Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics

Supplementary Information

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

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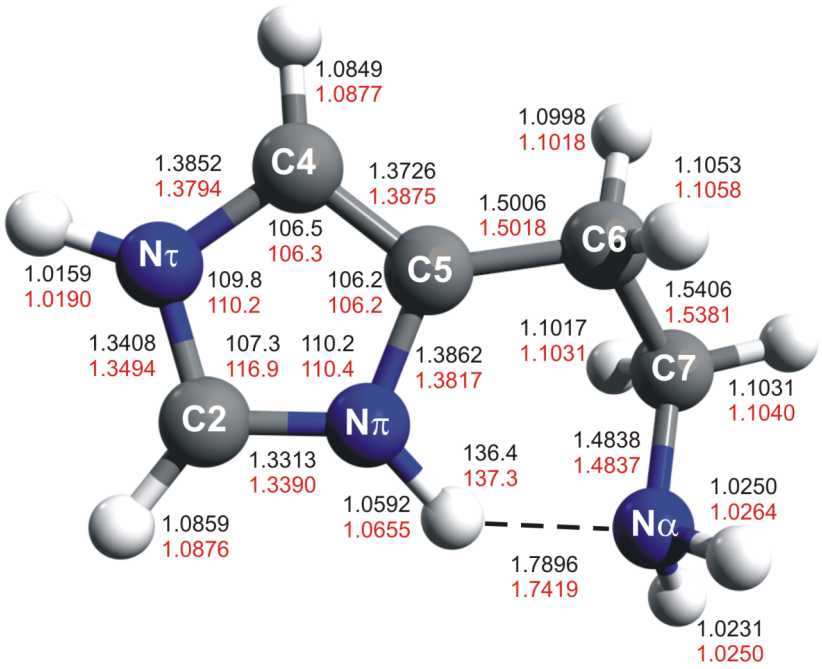
Table S1. Selected bond distances (in Å), dihedral angles (in degrees), and relative energies and relative free energies at 298 K (in kJ/mol) of all considered isomers of histamineH^+ calculated at the B3LYP/cc-pVDZ and MP2/cc-pVDZ levels (Fig. 3).

	A		**B**		**C**		**D**		**E**	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
ϕ_1 ϕ_2	-57.9 36.2	-59.4 36.4	-56.9 37.3	-59.4 38.6	59.5 146.0	60.7 144.7	174.5 66.8	174.8 70.7	176.4 -173.9	176.5 -175.9
$R_{N_a\cdots H}$ $R_{N_s\cdots H}$ $R_{N\cdots H}$	1.790 1.059 1.016	1.742 1.065 1.019	1.106 1.587 1.015	1.092 1.614 1.018	- 1.016 1.016	- 1.020 1.019	- 1.017 1.017	- 1.020 1.020	- 1.017 1.017	- 1.020 1.020
ΔE	0.0	1.6	6.2	0.0	34.3	37.1	52.6	59.4	53.2	60.7
ΔG	0.0	1.7	6.3	0.0	32.2	35.1	48.1	54.7	48.1	55.3

	F		**G**		**H**		**I**		**J**	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
ϕ_1 ϕ_2	-167.2 46.2	-168.7 47.1	51.8 -151.8	52.1 -150.8	176.6 90.0	176.7 93.2	177.8 -68.3	177.3 -66.4	180.0 180.0	180 180
$R_{N_a\cdots H}$ $R_{N_s\cdots H}$ $R_{N\cdots H}$	1.030 - 1.014	1.030 - 1.017	- 1.014 1.044	- 1.017 1.042	1.030 1.014 -	1.030 1.016 -	- - 1.035	- - 1.037	- - 1.035	- - 1.037
ΔE	77.1	69.6	102.4	93.5	123.1	117.8	258.1	27.0	261.0	273.5
ΔG	73.1	65.7	99.9	91.2	117.8	112.4	253.7	266.8	256.4	269.7

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.

A



B

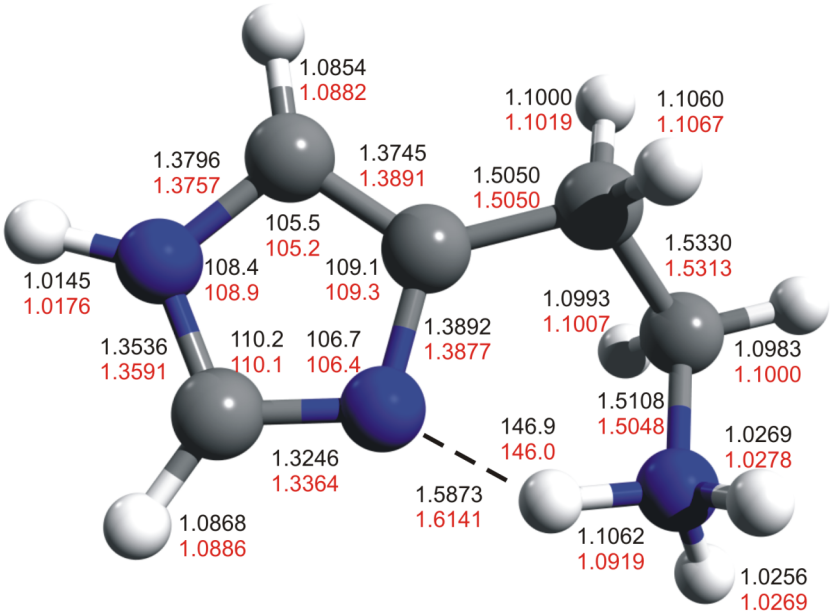
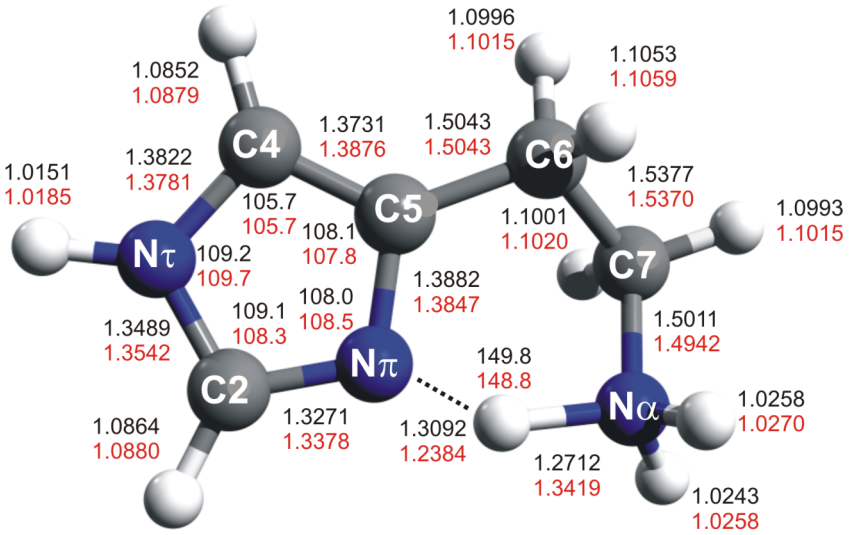


