Supporting Information

Infrared spectra of protonated neurotransmitters: dopamine

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Figure F1. Bond distances (in Å) of the most stable isomers of protonated and neutral dopamine calculated at the B3LYP and MP2 levels using the cc-pVDZ basis set.

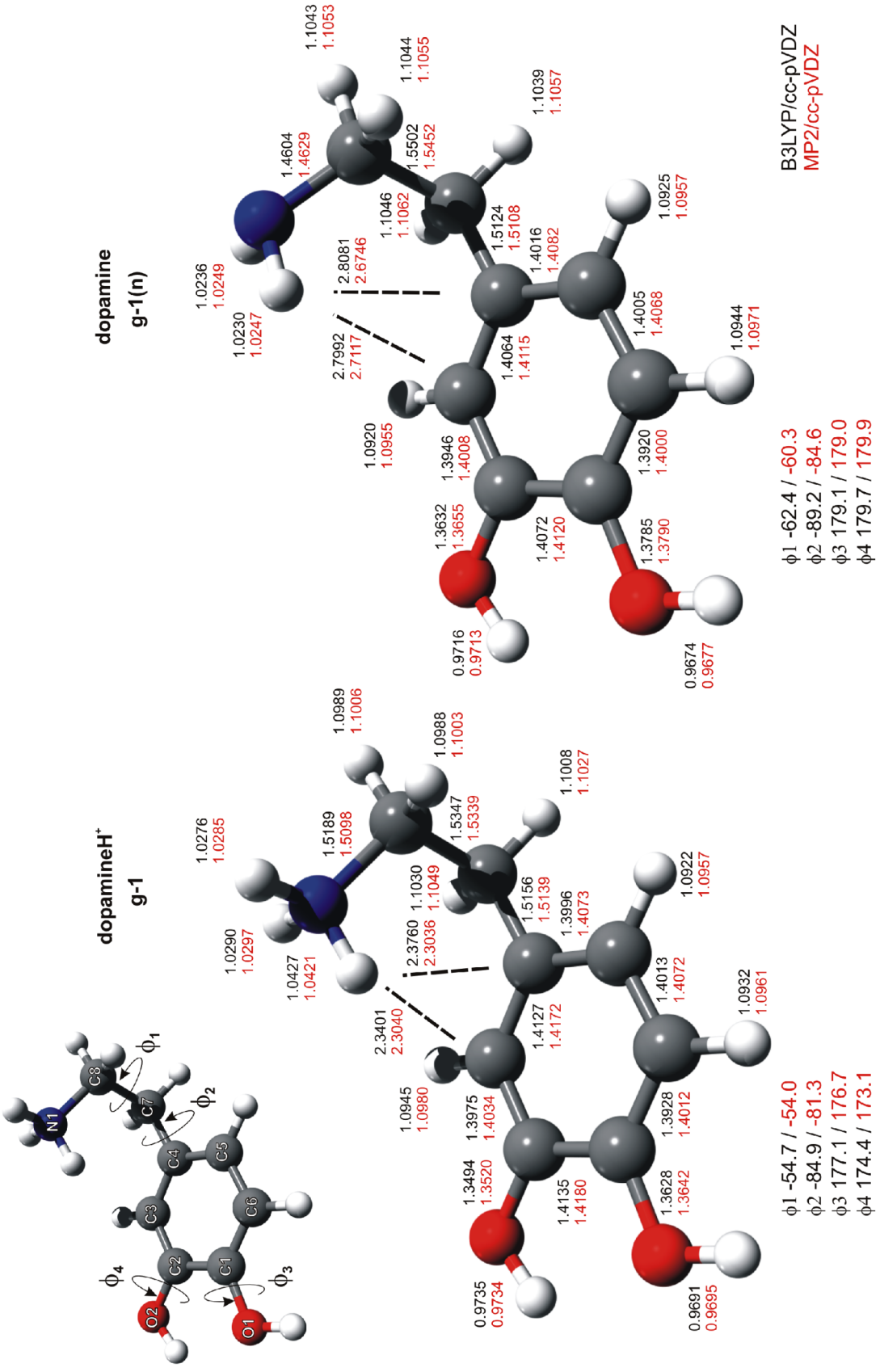


Figure F2. NBO charge distribution of the most stable isomers of protonated and neutral dopamine calculated at the B3LYP and MP2 levels using the cc-pVDZ basis set.

