Electronic Supplementary Information for: "Position Matters: Competing O–H and N–H Photodissociation Pathways in Hydroxy- and Methoxy- substituted Indoles"

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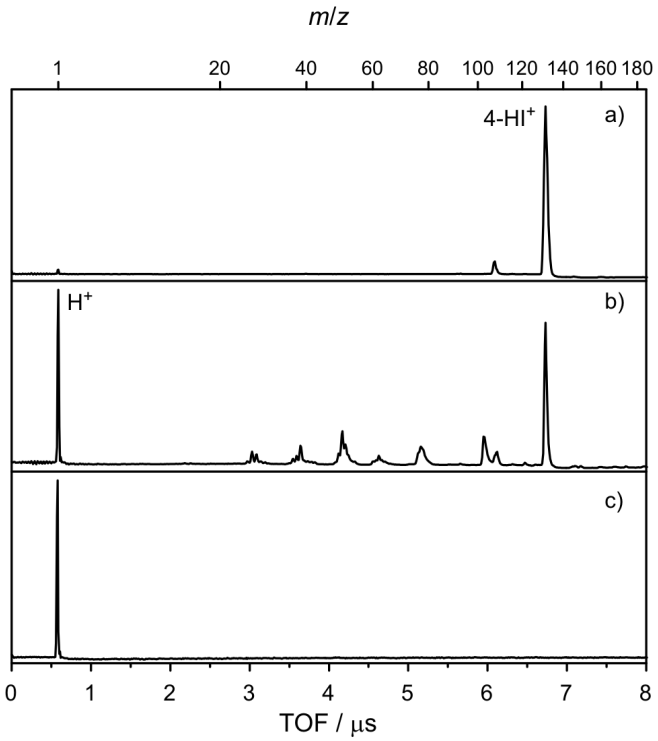
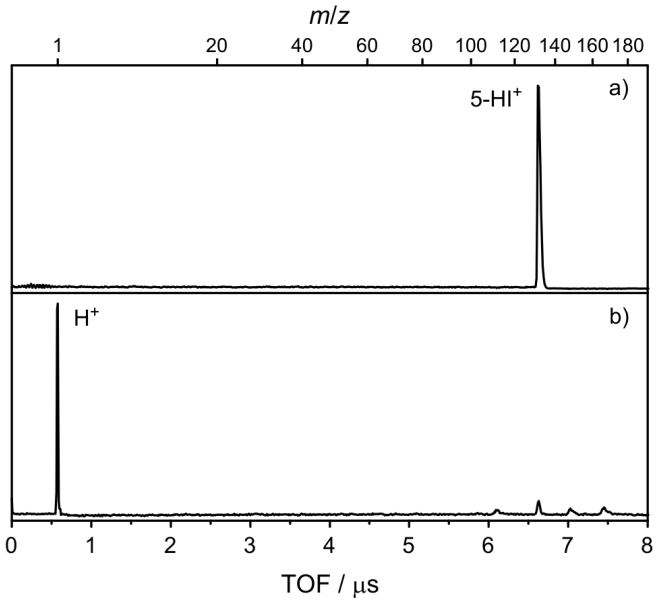
1. Photoionisation Mass Spectrometry

(a) 4-HI



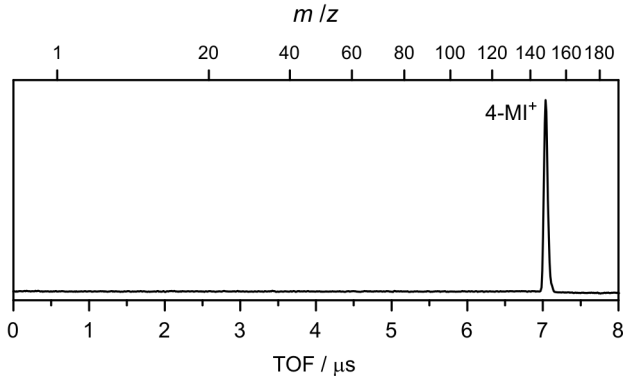
Ion TOF mass spectra obtained following excitation of jet cooled 4-HI at λ_{phot} = (a) 284.893 nm, (b) 284.893 nm with Lyman-α radiation (c) 193.3 nm and Lyman-α radiation.