Figure S2. Bond distances (in Å), selected bond angles, and NBO charge distribution (bottom) of the transition state **TS** between the two low-energy isomers **A** and **B** of histamineH^+, calculated at the B3LYP (black) and MP2 (red) levels using the cc-pVDZ basis set.



TS_AB

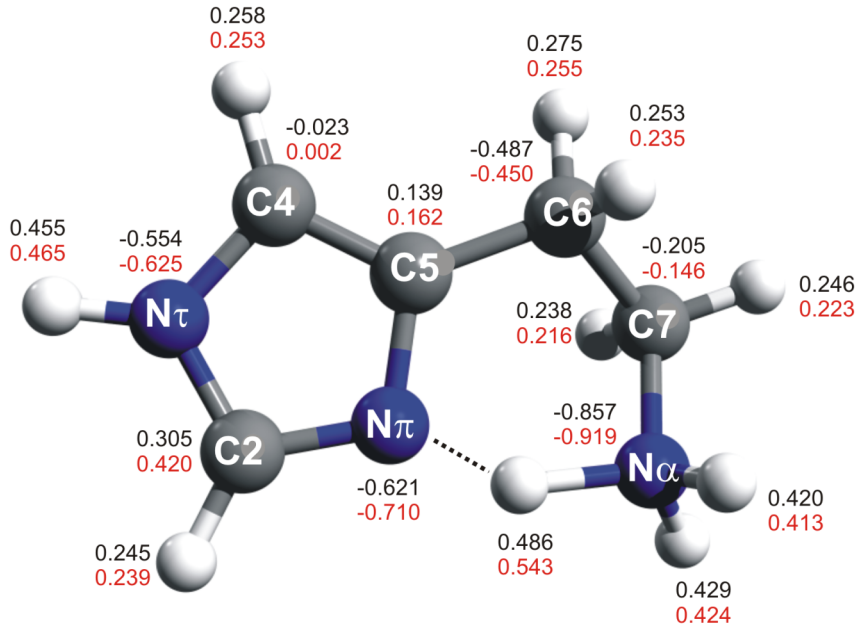


Figure S3. Potential energy scan of histamineH^+ along the proton transfer isomerization coordinate connecting the two minima **A** and **B** via a transition state **TS** (B3LYP/cc-pVDZ). The energies were obtained by changing the Nπ-H bond distance and optimizing all other coordinates.