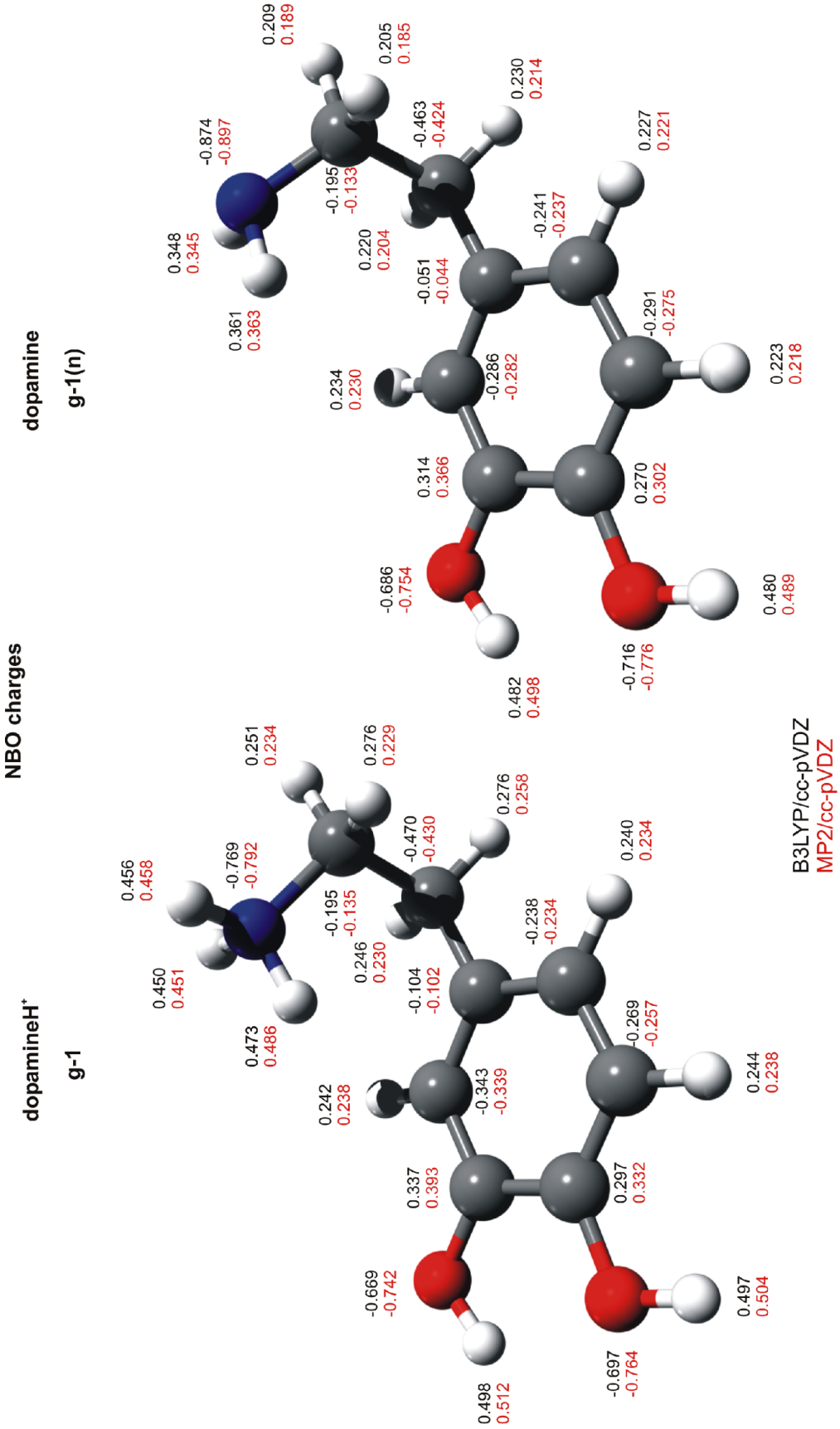
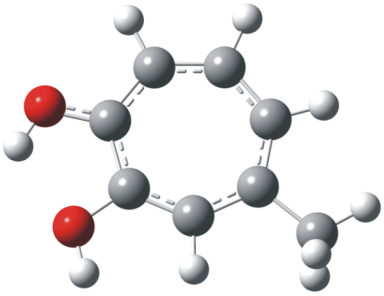


Figure F3. Possible structures of the fragment ion with m = 137 u calculated at the B3LYP/cc-pVDZ (MP2/cc-pVDZ) level. Relative energies ΔE_{rel} are given with respect to the **FIII** ion. The D_0 values correspond to binding energies for NH_3 elimination from the **g-1** isomer of dopamineH^+.

