Supplementary Information

Infrared spectra of the protonated neurotransmitter histamine: 
Competition between imidazolium and ammonium isomers in the gas phase

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Table S1. Selected bond distances (in Å), dihedral angles (in degrees), and relative energies and relative free energies at 298 K (in kJ/mol) of all considered isomers of histamineH⁺ calculated at the B3LYP/cc-pVDZ and MP2/cc-pVDZ levels (Fig. 3).

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Figure S1. Bond distances (in Å) and selected bond angles of the two low-energy isomers A and B of histamineH+, calculated at the B3LYP (black) and MP2 (red) levels using the cc-pVDZ basis set.
**Figure S2.** Bond distances (in Å), selected bond angles, and NBO charge distribution (bottom) of the transition state TS between the two low-energy isomers A and B of histamineH⁺, calculated at the B3LYP (black) and MP2 (red) levels using the cc-pVDZ basis set.
Figure S3. Potential energy scan of histamineH⁺ along the proton transfer isomerization coordinate connecting the two minima A and B via a transition state TS (B3LYP/cc-pVDZ). The energies were obtained by changing the Nₓ-H bond distance and optimizing all other coordinates.
Figure S4. NBO charge distribution of the two low-energy isomers A and B of histamineH⁺, calculated at the B3LYP (black) and MP2 (red) levels using the cc-pVDZ basis set.
Figure S5. Calculated absorption spectra (B3LYP/cc-pVDZ) of isomers A–J of histamineH⁺ compared to the IRMPD spectrum. Intensities are all on the same scale. Relative energy differences (ΔE in kJ/mol) are given in parentheses.
Figure S6. Comparison of linear IR absorption spectra of the isomers A and B of histamineH⁺ in harmonic (scaling factor 0.98) and anharmonic approximation (B3LYP/cc-pVDZ).
Figure S7. Comparison of linear IR absorption spectra of the isomers A and B of histamineH⁺ and the corresponding transition state TS (B3LYP/cc-pVDZ) with the experimental IRMPD spectrum. Calculated intensities are all drawn to the same scale. The most intense for isomer B peak is cut at approximately 50%. 

![Spectral Comparison](image-url)
**Figure S8.** Possible structures of the m/z=95 fragment ion calculated at the B3LYP/cc-pVDZ level. Relative energies $\Delta E$ are given with respect to the most stable FI_{95} ion. The $D_0$ values correspond to binding energies for NH$_3$ elimination from the A isomer of histamineH$^+$. 

- **FI_{95}**
  - $\Delta E_{ua} = 0$ kJ/mol
  - $D_0 = 79$ kJ/mol

- **FI_{II~95}**
  - $\Delta E_{ua} = 3$ kJ/mol
  - $D_0 = 82$ kJ/mol

- **FI_{III~95}**
  - $\Delta E_{ua} = 17$ kJ/mol
  - $D_0 = 96$ kJ/mol

- **FI_{IV~95}**
  - $\Delta E_{ua} = 75$ kJ/mol
  - $D_0 = 153$ kJ/mol

- **FI_{V~95}**
  - $\Delta E_{ua} = 102$ kJ/mol
  - $D_0 = 181$ kJ/mol

- **FI_{VI~95}**
  - $\Delta E_{ua} = 108$ kJ/mol
  - $D_0 = 187$ kJ/mol
**FVII.95**
\[ \Delta E_m = 132 \text{ kJ/mol} \]
\[ D_o = 211 \text{ kJ/mol} \]

**FVIII.95**
\[ \Delta E_m = 142 \text{ kJ/mol} \]
\[ D_o = 220 \text{ kJ/mol} \]

**FIX.95**
\[ \Delta E_m = 156 \text{ kJ/mol} \]
\[ D_o = 234 \text{ kJ/mol} \]

**FX.95**
\[ \Delta E_m = 158 \text{ kJ/mol} \]
\[ D_o = 237 \text{ kJ/mol} \]

**FXI.95**
\[ \Delta E_m = 217 \text{ kJ/mol} \]
\[ D_o = 296 \text{ kJ/mol} \]

**FXII.95**
\[ \Delta E_m = 329 \text{ kJ/mol} \]
\[ D_o = 408 \text{ kJ/mol} \]

**FXIII.95**
\[ \Delta E_m = 354 \text{ kJ/mol} \]
\[ D_o = 433 \text{ kJ/mol} \]
Figure S9. Structures of neutral histamine isomers calculated at the B3LYP/cc-pVDZ level. Relative energies ($\Delta E$) and relative free energies ($\Delta G$ at 298 K) are given with respect to the most stable structure $A(n)$. Values in parentheses are calculated at the MP2/cc-pVDZ level. All values are given in kJ/mol.
Figure S10. Bond distances (in Å) and selected bond angles of the most stable structures of neutral (A(n)) and protonated histamine (A) calculated at the B3LYP (black) and MP2 (red) levels using the cc-pVDZ basis set.
Figure S11. NBO charge distribution of the most stable structures of neutral (A(n)) and protonated histamine (A), calculated at the B3LYP (black) and MP2 (red) levels using the cc-pVDZ basis set.
Figure S12. Comparison of linear IR absorption spectra of the histamine(H⁺) isomers A and A(n) (B3LYP/cc-pVDZ) with the experimental IRMPD spectrum of histamineH⁺ and the solid-state spectrum available from the NIST database. Note that the NIST spectrum is spectrally contaminated by oil resonances at 1450 and 1380 cm⁻¹.