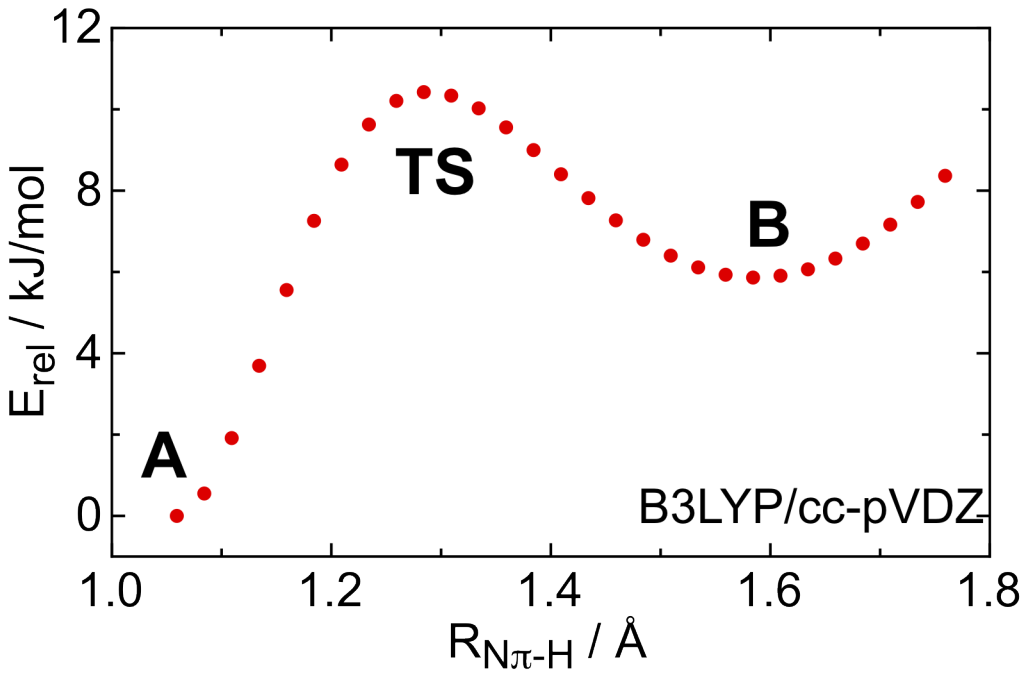


Figure S4. NBO charge distribution of the two low-energy isomers **A** and **B** of histamineH$^+$, calculated at the B3LYP (black) and MP2 (red) levels using the cc-pVDZ basis set.

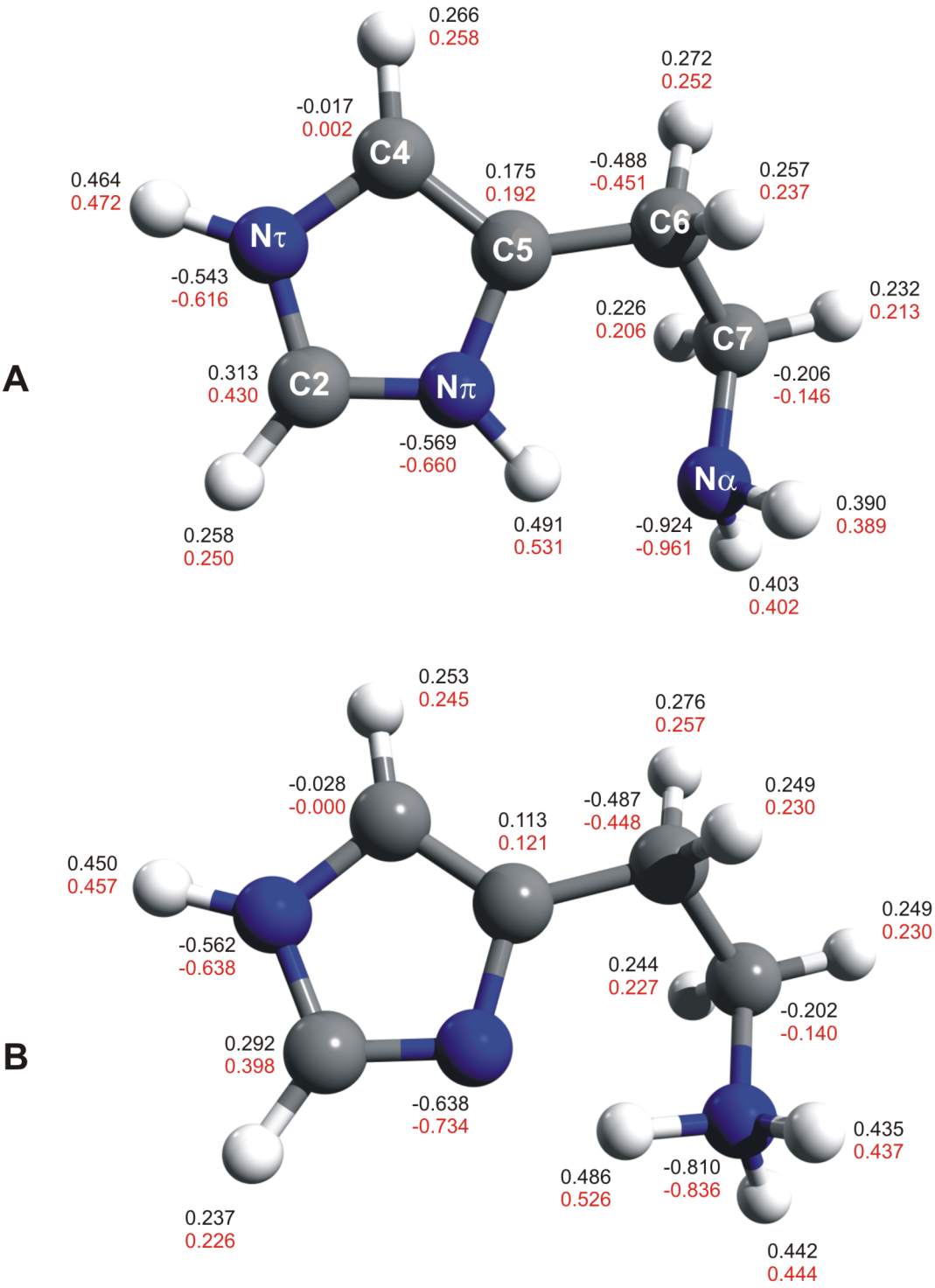


Figure S5. Calculated absorption spectra (B3LYP/cc-pVDZ) of isomers **A**-**J** of histamineH^+ compared to the IRMPD spectrum. Intensities are all on the same scale. Relative energy differences (ΔE in kJ/mol) are given in parentheses.