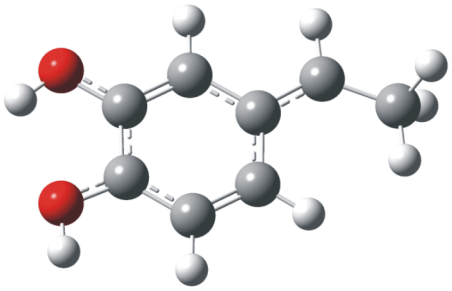


FIII

1,2-dihydroxy-4-methyl-cycloheptatrienyl cation

ΔE_{rel}= 0 (0) kJ/mol

D_0= 62 (98) kJ/mol

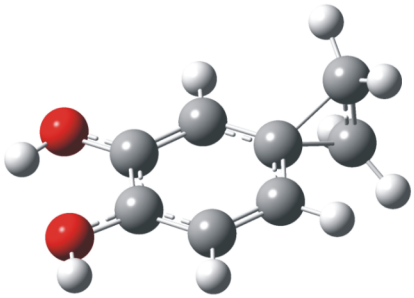


FI

1,2-dihydroxy-2,5-cyclohexa-dienyl-4-ethylidene cation

ΔE_{rel}= 19 (34) kJ/mol

D_0= 81 (133) kJ/mol



FII

phenonium cation

ΔE_{rel}= 83 (71) kJ/mol

D_0= 145 (169) kJ/mol

In an effort to identify the structure of the fragment ion with m = 137 u, several prospective candidates are considered. After elimination of NH_3 from N-protonated dopamineH^+, several 137 u fragment ions can be formed (Fig. F3). These ions are found after cutting off the NH_3 fragment from various low-lying conformers of dopamineH^+. The three ions obtained are the 1,2-dihydroxy-2,5-cyclo-hexadienyl-4-ethylidene cation (**FI**), with a dissociation energy of D_0 = 81 (133) kJ/mol at B3LYP (MP2), a phenonium-type cation obtained after ring closure (**FII**), with D_0 = 145 (169) kJ/mol, and a seven-membered ring of a cycloheptatrienyl-type ion (**FIII**), with D_0 = 62 (98) kJ/mol. All D_0 values are given with respect to the **g-1** isomer. The **FI** ion is obtained after a simple H-shift following NH_3 elimination from **t1** with an activation barrier of 112 (130) kJ/mol. The **FII** ion is an arenium ion, in which a cyclohexadienyl cation is spiro-annulated with a cyclopropane unit. It is obtained after NH_3 elimination from **g-1** with an activation barrier of 182 (230) kJ/mol. Ion **FIII** can be derived after substantial rearrangement of either the ethylidene-type or the phenonium-type ion. However, this process involves a much higher barrier as compared to dissociation in **FI** and **FII**. In order to evaluate which of the ions **FI**-**FIII** are likely candidates for the observed 137 u fragment ion, the IR spectra calculated for **FI**-**FIII** are compared to the experimental IR action spectra measured in the 137, 119 and 91 u fragment channels in Fig. F4. The likely candidates need to have significant absorption cross sections for the bands observed in all experimental spectra (137, 119 and 91 u). However, as the sequential IRMPD process is complex and involving the 137 u intermediate fragment with unknown amount of internal energy, it is difficult to predict the IR action spectra observed in the 137, 199 and 91 u channels from the calculated linear absorption spectra. In general, the IR spectra of **FI** and **FIII** are rather different in appearance. The fact that bands L and M in the experimental 91, 119 and 137 u spectra are rather intense and fragment **FIII** has no strong band in this spectra range, indicates that the **FIII** is not likely to contribute much to the 137 u ion population. On the other hand, the **FII** and **FI** spectra are both compatible with the experimental IR action spectra, leaving both ions as possible candidates for the 137 u ion. According to the above energetics, fragmentation of **g-1** into **FI** and NH_3 has by far the lowest predicted activation barrier and is thus a likely IRMPD dissociation pathway.