(b) 5-HI



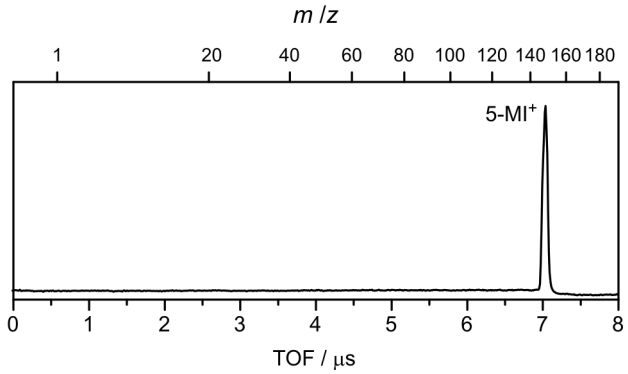
Ion TOF mass spectra obtained following excitation of jet cooled 5-HI at λ_{phot} = (a) 303.878 nm, (b) 193.3 nm and Lyman-α.

(c) 4-MI



Ion TOF mass spectrum obtained following excitation of jet cooled 4-MI at λ_{phot} = 283.255 nm.

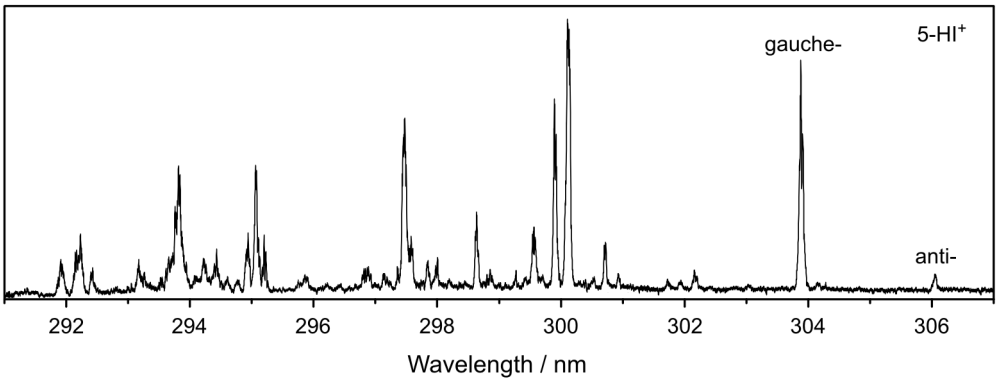
(d) 5-MI



Ion TOF mass spectrum obtained following excitation of jet cooled 5-MI at λ_{phot} = 301.920 nm.

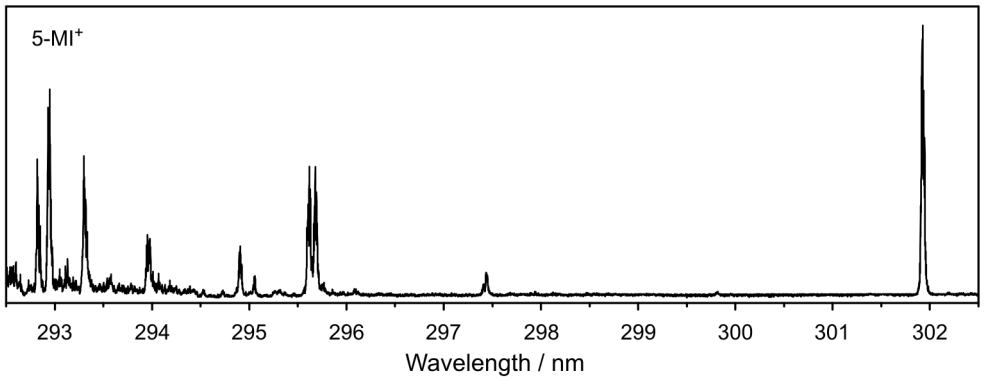
2. Resonance Enhanced Multiphoton Absorption Spectroscopy