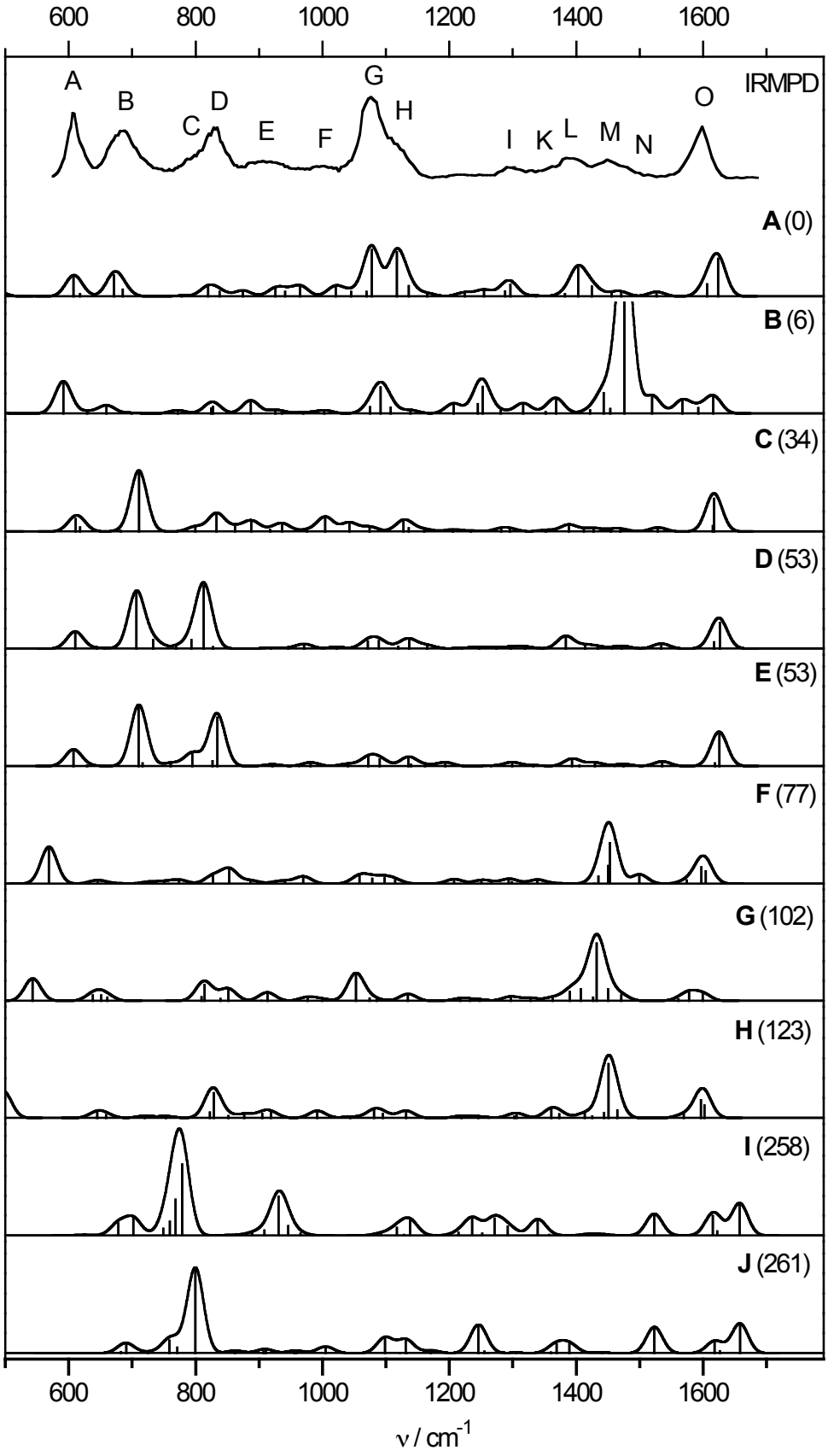


Figure S6. Comparison of linear IR absorption spectra of the isomers **A** and **B** of histamineH^+ in harmonic (scaling factor 0.98) and anharmonic approximation (B3LYP/cc-pVDZ).

