 1533 s | δ(As(NH₃)+) | [6, 25, 26] |
| 1456 m | δ(CH₃) | [6, 25, 26] |
| 1401 w | δ(CH₃) | [6] |
| 985 m | υ(CN) | [6, 27] |
| 907 m | ρ(CH₃) | [6] |
| 108 m | T(MA⁺) | [6] |
| 1372 s | δ(CH) + υ(As(CN)) | [9, 19] |
| 1333 m | ρ(NH₂) | [9, 19] |
| 1190 m | υ(As(CN)) | [9, 19] |
| 1036 w | ρ(NH₂) + γ(CH) | [9, 19] |
| 1017 w | ρ(NH₂) | [9] |
| 740 w | τ(NH₂) + γ(CH) | [19] |
| 677 m | ω(NH₂) | [9] |
| 627 sh | δ(CN) | [19] |
| 607 w | τ(NH₂) | [9, 19] |
| 512 m | δ(CN) | [19] |
| 142 s | T(FA⁺) | [19] |
| 116 s | L(FA⁺) | [19] |

4. CONCLUSION

For the first time the vibrational spectra of MAI and FAI in wide temperature range (~170 °C to 200 °C) have been fully characterized by the means of infrared spectroscopy. Transmission IR, ATR and Raman spectra were taken into account while making the assignation of the bands for both compounds. Many ambiguities concerning the origin of the bands and their assignation have been resolved. Recorded temperature-dependent spectra enables following of the appearance/disappearance of the bands that may be correlated with the bands assignation.

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REFERENCES

[1] L. K. Ono, E. J. Juarez-Perez, Y. Qi, Progress on perovskite materials and solar cells with mixed cations and Halide Anions, ACS Appl. Mater. Interfaces., 9, 30197–30246 (2017). https://doi.org/10.1021/acsmi.7b06601.

[2] J. Navas, A. Sánchez-Coronilla, I. J. Gallardo, N. Cruz Hernández, J. C. Piñero, R. Alcántara, C. Fernández-Lorenzo, D. M. De los Santos, T. Aguilar, J. Martín-Caldejo, New insights into organic–inorganic hybrid perovskite CH$_3$NH$_3$PbI$_3$ nanocrystals. An experimental and theoretical study of doping in Pb$_2^+$ sites with Sn$_2^+$, Sr$_2^+$, Cd$_2^+$ and Ca$_2^+$, Nanoscale, 7, 6216–6229 (2015). https://doi.org/10.1039/C5NR00041F.

[3] G. E. Eperon, S. D. Stranks, C. Meneou, M. B. Johnston, L. M. Herz, H. J. Snaith, Formamidinium lead trihalide: A broadly tunable perovskite for efficient planar heterojunction solar cells, Energy Environ. Sci., 7, 982–988 (2014). https://doi.org/10.1039/c3ee43822h.

[4] J. Breternitz, F. Lehmann, S. A. Barnett, H. Nowell, S. Schorr, Role of the iodide-methylammonium interaction in the ferroelectricity of CH$_3$NH$_3$PbI$_3$, Angew. Chemie Int. Ed. (2019). https://doi.org/10.1002/anie.201910595.

[5] A. Cabana, C. Sandorfy, The infrared spectra of solid methylammonium halides, Spectrochim. Acta., 18 843–861 (1962). https://doi.org/10.1016/0037-1951(62)80089-7.

[6] E. Castellucci, β and γ crystal forms of methylammonium chloride: polarized light infrared spectra and Raman spectra: Infrared spectra of matrix isolated methylammonium ion, J. Mol. Struct., 23, 449–461 (1974). https://doi.org/10.1016/0022-2860(74)87013-4.

[7] A. Théorêt, C. Sandorfy, The infrared spectra of solid methylammonium halides-II, Spectrochim. Acta Part A Mol. Spectrosc., 23, 519–542 (1967). https://doi.org/10.1016/0037-5975(67)80310-6.

[8] O. Yamamuro, M. Oguni, T. Matsuo, H. Suga, Calorimetric and dilatometric studies on the phase transitions of crystalline CH$_3$NH$_3$I, J. Chem. Thermodyn., 18 939–954 (1986). https://doi.org/10.1016/0009-9563(86)90152-7.

[9] M. Mączka, A. Ciupa, A. Gagor, A. Sieradzki, A. Pikul, B. Macalik, M. Drozd, Perovskite Metal Fornate Framework of [NH$_3$CH$_3$NH$_3$][Hg(HCO$_3$)$_2$]: Phase Transition, Magnetic, Dielectric, and Phonon Properties, Inorg. Chem., 53 (2014) 5260–5268. https://doi.org/10.1021/ic500479e.

[10] K. Hills-Kimball, Y. Nagaoka, C. Cao, E. Chaykovsky, Q. Chen, Synthesis of formamidinium lead halide perovskite nanocrystals through solid-liquid-solid cation exchange, J. Mater. Chem. C, 5, 5680–5684 (2017). https://doi.org/10.1039/c7tc00598a.

