Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic supplementary information for: “Influence of the N atom position on the excited state photodynamics of protonated azaindole.”

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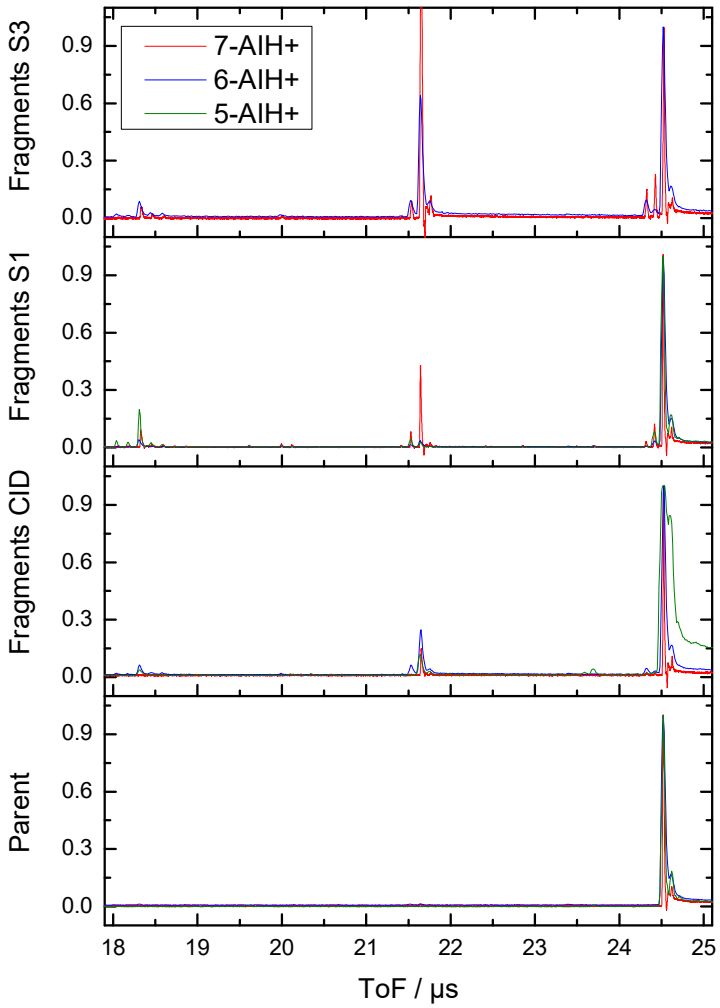

Figure SI-1: Time of flight mass spectra of protonated 7-, 6-, and 5-azaindole upon collision induced dissociation (CID), and photofragmentation in excited states S_1 and S_3 (7-AIH$^+$ and 6-AIH$^+$ only).

Figure SI-2: Optimised geometries in S_0 of (l-r) 7-AIH$^+$, 6-AIH$^+$, and 5-AIH$^+$; $C_7N_2H_7^+$, where C atoms are grey, N atoms are blue, H atoms are white.

7-AIH$^+$ S_0 optimised geometry (x,y,z co-ordinates)

C	-0.8767320140	1.6717162266	2.0654094722
C	-0.6368294839	1.3712455317	3.3777476827
H	-0.0032388405	0.6071661170	3.8209409215
C	-1.7975953368	2.7760761521	2.0501402820
N	-1.3639669477	2.2350922383	4.2063032204
C	-2.0648846364	3.0828896708	3.4194425251
C	-2.4314779564	3.5445130402	1.0714804547
H	-2.2605142210	3.3494940210	0.0106495248
N	-2.9030968175	4.0838695289	3.7689610482
C	-3.2970881107	4.5772749895	1.4687415571
H	-3.8065858366	5.1943416292	0.7288615517
C	-3.5202572822	4.8316384028	2.8128678216
H	-4.1809734604	5.6189747229	3.1739242849
H	-0.4492415964	1.1675281443	1.2034126873
H	-3.0841989123	4.2915746450	4.7498750759
H	-1.3523231460	2.2106098049	5.2202451849

6-AIH$^+$ S_0 optimised geometry (x,y,z co-ordinates)