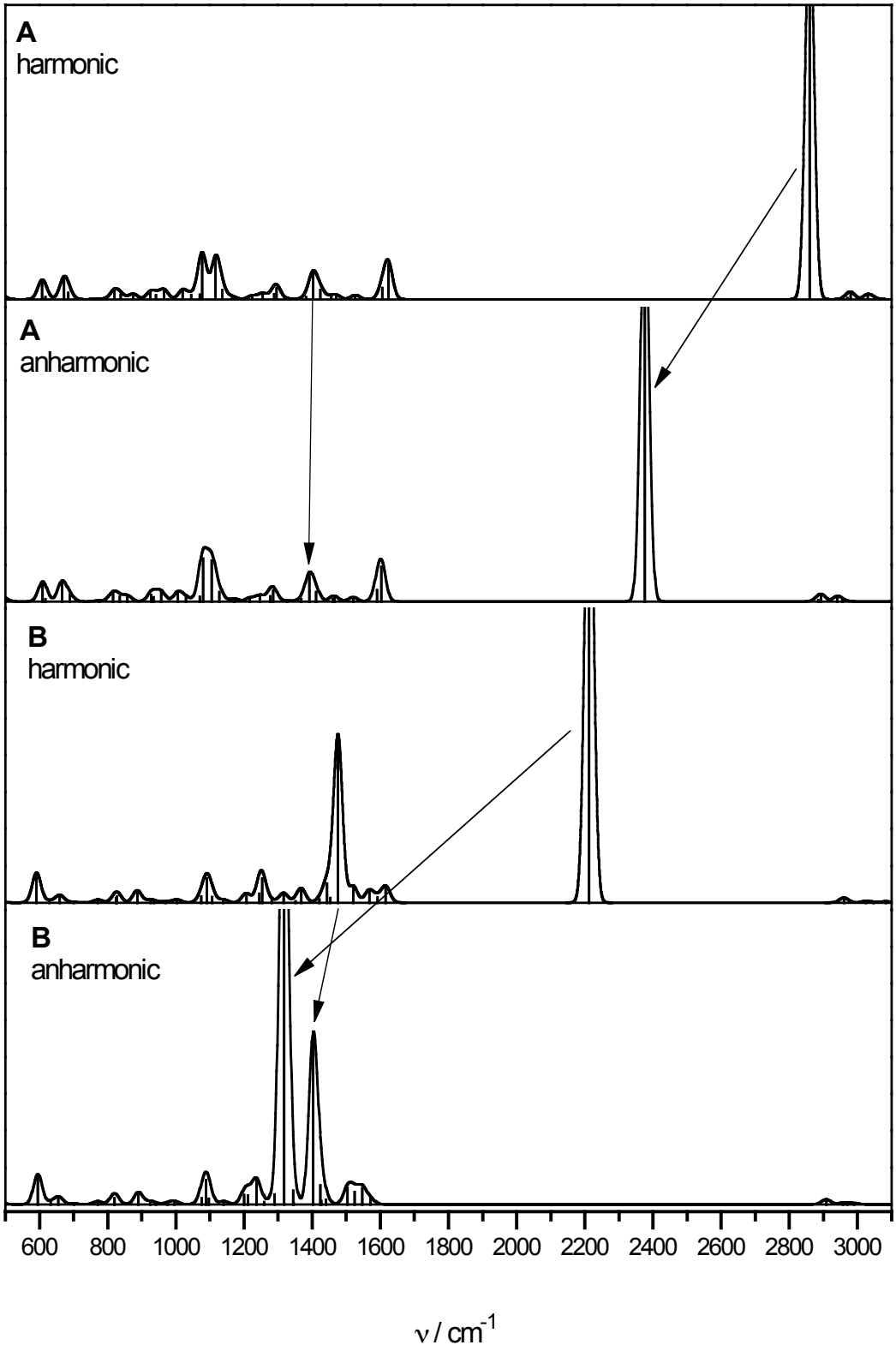


Figure S7. Comparison of linear IR absorption spectra of the isomers **A** and **B** of histamineH^+ and the corresponding transition state **TS** (B3LYP/cc-pVDZ) with the experimental IRMPD spectrum. Calculated intensities are all drawn to the same scale. The most intense for isomer **B** peak is cut at approximately 50%.

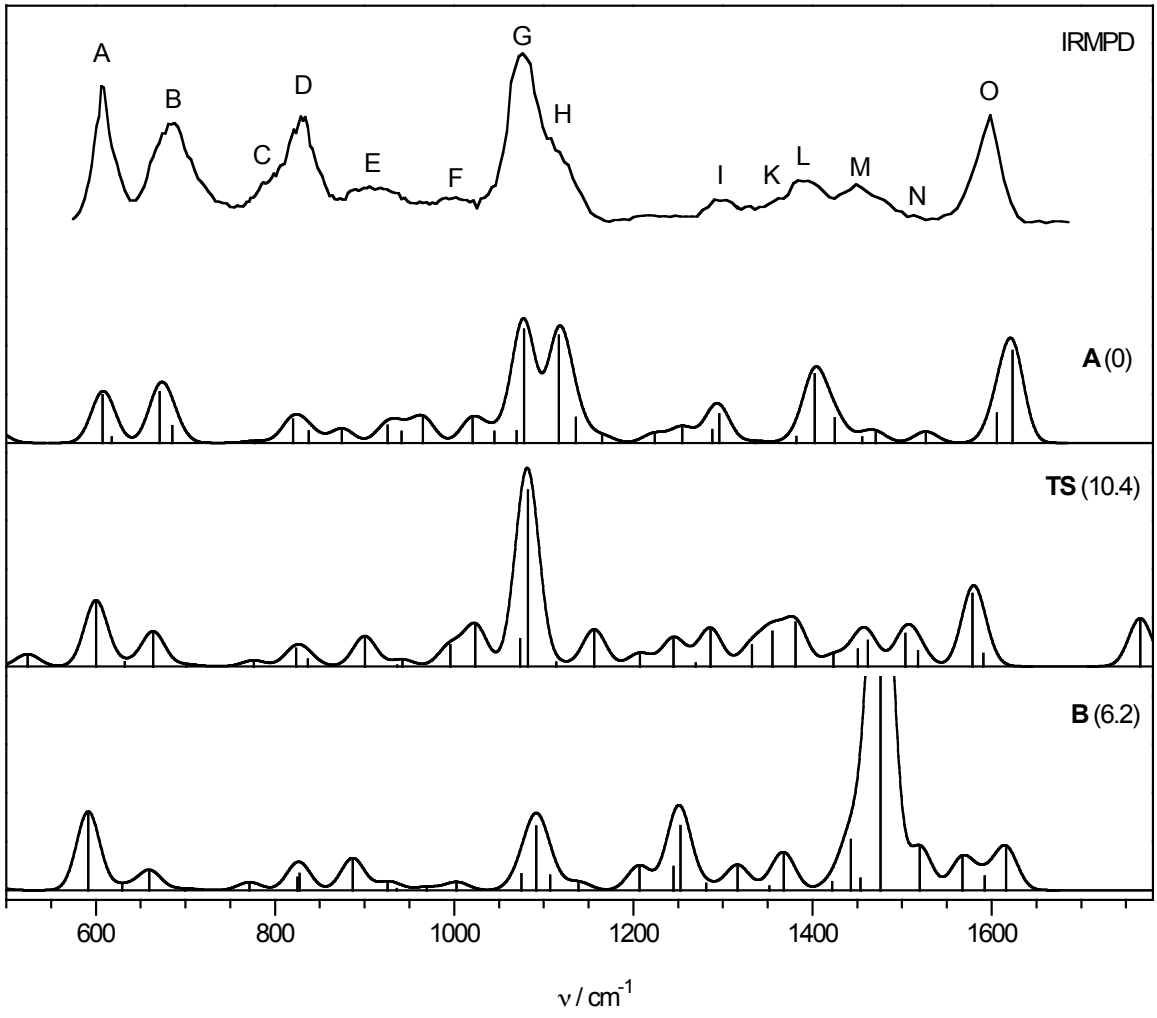
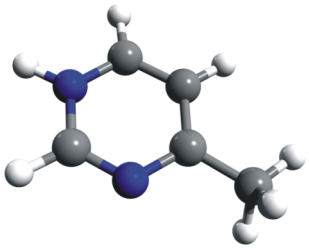