(a) 5-HI



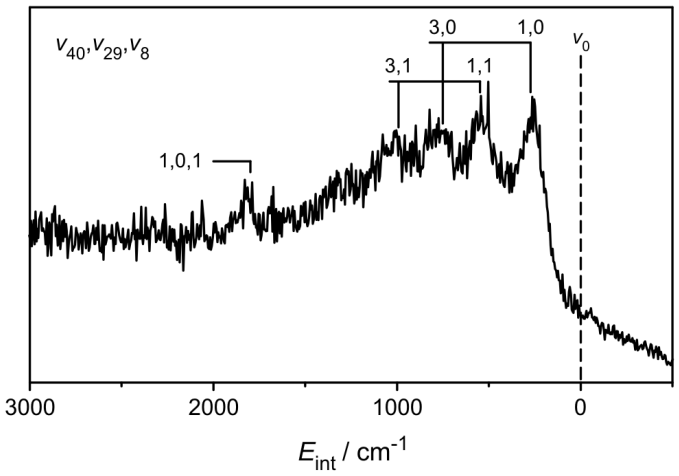
REMPI excitation spectrum of 5-HI between 306.5 nm > λ > 291.5 nm, with the ^1L_b-S_0 origin features for both conformers indicated.

(b) 5-MI



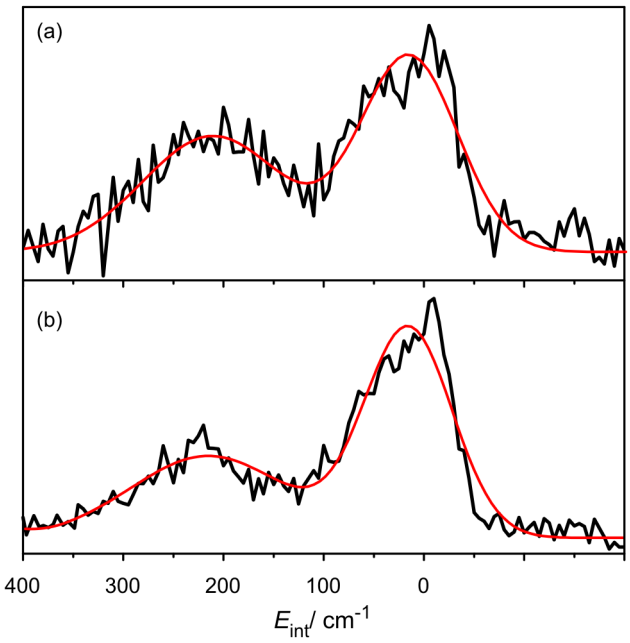
REMPI excitation spectrum of jet-cooled 5-MI molecules between 302.5 nm > λ > 292.5 nm.

3. H(Rydberg) Atom Photofragment Translational Spectroscopy



E_{int} spectrum resulting from the photodissociation of the 4-HI$_{(gauche)}$ conformer at λ_{phot} = 287.0 nm.

4. Baseline subtraction of 4-MI E_{int} spectra at λ_{phot} = 270.176 and 270.0 nm



The underlying featureless background was fitted to the side of a gaussian and subtracted from the respective raw E_{int} spectrum (see main paper fig. 12). The peaks at E_{int} = 0 cm^{-1} and 220 cm^{-1} were then each fitted to a gaussian, allowing us to deduce the relative integrated areas for λ_{phot} = (a) 270.176 nm and (b) 270.0 nm. The ratio of the E_{int} = 0 cm^{-1}/E_{int} = 220 cm^{-1} peaks was deduced for (a) to be 1.2:1 and (b) 1.4:1. The peak intensities, however, show a marked difference in ratios: (a) = 1.69:1 and (b) 2.7:1.