C	-1.5911460688	-1.2653543711	0.0000000000
C	-0.2613745458	-0.7687925694	0.0000000000
C	-0.3521257213	0.6693304023	0.0000000000
N	-1.6862267754	0.9961042094	0.0000000000
C	-2.4245718752	-0.1613890576	0.0000000000
C	1.0216825157	-1.3563164475	0.0000000000
C	2.1241588706	-0.5309523985	0.0000000000
N	1.9751854938	0.8291904407	0.0000000000
C	0.7785723896	1.4609535620	0.0000000000
H	-3.5119402382	-0.1180917017	0.0000000000
H	-2.0732388462	1.9331261715	0.0000000000
H	1.1580018465	-2.4380463826	0.0000000000
H	-1.9082701319	-2.3043913191	0.0000000000
H	0.7849749019	2.5508205366	0.0000000000
H	3.1496779026	-0.8976664246	0.0000000000
H	2.8166402821	1.4014753496	0.0000000000

5-AIH$^+$ S_0 optimised geometry (x,y,z co-ordinates)

C	-3.1562555879	3.5624946268	5.6358485426
C	-2.0608820652	2.7934831227	5.2121702906
C	-1.7726690859	2.5956936069	3.8146703215
C	-2.6132144362	3.1894307190	2.8856532811
N	-3.6574824443	3.9221765331	3.3328696840
C	-3.9464633158	4.1214557046	4.6541369076
N	-1.1100596790	2.1214877356	5.9077638443
C	-0.2299670229	1.5051860691	5.0241361258
C	-0.6010692899	1.7713637388	3.7322975853
H	0.6027924176	0.9173040583	5.4029853895
H	-1.0448638176	2.0705520342	6.9189151086
H	-2.4919991883	3.1070772524	1.8054463955
H	-4.2692827253	4.3541897239	2.6432775959
H	-4.8200370931	4.7352420726	4.8683770996
H	-0.1001501777	1.4220793918	2.8338901755
H	-3.3942101355	3.7259381163	6.6872131019

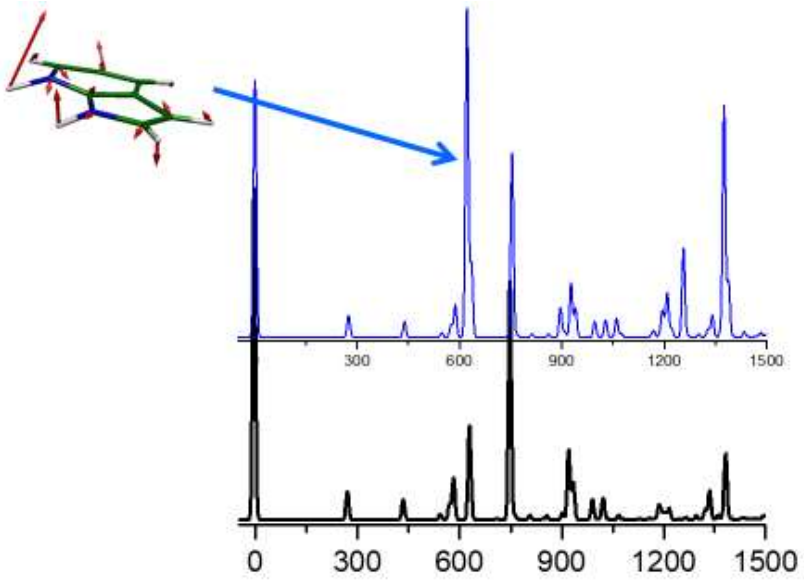

Figure SI-3: Two simulated spectra of 7-AIH$^+$ (cm^{-1}). The simulation in blue includes the v9 out-of-plane vibration. The one in black does not include this vibration and is much closer to the experimental spectrum (Figure 2), indicating that the first calculation overestimated the out-of-plane character of the excited state.