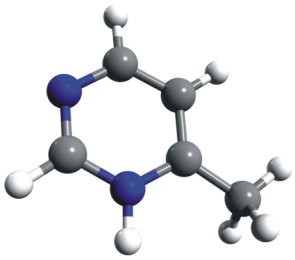
Figure S8. Possible structures of the m/z=95 fragment ion calculated at the B3LYP/cc-pVDZ level. Relative energies ΔE are given with respect to the most stable **FI_95** ion. The D_0 values correspond to binding energies for NH_3 elimination from the **A** isomer of histamineH^+.



FI_95

ΔE_{rel}= 0 kJ/mol

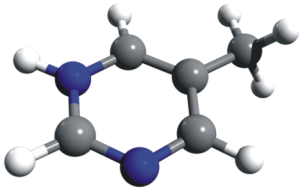
D_0= 79 kJ/mol



FII_95

ΔE_{rel}= 3 kJ/mol

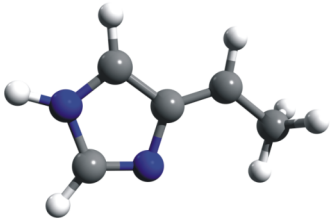
D_0= 82 kJ/mol



FIII_95

ΔE_{rel}= 17 kJ/mol

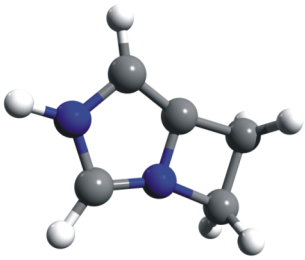
D_0= 96 kJ/mol



FIV_95

ΔE_{rel}= 75 kJ/mol

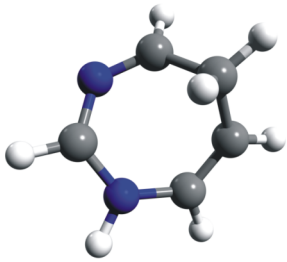
D_0= 153 kJ/mol



FV_95

ΔE_{rel}= 102 kJ/mol

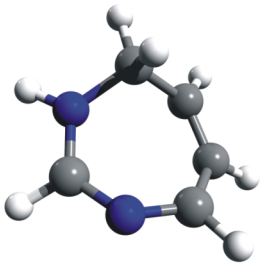
D_0= 181 kJ/mol



FVI_95

ΔE_{rel}= 108 kJ/mol

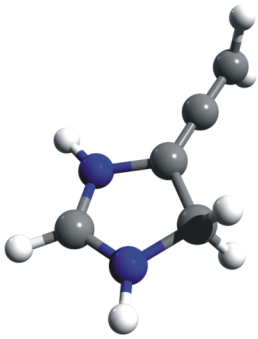
D_0= 187 kJ/mol



FVII_95

ΔE_{rel}= 132 kJ/mol

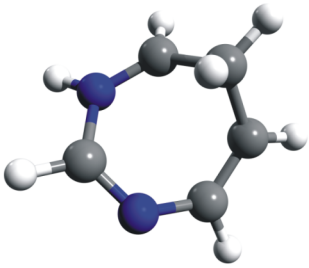
D_0= 211 kJ/mol



FVIII_95

ΔE_{rel}= 142 kJ/mol

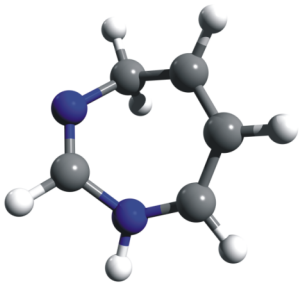
D_0=220 kJ/mol



FIX_95

ΔE_{rel}= 156 kJ/mol

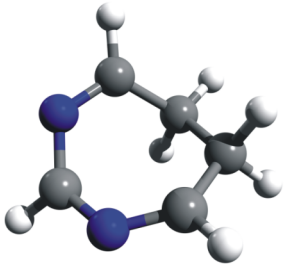
D_0= 234 kJ/mol



FX_95

ΔE_{rel}=158 kJ/mol

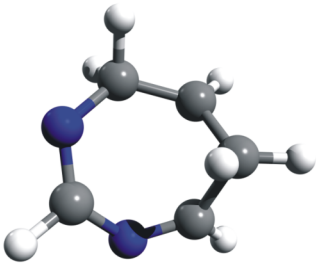
D_0= 237 kJ/mol



FXI_95

ΔE_{rel}= 217 kJ/mol

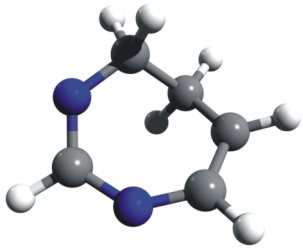