5. Calculated normal mode wavenumbers

(a) 4-HI and 4-HI-Oyl and 4-HI-Nyl radical products

4-HI ($\tilde{X}\ ^1A'$)				4-HI-Oyl ($\tilde{X}\ ^2A''$)				4-HI-Nyl ($\tilde{X}\ ^2A''$)			
Mode	Sym.	Harm.	Anharm.	Mode	Sym.	Harm.	Anharm.	Mode	Sym.	Harm.	Anharm.
ν_1	*a*'	3831	3634	Disappearing Mode				ν_1	*a*'	3816	3614
ν_2	*a*'	3676	3504	ν_1	*a*'	3663	3479	Disappearing Mode			
ν_3	*a*'	3264	3132	ν_2	*a*'	3264	3135	ν_2	*a*'	3236	3093
ν_4	*a*'	3243	3122	ν_3	*a*'	3246	3123	ν_4	*a*'	3191	3054
ν_5	*a*'	3188	3054	ν_4	*a*'	3196	3055	ν_3	*a*'	3202	3058
ν_6	*a*'	3171	3043	ν_5	*a*'	3184	3046	ν_5	*a*'	3181	3063
ν_7	*a*'	3147	3005	ν_6	*a*'	3167	3045	ν_6	*a*'	3154	3064
ν_8	*a*'	1665	1621	ν_7	*a*'	1599	1559	ν_8	*a*'	1618	1577
ν_9	*a*'	1630	1591	ν_8	*a*'	1557	1523	ν_7	*a*'	1634	1593
ν_{10}	*a*'	1547	1512	ν_{10}	*a*'	1514	1481	ν_{10}	*a*'	1474	1420
ν_{11}	*a*'	1542	1506	ν_9	*a*'	1528	1492	ν_9	*a*'	1501	1463
ν_{12}	*a*'	1477	1443	ν_{13}	*a*'	1413	1382	ν_{11}	*a*'	1449	1410
ν_{13}	*a*'	1449	1410	ν_{11}	*a*'	1456	1415	Disappearing Mode			
ν_{14}	*a*'	1395	1365	ν_{12}	*a*'	1447	1410	ν_{13}	*a*'	1344	1314
ν_{15}	*a*'	1375	1342	ν_{14}	*a*'	1384	1351	ν_{12}	*a*'	1397	1363
ν_{16}	*a*'	1323	1292	Disappearing Mode				ν_{14}	*a*'	1312	1269
ν_{17}	*a*'	1268	1244	ν_{15}	*a*'	1321	1295	ν_{15}	*a*'	1308	1279
ν_{18}	*a*'	1260	1235	ν_{16}	*a*'	1256	1227	ν_{16}	*a*'	1230	1195
ν_{19}	*a*'	1211	1187	ν_{17}	*a*'	1202	1174	ν_{17}	*a*'	1213	1187
ν_{20}	*a*'	1178	1161	ν_{18}	*a*'	1174	1152	ν_{18}	*a*'	1182	1162