Figure F4. Ion currents of the protonated dopamine parent ion (m = 154 u) and the three fragment channels (m = 137, 91 and 119 u) compared to absorption spectra calculated for three possible fragment ions with m = 137 u (**FI**-**FIII**, see Fig. F3).

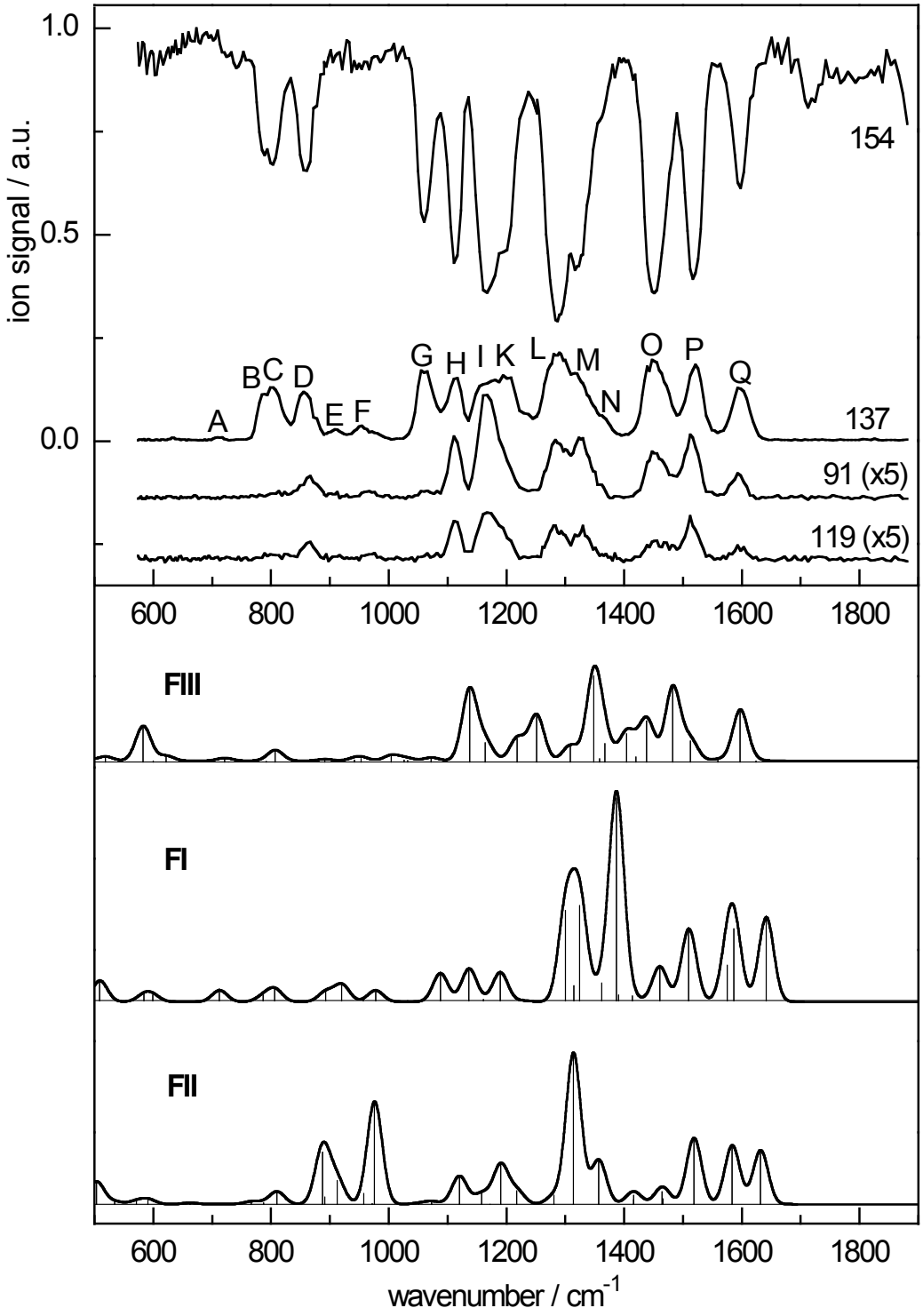


Figure F5. Most stable *gauche* and *trans* structures of dopamineH$^+$, dopamine, and dopamine*HCl calculated at the B3LYP/cc-pVDZ (MP2/cc-pVDZ) level. Relative energies are given in kJ/mol.