D_0= 296 kJ/mol



FXII_95

ΔE_{rel}= 329 kJ/mol

D_0= 408 kJ/mol

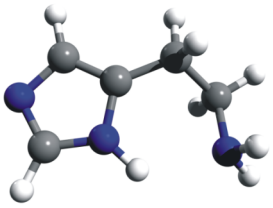


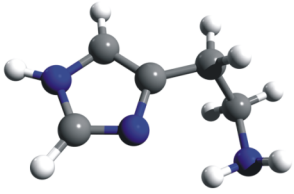
FXIII_95

ΔE_{rel}= 354 kJ/mol

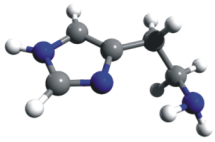
D_0= 433 kJ/mol

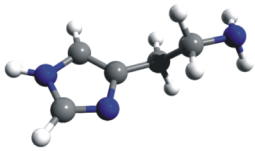
Figure S9. Structures of neutral histamine isomers calculated at the B3LYP/cc-pVDZ level. Relative energies (ΔE) and relative free energies (ΔG at 298 K) are given with respect to the most stable structure **A(n)**. Values in parentheses are calculated at the MP2/cc-pVDZ level. All values are given in kJ/mol.

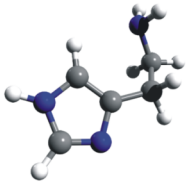


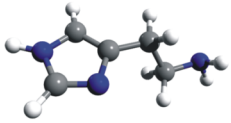


	A(n)	**B(n)**
ΔE	0.0 (0.0)	7.6 (9.2)
ΔG	0.0 (0.0)	6.1 (7.5)

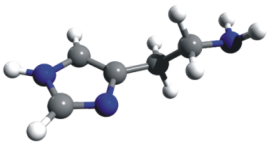


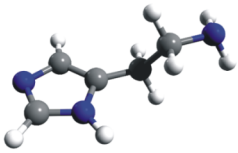


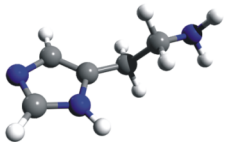


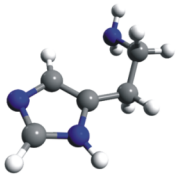


	C(n)	**D(n)**	**E(n)**	**F(n)**
ΔE	10.8 (12.3)	12.2 (15.8)	13.7 (15.1)	14.5 (17.4)
ΔG	9.4 (10.6)	9.3 (12.8)	12.0 (13.5)	11.4 (14.3)





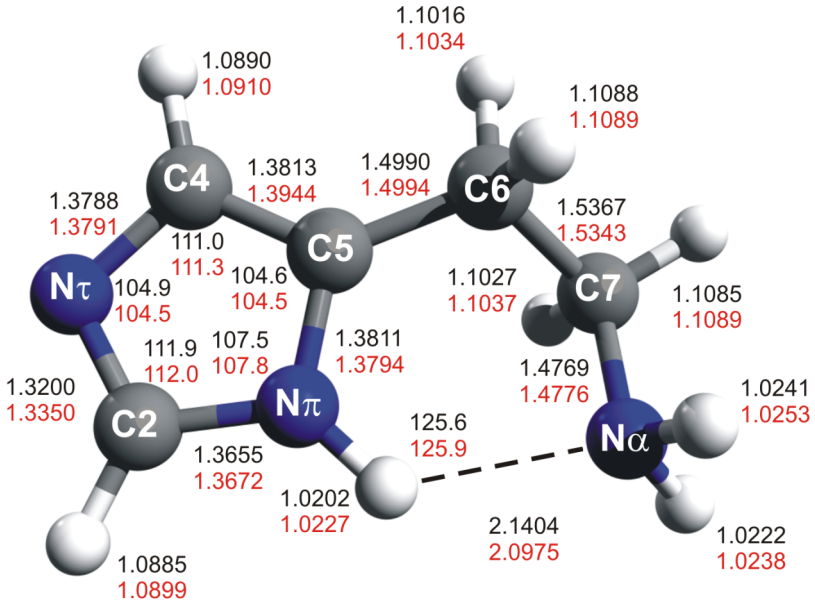




	G(n)	**H(n)**	**I(n)**	**J(n)**
ΔE	15.2 (18.5)	16.3 (20.1)	18.6 (22.1)	21.7 (23.6)
ΔG	12.1 (15.3)	13.2 (17.0)	15.2 (18.7)	19.3 (18.7)

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.

A(n)



