

Supporting information for:

Tagging Effects on the Mid-Infrared Spectrum of

Microsolvated Protonated Methane

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Mode Reconstruction

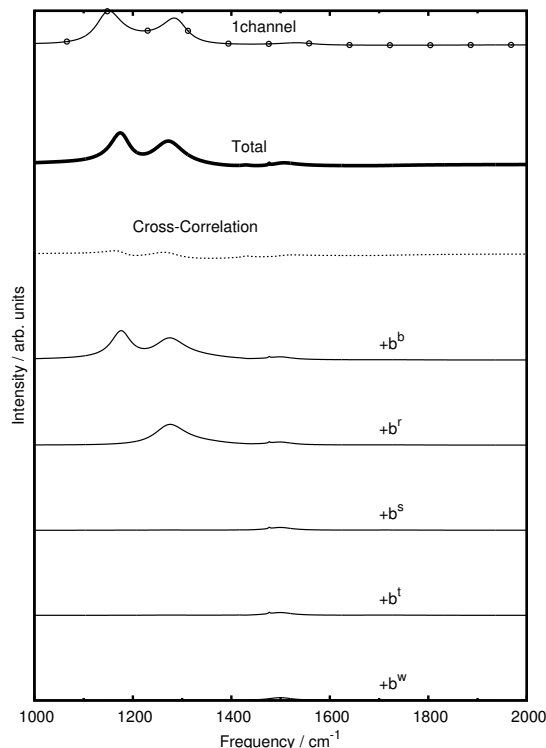


Figure S1: Close-up on the bending regions of the mode-by-mode re-construction of the total IR absorption cross section $\alpha(\omega)$ of bare CH_5^+ at 110 K based on successively adding up all mode-specific IR absorption cross sections $\alpha_k(\omega)$ according to Eq. (30) in the main text from bottom to top starting with the highest-frequency modes, as described in the main text.

Visualization of the Decomposed Modes

The generalized normal modes of bare and microsolvated protonated methane are displayed on the following pages in the mid-IR frequency range as discussed in the main text. Each page shows one mode for each of the four cases $\text{CH}_5^+ \bullet (\text{H}_2)_n$, $n = 0, 1, 2, 3$ (where the singly tagged species requires two reference structures and thus two animations for reasons explained in the main text). Each of the dynamical animations can be controlled via the panel below the respective image.

Table S1: Butterfly Bending Mode b^b

CH_5^+ 1176 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_1\text{-I}$ 1207 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_1\text{-II}$ 1161 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_2$ 1176 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_3$ 1171 cm^{-1}

Table S2: Rocking Bend Mode b^r

CH_5^+ 1276 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_1\text{-I}$ 1284 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_1\text{-II}$ 1309 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_2$ 1308 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_3$ 1324 cm^{-1}

Table S3: Scissoring Bend Mode b^s

CH_5^+ 1430 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_1\text{-I}$ 1442 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_1\text{-II}$ 1444 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_2$ 1446 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_3$ 1439 cm^{-1}

Table S4: Twisting Mode b^t

CH_5^+ 1477 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_1\text{-I}$ 1466 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_1\text{-II}$ 1473 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_2$ 1472 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_3$ 1473 cm^{-1}

Table S5: Wagging Mode b^w

CH_5^+ 1500 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_1\text{-I}$ 1501 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_1\text{-II}$ 1509 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_2$ 1513 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_3$ 1498 cm^{-1}

Table S6: Asymmetric Moiety Stretching Mode m^a

CH_5^+ 2429 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_1\text{-I}$ 2288 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_1\text{-II}$ 2293 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_2$ 2242 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_3$ 2286 cm^{-1}

Table S7: Symmetric Moiety Stretching Mode m^s

CH_5^+ 2706 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_1\text{-I}$ 2710 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_1\text{-II}$ 2718 cm^{-1}

2H_2 2673 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_3$ 2660 cm^{-1}

Table S8: In-plane Tripod Stretching Mode tⁱ

CH_5^+ 3080 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_1\text{-I}$ 3081 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_1\text{-II}$ 3099 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_2$ 3098 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_3$ 3058 cm^{-1}

Table S9: Symmetric Tripod Stretching Mode t^s

CH_5^+ 3218 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_1\text{-I}$ 3198 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_1\text{-II}$ 3203 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_2$ 3200 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_3$ 3203 cm^{-1}

Table S10: Asymmetric Tripod Stretching Mode t^a

CH_5^+ 3309 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_1\text{-I}$ 3291 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_1\text{-II}$ 3294 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_2$ 3294 cm^{-1}

$\text{CH}_5^+(\text{H}_2)_3$ 3304 cm^{-1}

Table S11: Inner Moiety H₂ Mode H₂ⁱ

not present	CH ₅ ⁺ (H ₂) ₁ -I 4327 cm ⁻¹	not present
CH ₅ ⁺ (H ₂) ₂ 4334 cm ⁻¹	CH ₅ ⁺ (H ₂) ₃ 4340 cm ⁻¹	

Table S12: Outer Moiety H₂ Mode H₂^{om}

not present

not present

CH₅⁺(H₂)₁-II 4336 *cm*⁻¹

CH₅⁺(H₂)₂ 4343 *cm*⁻¹

CH₅⁺(H₂)₃ 4343 *cm*⁻¹

Table S13: In-plane H_2 Mode H_2^{im}

not present

not present

not present

not present

$\text{CH}_5^+(\text{H}_2)_3$ 4374 cm^{-1}