5-AIH$^+$				
S_0			S_1 (1A')	
1	a"	226	a"	153
2	a"	244	a"	221
3	a'	411	a"	338
4	a"	430	a"	379
5	a'	558	a'	388
6	a"	576	a"	466
7	a"	598	a'	514
8	a'	617	a"	524
9	a"	621	a"	556
10	a"	739	a"	609
11	a"	760	a'	619
12	a'	787	a"	696
13	a"	800	a"	717
14	a"	849	a'	754
15	a'	902	a"	791
16	a'	908	a'	878
17	a"	919	a"	893
18	a"	935	a'	907
19	a"	963	a"	958
20	a'	1045	a'	1002
21	a'	1082	a'	1045
22	a'	1107	a'	1121
23	a'	1171	a'	1156
24	a'	1219	a'	1184
25	a'	1267	a'	1219
26	a'	1291	a'	1228
27	a'	1346	a'	1283
28	a'	1385	a'	1357
29	a'	1427	a'	1408
30	a'	1465	a'	1439
31	a'	1520	a'	1484
32	a'	1545	a'	1522
33	a'	1596	a'	1574
34	a'	1650	a'	1625
35	a'	1675	a'	1677
36	a'	3223	a'	3224
37	a'	3232	a'	3251
38	a'	3248	a'	3257
39	a'	3262	a'	3271
40	a'	3279	a'	3295
41	a'	3570	a'	3590
42	a'	3616	a'	3613

6-AIH$^+$				
S_0			S_1 (1A')	
1	a"	229	a"	186
2	a"	252	a"	268
3	a'	411	a"	331
4	a"	434	a"	341
5	a"	521	a'	393
6	a'	560	a'	517
7	a"	588	a"	519
8	a'	613	a"	564
9	a"	620	a'	619
10	a"	729	a"	662
11	a"	774	a"	693
12	a'	789	a"	727
13	a"	814	a'	750
14	a"	867	a"	760
15	a'	899	a"	807
16	a'	910	a"	874
17	a"	914	a'	887
18	a"	941	a'	909
19	a"	983	a"	969
20	a'	1043	a'	1010
21	a'	1087	a'	1058
22	a'	1124	a'	1117
23	a'	1165	a'	1142
24	a'	1235	a'	1174
25	a'	1270	a'	1222
26	a'	1275	a'	1228
27	a'	1339	a'	1289
28	a'	1383	a'	1343
29	a'	1422	a'	1384
30	a'	1478	a'	1435
31	a'	1518	a'	1450
32	a'	1537	a'	1519
33	a'	1574	a'	1555
34	a'	1638	a'	1633
35	a'	1692	a'	1668
36	a'	3224	a'	3227
37	a'	3232	a'	3251
38	a'	3245	a'	3265
39	a'	3258	a'	3285
40	a'	3276	a'	3299
41	a'	3575	a'	3571
42	a'	3624	a'	3599

7-AIH$^+$				
S_0			S_1 bend	
1	a"	221	a	209
2	a"	249	a	273
3	a"	405	a	414
4	a'	423	a	438
5	a"	502	a	517
6	a'	558	a	538
7	a"	574	a	574
8	a"	608	a	587
9	a'	619	a	621
10	a"	718	a	634
11	a"	746	a	723
12	a'	771	a	753
13	a"	795	a	768
14	a"	826	a	811
15	a'	901	a	852
16	a'	909	a	884
17	a"	913	a	926
18	a"	954	a	939
19	a"	1014	a	995
20	a'	1060	a	1005
21	a'	1070	a	1039
22	a'	1104	a	1096
23	a'	1136	a	1149
24	a'	1220	a	1184
25	a'	1237	a	1198
26	a'	1299	a	1220
27	a'	1325	a	1244
28	a'	1376	a	1328
29	a'	1399	a	1368
30	a'	1476	a	1435
31	a'	1533	a	1459
32	a'	1542	a	1506
33	a'	1576	a	1534
34	a'	1656	a	1589
35	a'	1685	a	1736
36	a'	3209	a	3214
37	a'	3228	a	3251
38	a'	3245	a	3252
39	a'	3264	a	3268
40	a'	3281	a	3269
41	a'	3556	a	3576
42	a'	3619	a	3586

Table SI-1: All calculated vibrational modes for S_0 and S_1 of 5-, 6-, and 7-AIH$^+$ (cm^{-1}).