A

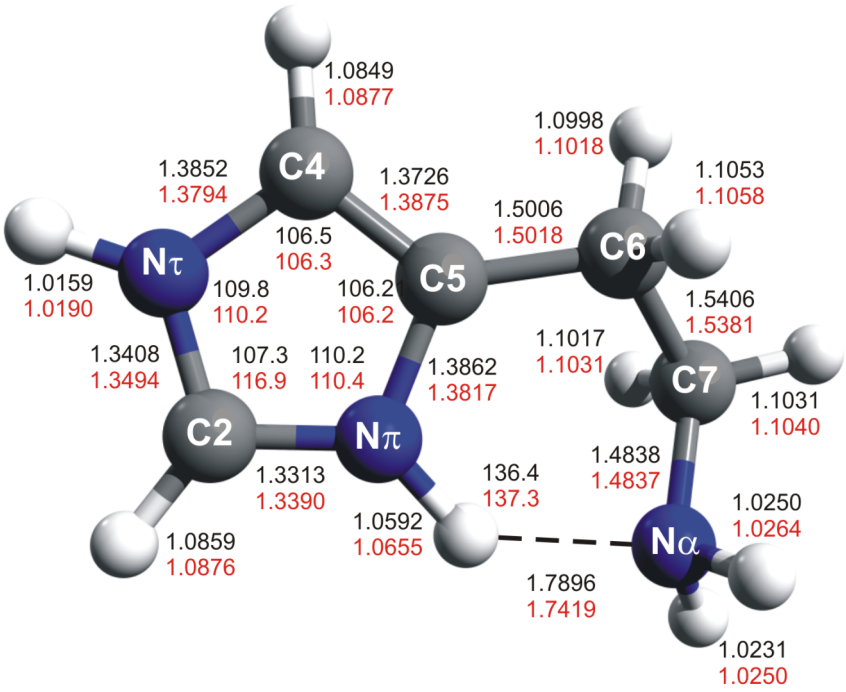


Figure S11. NBO charge distribution of the most stable structures of neutral (**A(n)**) and protonated histamine (**A**), calculated at the B3LYP (black) and MP2 (red) levels using the cc-pVDZ basis set.

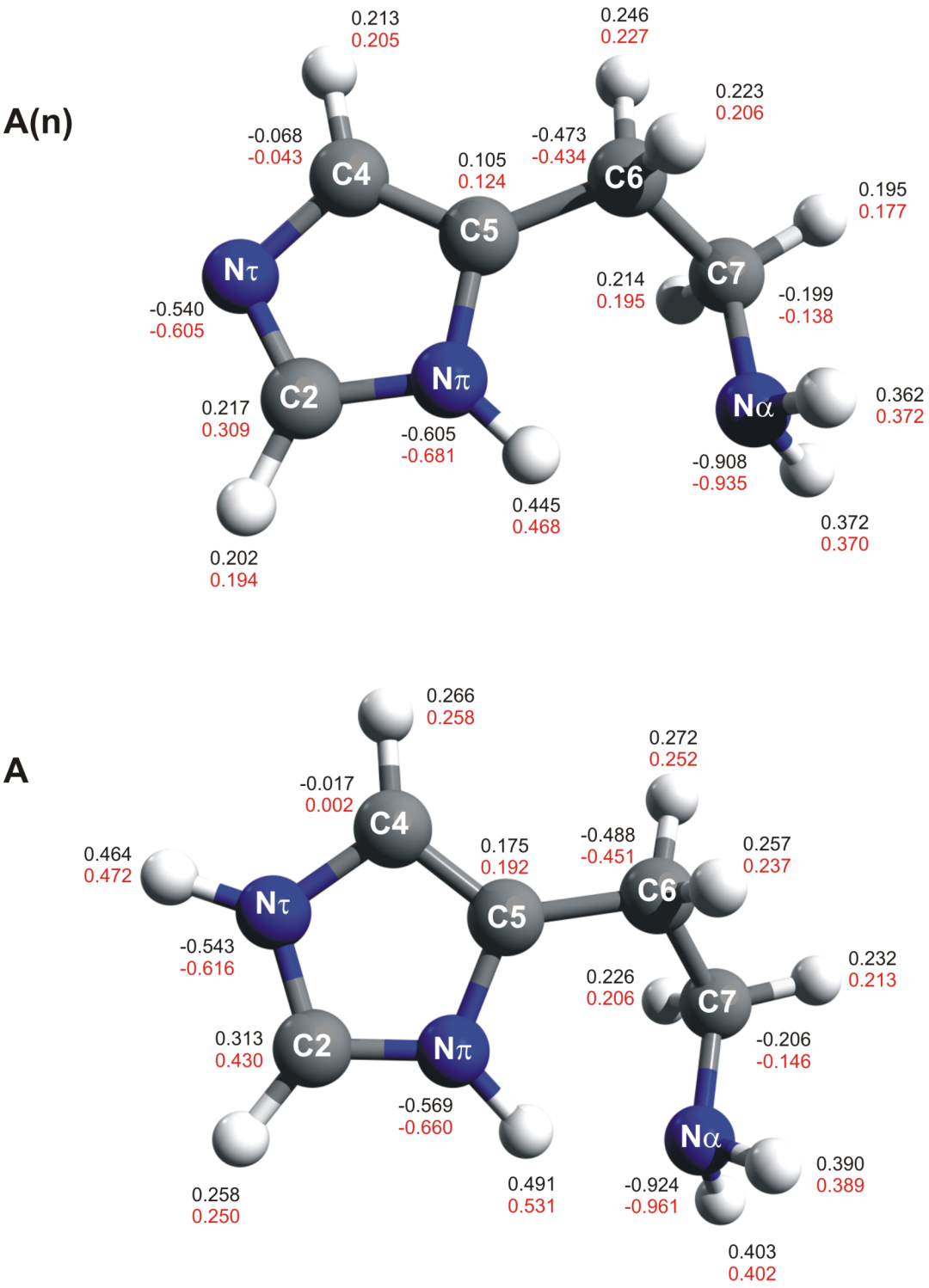


Figure S12. Comparison of linear IR absorption spectra of the histamine(H^+) isomers **A** and **A(n)** (B3LYP/cc-pVDZ) with the experimental IRMPD spectrum of histamineH^+ and the solid-state spectrum available from the NIST database. Note that the NIST spectrum is spectrally contaminated by oil resonances at 1450 and 1380 cm^{-1}.