ν_{21}	*a*'	1128	1113	ν_{19}	*a*'	1121	1102	ν_{19}	*a*'	1170	1147
ν_{22}	*a*'	1093	1071	ν_{20}	*a*'	1100	1078	ν_{22}	*a*'	983	961
ν_{23}	*a*'	1077	1055	ν_{21}	*a*'	1064	1045	ν_{20}	*a*'	1058	1042
ν_{24}	*a*'	1034	1018	ν_{22}	*a*'	1036	1018	ν_{21}	*a*'	1012	992
ν_{25}	*a*'	915	904	ν_{23}	*a*'	910	906	ν_{23}	*a*'	892	879
ν_{26}	*a*'	851	846	ν_{24}	*a*'	860	842	ν_{24}	*a*'	852	840
ν_{27}	*a*'	687	678	ν_{25}	*a*'	680	670	ν_{25}	*a*'	680	669
ν_{28}	*a*'	603	595	ν_{26}	*a*'	590	583	ν_{26}	*a*'	595	585
ν_{29}	*a*'	512	507	ν_{27}	*a*'	505	499	ν_{27}	*a*'	497	491
ν_{30}	*a*'	489	484	ν_{28}	*a*'	486	481	ν_{28}	*a*'	491	486
ν_{31}	*a*'	281	280	ν_{29}	*a*'	293	292	ν_{29}	*a*'	287	283
ν_{32}	*a*"	934	939	ν_{30}	*a*"	970	952	ν_{30}	*a*"	956	949
ν_{33}	*a*"	864	849	ν_{31}	*a*"	891	870	ν_{31}	*a*"	909	896
ν_{34}	*a*"	826	829	ν_{32}	*a*"	867	848	ν_{32}	*a*"	882	867
ν_{35}	*a*"	781	801	ν_{33}	*a*"	811	800	ν_{33}	*a*"	776	793
ν_{36}	*a*"	738	729	ν_{35}	*a*"	714	698	ν_{35}	*a*"	737	730
ν_{37}	*a*"	717	708	ν_{34}	*a*"	754	745	ν_{34}	*a*"	768	748
ν_{38}	*a*"	637	628	ν_{36}	*a*"	649	637	ν_{36}	*a*"	641	633
ν_{39}	*a*"	600	595	ν_{37}	*a*"	608	596	ν_{37}	*a*"	559	548
ν_{40}	*a*"	544	539	ν_{38}	*a*"	494	485	ν_{38}	*a*"	512	507
ν_{41}	*a*"	396	420	ν_{39}	*a*"	448	455	Disappearing Mode			
ν_{42}	*a*"	347	279	Disappearing Mode				ν_{39}	*a*"	401	317
ν_{43}	*a*"	275	274	ν_{40}	*a*"	257	254	ν_{40}	*a*"	269	264
ν_{44}	*a*"	214	212	ν_{41}	*a*"	209	206	ν_{41}	*a*"	210	205
ν_{45}	*a*"	181	180	ν_{42}	*a*"	154	152	ν_{42}	*a*"	172	169