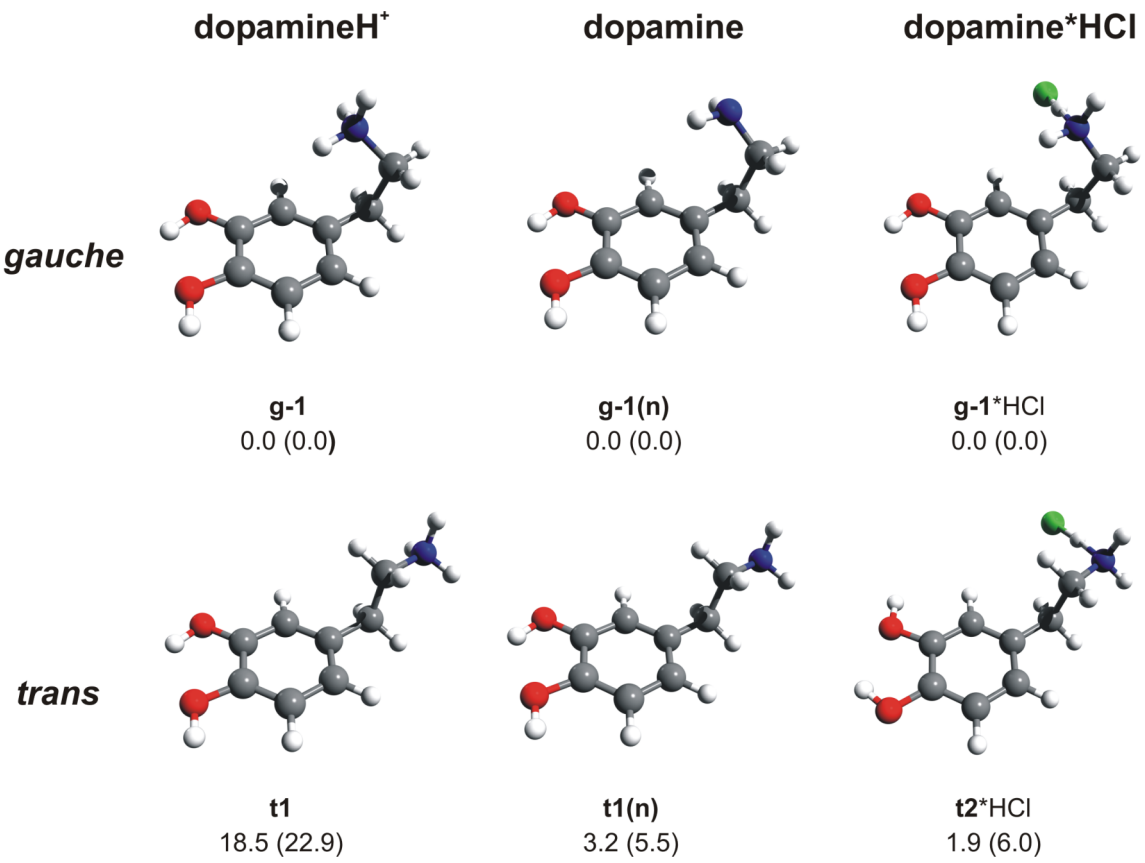


Figure F6. Comparison of the IRMPD spectrum of dopamineH^+ with the experimental IR spectrum of dopamine*HCl (taken from the NIST database) and IR spectra calculated for the most stable *gauche* isomers of dopamineH^+, **g-1**, and neutral dopamine, **g-1(n)**, as well as the most stable *trans* isomer of neutral dopamine, **t1(n)**, calculated at the B3LYP level.