[11] K. Mencel, P. Durlak, M. Rok, R. Jakubas, J. Baran, W. Medycki, A. Cízma, A. Piecha-Bisiorek, Widely used hardly known. An insight into electric and dynamic properties of formamidinium iodide, RSC Adv., 8, 26506–26516 (2018). https://doi.org/10.1039/c8ra03871f.

[12] O. Yamamuro, M. Oguni, T. Matsuo, H. Suga, P-T phase relations of methylammonium halides, Thermochim. Acta., 98, 327–338 (1986). https://doi.org/10.1016/0040-6031(86)87103-9.

[13] H. Ishida, R. Ikeda, D. Nakamura, 1H NMR studies on the reorientational motions of cations in four solid phases of methylammonium iodide and the self-diffusion of ions in its highest-temperature solid phase, Bull. Chem. Soc. Jpn., 59, 915–924 (1986). https://doi.org/10.1246/bcsj.59.915.

[14] H. Ishida, R. Ikeda, D. Nakamura, Pre-melting state of methylammonium iodide as revealed by proton magnetic resonance, Phys. Status Solidi., 70, 151–154 (1982). https://doi.org/10.1002/pssa.22110700261.

[15] A. A. Petrov, E. A. Goodlin, A. B. Tarasov, V. A. Lazarenko, P. V. Dorovatovskii, V. N. Khrustalev, Formamidinium iodide: Crystal structure and phase transitions, Acta Crystallogr. Sect. E Crystallogr. Commun., 73 (2017) 569–572. https://doi.org/10.1107/S160053681700425X.

[16] K. M. Boopathi, M. Ramesh, P. Perumal, Y. C. Huang, C. S. Tsao, Y. F. Chen, C. H. Lee, C. W. Chu, Preparation of metal halide perovskite solar cells through a liquid droplet assisted method, J. Mater. Chem. A, 3, 9257–9263 (2015). https://doi.org/10.1039/c4ta06392a.

[17] M. Buklesi, S. Dimitrovskaja-Lazova, V. Makrievski, S. Aleksovska, A simple approach for determination of the phase transition temperature using infrared temperature induced isosbestic points, Spectrochim. Acta Part A Mol. Spectrosc., in prep. (n.d.) 1–15.

[18] N. Pellet, P. Gao, G. Gregori, Y. T. Yang, M. K. Nazareuddin, J. Maier, M. Grätzel, Mixed-organic cation perovskite photovoltaics for enhanced solar-light harvesting, Angew. Chemie – Int. Ed., 53, 3151–3157 (2014). https://doi.org/10.1002/anie.201309361.

[19] E. Kučharska, J. Hanuza, A. Ciupa, M. Mączka, L. Macalik, Vibrational properties and DFT calculations of formamide-templated Co and Fe formates, Vib. Spectrosc., 75, 45–50 (2014). https://doi.org/10.1016/j.vibspect.2014.09.001.

[20] O. Yamamuro, T. Matsuo, H. Suga, W. I. F. David, R. M. Ibberson, A. J. Leadbetter, Neutron diffraction and calorimetric studies of methylammonium iodide, Acta Crystallogr. Sect. B., 48, 329–336 (1992). https://doi.org/10.1107/S0108768192000260.

[21] T. Glaser, C. Müllner, M. Sendner, C. Kekeler, O. E. Semonin, T. D. Hull, O. Yaffe, J. S. Owen, W. Kowalski, A. Pucci, R. Lovrinčič, Infrared spectroscopic study of vibrational modes in methylammonium lead halide perovskites, J. Phys. Chem. Lett., 6, 2913–2918 (2015). https://doi.org/10.1021/acs.jpclett.5b01309.

[22] A. Möller, J. George, R. Dronskowski, First full structural characterization of chloro formamidinium salts, Zeitschrift Fur Anorg. Und Allg. Chemie., 644, 1485–1491 (2018). https://doi.org/10.1002/zaac.201800164.
[23] G. Bator, R. Jakubas, J. Baran, H. Ratajczak, Infrared studies of structural phase transitions in (CH$_3$NH)$_3$Bi$_3$I$_6$ (MAIB), *J. Mol. Struct.*, 325, 45–51 (1994). https://doi.org/10.1016/0022-2860(94)80016-2.

[24] L. Wang, K. Wang, B. Zou, Pressure-induced structural and optical properties of organometal halide perovskite-based formamidinium lead bromide, *J. Phys. Chem. Lett.*, 7, 2556–2562 (2016). https://doi.org/10.1021/acs.jpcl.6b00999.

[25] T. K. K. Srinivasan, M. Mylrajan, Phase transitions in CH$_3$NH$_3$ClO$_4$ and CH$_3$ND$_3$ClO$_4$, *Phase Transitions*, 38, 97–113 (1992). https://doi.org/10.1080/01411599208203466.

[26] J. T. Edsall, H. Scheinberg, Raman spectra of amino acids and related compounds. V. Deuterium substitution in the amino group, *J. Chem. Phys.*, 8, 520–525 (1940). https://doi.org/10.1063/1.1750705.

[27] M. Mylrajan, T. K. K. Srinivasan, Raman and infrared spectra of phase transition in CH$_3$NH$_3$ClO$_4$, *J. Mol. Struct.*, 143, 105–108 (1986). https://doi.org/10.1016/0022-2860(86)85215-2.