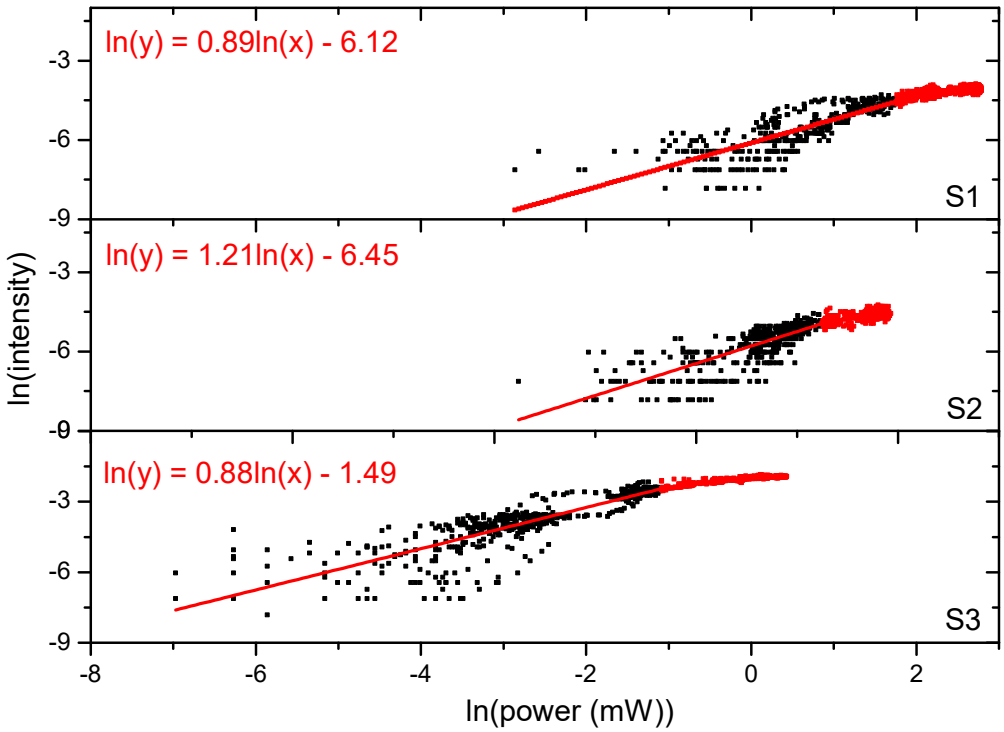

Figure SI-4: Power dependence of fragment m/z 92 in each excited state for 6-AIH$^+$. Linear fits to log-log plots are plotted in red. In all three states, the transition exhibits linearity at the beginning, before saturating at higher power (red data points not included in fit). From the power dependency, all transitions appear to involve one photon.

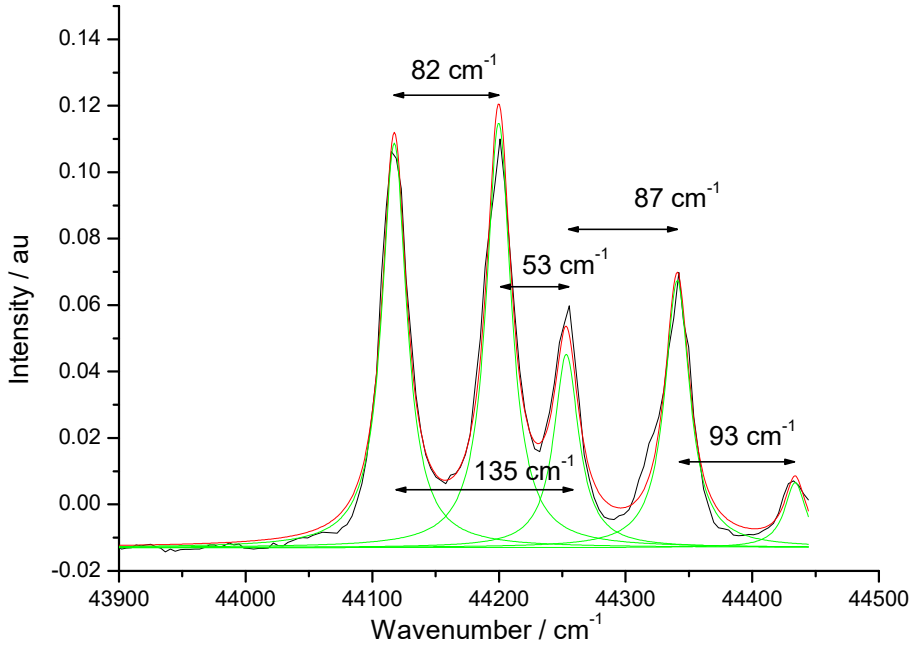

Figure SI-5: Photofragmentation bands of m/z 92 for 7-AIH$^+$ in the S_3 state. The vibrational progression of ~70 cm^{-1} is indicated in black, while the fitted Lorentzian functions reveal a width of ~23 cm^{-1} (i.e. without taking into consideration the laser spectral width of ~10 cm^{-1}).