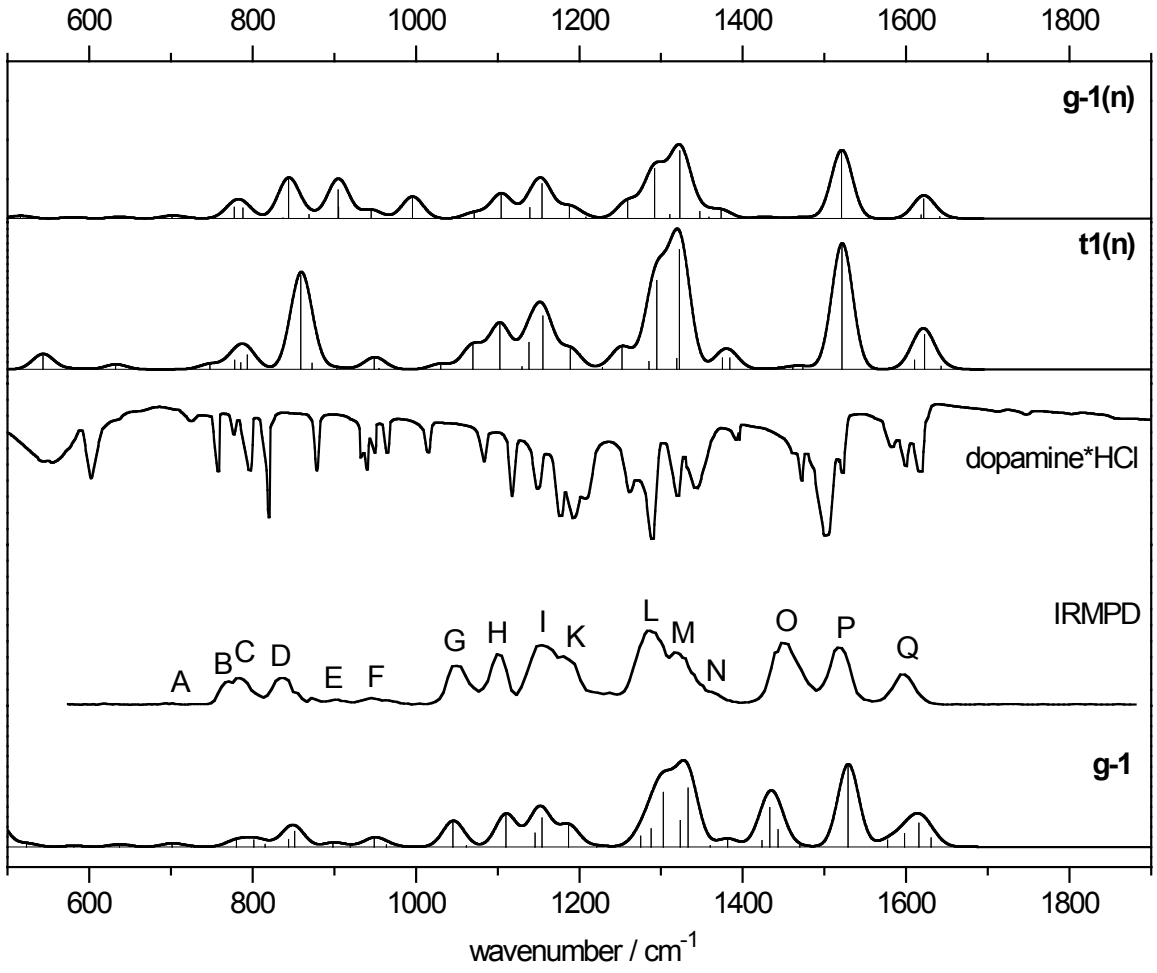


Table T1. Relative energies (ΔE) and free energies (ΔG, in parentheses) at 298 K (in kJ/mol) of selected isomers of dopamineH^+ calculated at different levels of theory using the cc-pVDZ basis set. Zero-point energies are scaled with 0.98 for all density functionals and with 0.97 for MP2.

	B2PLYP	B2PLYP-D	M06-2X	B3LYP	MP2	B3PLYP*	B3PLYP-D*
g-1	0.0 (0.4)	0.0 (0.0)	0.0 (0.9)	0.0 (0.1)	0.0 (0.2)	0.0 (0.0)	0.0 (0.0)
g+1	0.5 (0.0)	0.7 (0.1)	0.2 (0.0)	0.5 (0.0)	0.5 (0.0)	0.6 (0.2)	0.8 (0.3)
t1	19.7 (17.8)	22.7 (20.6)	22.7 (22.5)	18.5 (16.4)	22.9 (20.7)	18.4 (16.1)	24.1 (21.9)

* Calculated with TURBOMOLE 6.0.