Calculated harmonic (harm.) and anharmonically (anharm.) corrected vibrational wavenumbers (in cm^{-1}) at the DFT/B3LYP/6-311+G** level for 4-HI and the corresponding radicals arising from O–H (4-HI-Oyl) or N–H (4-HI-Nyl) bond fission. The parent modes are labelled according to Herzberg notation[i], whereas the ordering of radical modes has been adjusted so as to map through from those of the parent molecule.

(b) 4-MI and 4-MI-Nyl

4-MI($\tilde{X}\ ^1A'$)				4-MI-Nyl($\tilde{X}\ ^2A''$)			
Mode	Sym.	Harm.	Anharm.	Mode	Sym.	Harm.	Anharm.
ν_1	*a*'	3676	3503		Disappearing Mode		
ν_2	*a*'	3265	3131	ν_1	*a*'	3236	3094
ν_3	*a*'	3245	3118	ν_4	*a*'	3192	3052
ν_4	*a*'	3207	3092	ν_2	*a*'	3212	3085
ν_5	*a*'	3185	3053	ν_3	*a*'	3200	3054
ν_6	*a*'	3168	3027	ν_5	*a*'	3175	3045
ν_7	*a*'	3131	2984	ν_6	*a*'	3143	2995
ν_8	*a*'	3004	2885	ν_7	*a*'	3019	2985
ν_9	*a*'	1650	1617	ν_9	*a*'	1598	1560
ν_{10}	*a*'	1622	1586	ν_8	*a*'	1625	1582
ν_{11}	*a*'	1541	1507	ν_{10}	*a*'	1509	1474
ν_{12}	*a*'	1536	1503	ν_{12}	*a*'	1477	1432
ν_{13}	*a*'	1504	1472	ν_{11}	*a*'	1502	1466
ν_{14}	*a*'	1474	1450	ν_{13}	*a*'	1471	1407
ν_{15}	*a*'	1459	1430	ν_{14}	*a*'	1415	1383
ν_{16}	*a*'	1442	1402		Disappearing Mode		
ν_{17}	*a*'	1388	1356	ν_{16}	*a*'	1343	1317
ν_{18}	*a*'	1373	1345	ν_{15}	*a*'	1378	1342
ν_{19}	*a*'	1300	1272	ν_{17}	*a*'	1314	1271
ν_{20}	*a*'	1265	1240	ν_{18}	*a*'	1292	1259
ν_{21}	*a*'	1228	1205	ν_{19}	*a*'	1217	1191
ν_{22}	*a*'	1204	1190	ν_{20}	*a*'	1200	1182
ν_{23}	*a*'	1191	1169	ν_{22}	*a*'	1179	1158
ν_{24}	*a*'	1151	1133	ν_{21}	*a*'	1189	1167
ν_{25}	*a*'	1101	1086	ν_{23}	*a*'	1095	1073
ν_{26}	*a*'	1084	1063	ν_{24}	*a*'	1063	1045
ν_{27}	*a*'	1079	1059	ν_{25}	*a*'	986	973
ν_{28}	*a*'	982	965	ν_{26}	*a*'	954	932
ν_{29}	*a*'	914	903	ν_{27}	*a*'	891	878
ν_{30}	*a*'	843	838	ν_{28}	*a*'	847	834
ν_{31}	*a*'	694	669	ν_{29}	*a*'	686	675
ν_{32}	*a*'	633	629	ν_{30}	*a*'	624	614
ν_{33}	*a*'	512	504	ν_{31}	*a*'	513	506
ν_{34}	*a*'	480	476	ν_{32}	*a*'	469	464
ν_{35}	*a*'	348	342	ν_{33}	*a*'	351	343
ν_{36}	*a*'	203	210	ν_{34}	*a*'	206	205
ν_{37}	*a*"	3062	2923	ν_{35}	*a*"	3084	2940
ν_{38}	*a*"	1490	1450	ν_{36}	*a*"	1494	1456
ν_{39}	*a*"	1168	1147	ν_{37}	*a*"	1166	1142
ν_{40}	*a*"	948	932	ν_{38}	*a*"	960	953
ν_{41}	*a*"	869	850	ν_{39}	*a*"	907	892
ν_{42}	*a*"	844	831	ν_{40}	*a*"	885	868
ν_{43}	*a*"	800	772	ν_{41}	*a*"	786	773
ν_{44}	*a*"	742	726	ν_{43}	*a*"	741	713
ν_{45}	*a*"	720	703	ν_{42}	*a*"	769	755
ν_{46}	*a*"	636	624	ν_{44}	*a*"	643	632
ν_{47}	*a*"	603	594	ν_{45}	*a*"	556	549
ν_{48}	*a*"	544	538	ν_{46}	*a*"	504	512
ν_{49}	*a*"	386	432		Disappearing Mode		
ν_{50}	*a*"	288	295	ν_{47}	*a*"	276	275
ν_{51}	*a*"	230	249	ν_{49}	*a*"	215	222
ν_{52}	*a*"	225	231	ν_{48}	*a*"	227	223
ν_{53}	*a*"	170	176	ν_{50}	*a*"	162	160
ν_{54}	*a*"	79	94	ν_{51}	*a*"	85	91

Calculated harm. and anharm. corrected vibrational wavenumbers (in cm^{-1}) at the DFT/B3LYP/6-311+G** level for 4-MI and the corresponding 4-MI-Nyl radical. Again labelled according to Herzberg notation[i], and the ordering of radical modes has been adjusted so as to map through from those of the parent molecule.

[i] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules*; van Nostrand: Princeton, NJ, 1945.