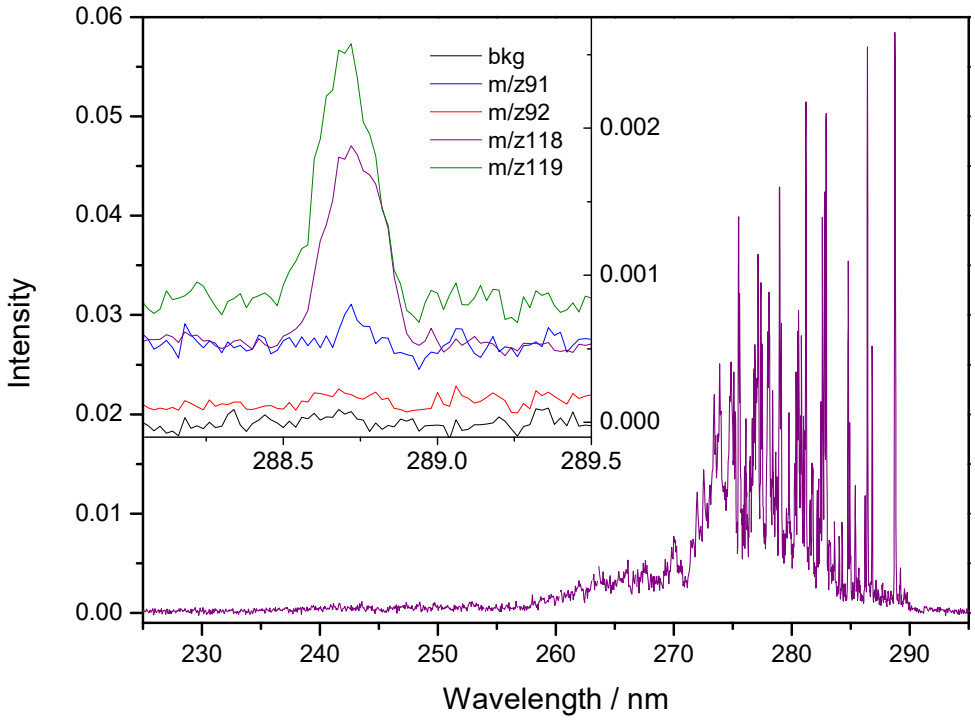

Figure SI-6: REMPI spectrum of neutral 7-azaindole at m/z 118 recorded in a molecular beam. Inset: Photofragmentation in the 0-0 band of the 7-azaindole molecule. The signal of the precursor molecule at m/z 118 (violet) has been divided by ten for ease of interpretation. The fragment m/z 91 (blue) is produced in the 0-0 band of neutral 7-azaindole, with a background signal (black) of approximately zero in this spectral range.