Table T2. Selected bond distances (in Å), dihedral angles (in degrees), and relative energies and free energies at 298 K (in kJ/mol) of all considered protonated dopamine isomers calculated at the B3LYP and MP2 levels (Figs. 1 and 2).[a]

	g-1		**g+1**		**g+2**		**g-2**		**t1**		**g+3**	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
ϕ_1	-54.7	-54.0	54.7	53.3	54.5	53.9	-49.0	-48.6	-178.4	-178.7	54.4	53.7
ϕ_2	-84.9	-81.3	-98.5	-101.6	-92.9	-94.4	-62.3	-63.6	-97.0	-95.1	-94.8	-96.7
ϕ_3	177.1	176.7	177.5	177.1	6.2	9.4	11.2	15.8	178.7	178.3	3.5	4.8
ϕ_4	174.4	173.1	174.5	173.0	1.9	2.6	2.7	3.4	177.7	176.6	177.0	176.3
$R_{NH\cdots C3/5}$	2.340	2.304	2.422	2.414	2.335	2.290	2.850	2.735	-	-	2.352	2.317
$R_{NH\cdots C4}$	2.376	2.303	2.339	2.264	2.350	2.281	2.326	2.265	-	-	2.334	2.265
$R_{OH\cdots OH}$	2.133	2.122	2.125	2.114	2.131	2.117	2.138	2.125	2.127	2.114	-	-
ΔE	0.0	0.0	0.5	0.5	4.2	4.3	8.7	8.1	18.5	22.9	20.7	20.7
ΔG	0.1	0.2	0.0	0.0	4.3	4.6	5.4	5.6	16.4	20.7	20.8	20.9

	g-3		**t2**		**t3**		**g-1(O2)**		**g-2(O1)**	
	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2	B3LYP	MP2
ϕ_1	-52.8	-51.5	178.3	178.6	179.4	179.6	-68.6	-70.5	-70.0	-71.8
ϕ_2	-75.2	-72.4	-84.5	-83.7	-87.8	-87.8	-138.1	-136.7	-136.1	-134.1
ϕ_3	7.4	8.9	4.8	7.2	2.5	3.0	175.0	174.7	-10.1	-17.9
ϕ_4	177.020	176.4	1.0	1.4	178.7	178.3	165.9	156.2	-4.3	-4.8
$R_{NH\cdots C3}$	2.516	2.467	-	-	-	-	-	-	-	-
$R_{NH\cdots C4}$	2.335	2.26	-	-	-	-	-	-	-	-
$R_{OH\cdots OH}$	-	-	2.130	2.116	-	-	1.827	1.806	1.823	1.805
ΔE	24.3	23.6	24.6	29.1	40.5	45.0	155.8	164.6	157.2	167.1
ΔG	23.5	22.7	22.6	26.7	38.3	42.8	154.9	163.8	156.5	166.1

[a] ϕ_1 = dihedral angle C4C7C8N1, ϕ_2 = dihedral angle C5C4C7C8, ϕ_3 = dihedral angle C2C1O1H, ϕ_4 = dihedral angle C3C2O2H.

Table T3. Experimental vibrational frequencies of dopamineH^+ (IRMPD spectrum) compared to values for the **g-1** isomer of dopamineH^+ and the **g-1(n)** isomer of dopamine calculated at the B3LYP/cc-pVDZ level.