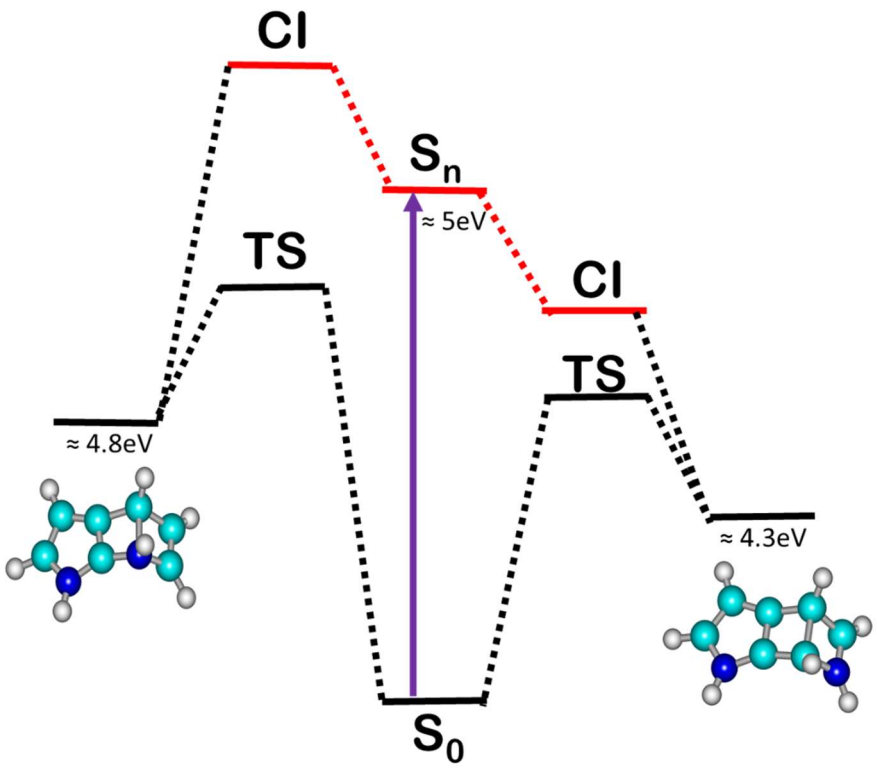

Figure SI-7: Schematic of the possible potential surface in n-AIH$^+$, derived from the work of Su[49] on pyridine.

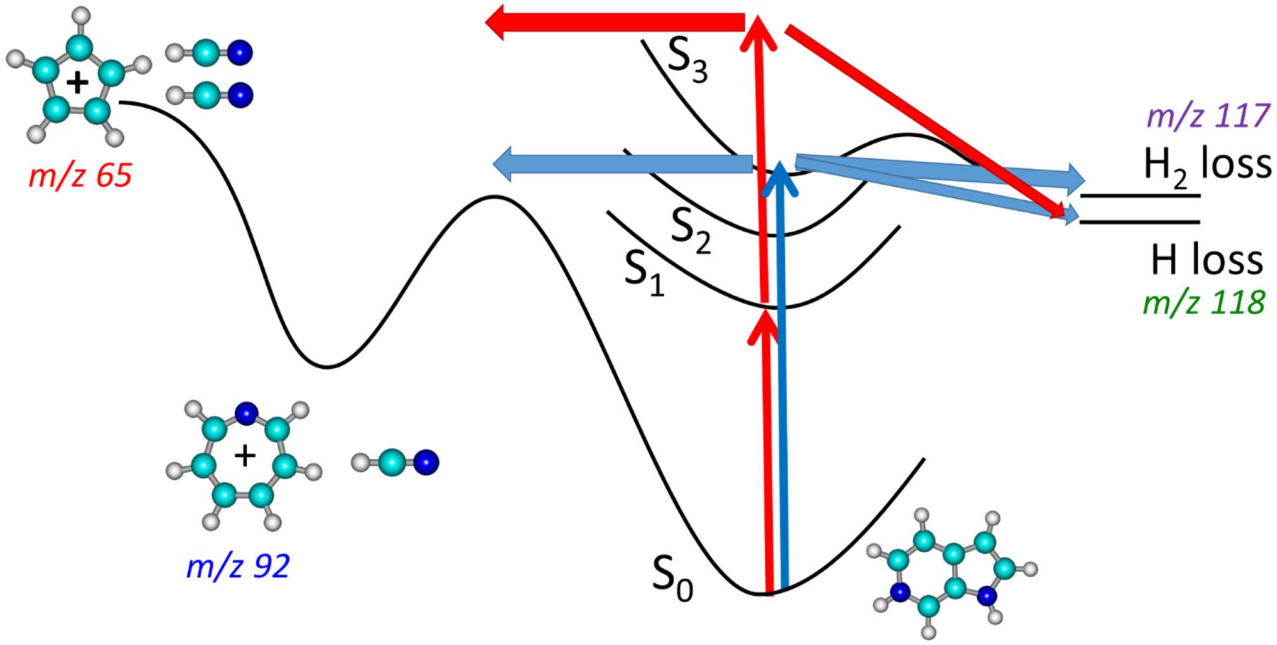

Figure SI-8: Schematic of the possible relaxation pathways from S_1 and S_3.