dopamineH^+ [a] ν_{exp} / cm^{-1}	**g-1** [b] ν_{calc} / cm^{-1}	vibration [c]	**g-1(n)** [b] ν_{calc} / cm^{-1}	vibration [c]
1595 (31) Q	1631 (22)	arom. σ_{CC} (ν_{8a})	1642 (5)	arom. σ_{CC} (ν_{8a})
	1616 (59)	arom. σ_{CC} (ν_{8b})	1622 (50)	arom. σ_{CC} (ν_{8b})
	1598 (33)	β_{NH3} asym.	1619 (8)	β_{NH2} sym.
	1577 (16)	β_{NH3} asym.	-	-
1516 (30) P	1529 (205)	arom. σ_{CC} (ν_{19b})	1521 (174)	arom. σ_{CC} (ν_{19b})
	1470 (2)	arom. σ_{CC} (ν_{19a})	1474 (4)	arom. σ_{CC} (ν_{19a})
1449 (40) O	1444 (42)	β_{CH2} sym. (scissoring, C8)	1433 (1)	β_{CH2} sym. (scissoring, C8)
	1433 (97)	β_{NH3} sym., umbrella	-	-
	1424 (15)	β_{CH2} sym. (scissoring, C7)	1426 (4)	β_{CH2} sym. (scissoring, C7)
1358 (?) N	1382 (20)	arom. σ_{CC}	1374 (21)	arom. σ_{CC}
	1361 (2)	β_{CH2} sym. (wagging, C8)	1348 (17)	β_{CH2} sym. (wagging, C8)
1319 (31) M	1333 (146)	β_{CH2} sym. (wagging, C7)	1311 (10)	β_{CH2} sym. (wagging, C7)
	1323 (65)	β_{COH} (in-plane, in-phase)	1323 (172)	β_{COH} (in-plane, in-phase)
1287(38) L	1303 (135)	σ_{CO}, (C1-O1)	1292 (127)	σ_{CO}, (C1-O1)
	1288 (45)	τCH_2 (torsion, C8) plus wag C7	1359 (3)	τCH_2 (tors, C8) plus scissor C7
	1275 (27)	σ_{CO} (C2-O2)	1259 (45)	σ_{CO} (C2-O2)
	1221 (3)	τCH_2 (torsion, C7)	1208 (4)	τCH_2 (torsion, C7)
1197 (33) K	1187 (54)	β_{COH} (in-plane, out-of-phase)	1188 (31)	β_{COH} (in-plane, out-of-phase)
1166 (40) I	1154 (71)	arom. β_{CH} (C3)	1154 (88)	arom. β_{CH} (C3)
	1146 (34)	arom. β_{CH} (C5/C6)	1140 (27)	arom. β_{CH} (C5/C6)
1114 (27) H	1110 (82)	arom. β_{CH} (C5/C6)	1105 (63)	arom. β_{CH} (C5/C6)
1060 (33) G	1062 (2)	CH_2 twist (CH_2/ CH_2/ NH_3)	1127 (0)	CH_2 twist (CH_2/ CH_2/ NH_2)
	1046 (64)	CH_2 twist (CH_2/ CH_2/ NH_3)	945 (22)	CH_2 twist (CH_2/ CH_2/ NH_2)
959 (50) F	964 (5)	aliph. σ_{CCN} (C7-C8-N1)	1072 (16)	aliph. σ_{CCN} (C7-C8-N1)
	949 (21)	aliph. σ_{CCN} (C7-C8-N1)	996 (56)	aliph. σ_{CCN} (C7-C8-N1)
909 (36) E	920 (2)	arom. γ_{CH} (C5/C6)	905 (29)	arom. γ_{CH} (C5/C6)
	899 (10)	CH_2 twist (CH_2/ CH_2/ NH_3)	905 (73)	CH_2 twist (CH_2/ CH_2/ NH_2)
858 (31) D	851 (38)	arom. γ_{CH} (C3)	869 (10)	arom. γ_{CH} (C3)
	844 (18)	σ_{CN}	844 (102)	σ_{CN}
	816 (6)	arom. γ_{CH} (C5/C6)	788 (26)	arom. γ_{CH} (C5/C6)
802 (22) C	802 (16)	delocalized[d]	837 (1)	delocalized[d]
786 (22) B	780 (16)	arom. γ_{CC} (ν_1)	777 (28)	arom. γ_{CC} (ν_1)
	725 (1)	arom. γ_{CC} (ν_4)	719 (1)	arom. γ_{CC} (ν_4)
712 (20) A	702 (9)	ring (ν_{-2})	702 (7)	ring (ν_{-2})

[a] Widths (in cm^{-1}) of the transitions are given in parentheses (see Fig. 3, 5 or F3 for labels of the transitions).

[b] IR intensities in km/mol are given in parentheses.

[c] The nomenclature for the modes of the aromatic ring is adopted from the Wilson notation for substituted benzene derivatives. The notation σ, γ, β, and τ is used to designate stretch, out-of-plane bend, in-plane bend, and torsional motions, respectively.

[d] Strongly coupled mode involving aromatic γ_{CH} and alkyl twist, torsion, and stretch motions.