

Ultraviolet Photodissociation of the
N-methylpyridinium Ion:
Action Spectroscopy and Product Characterization

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Electronic Supporting Information

Figure S1 Photodissociation mass spectrum ($\lambda = 250$ nm) of anilinium (m/z 94).

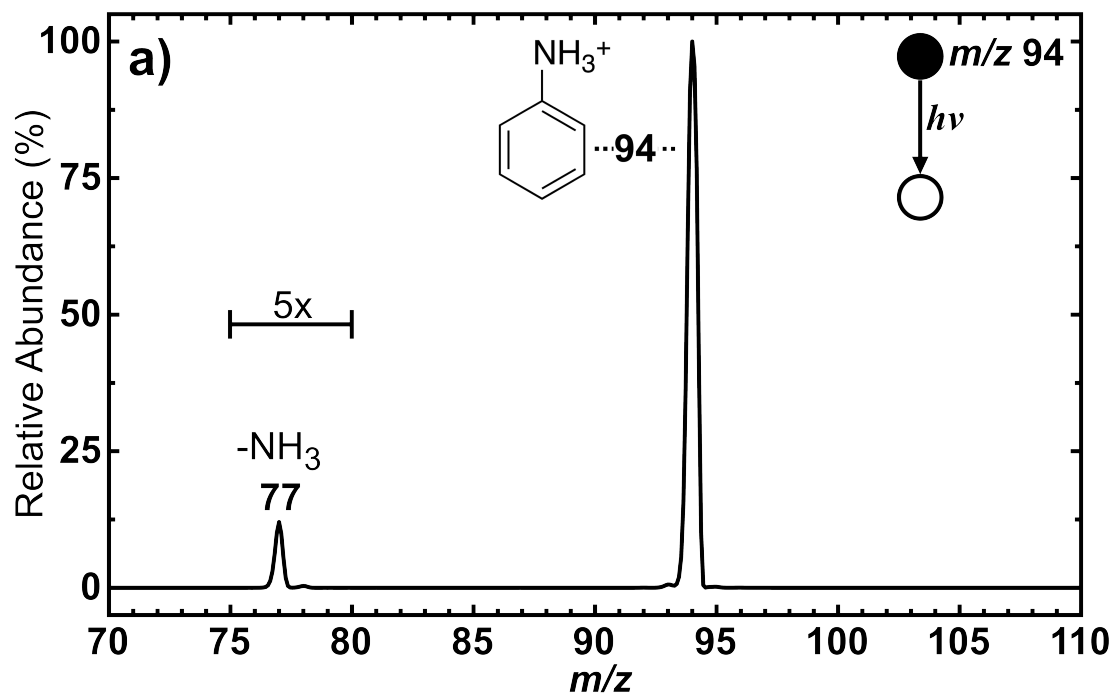
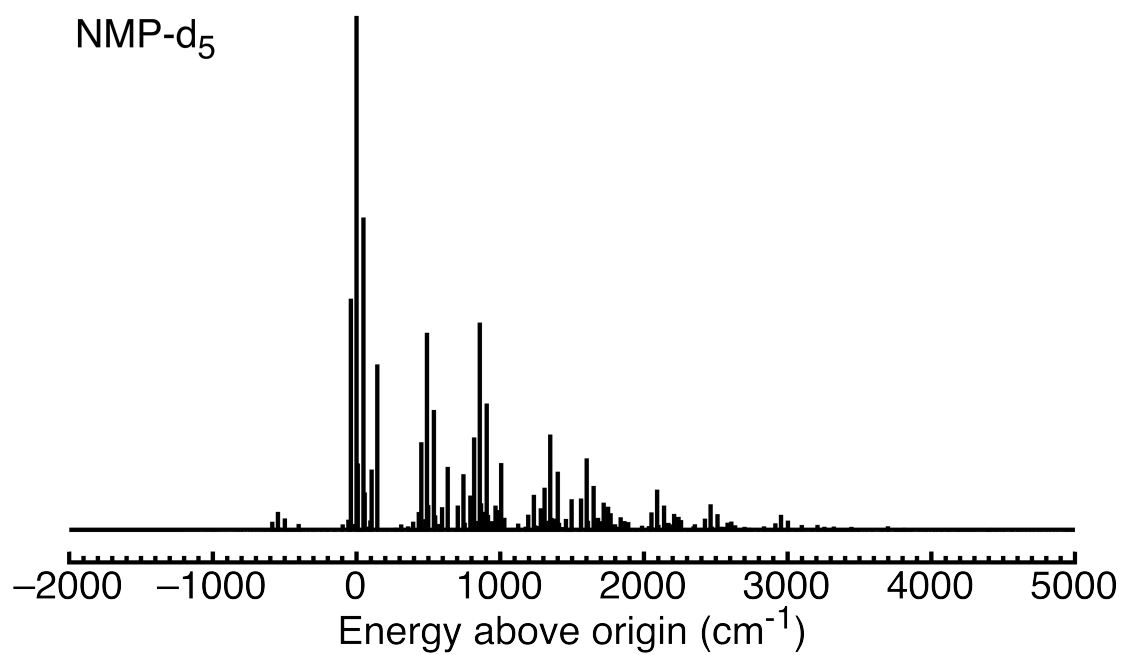
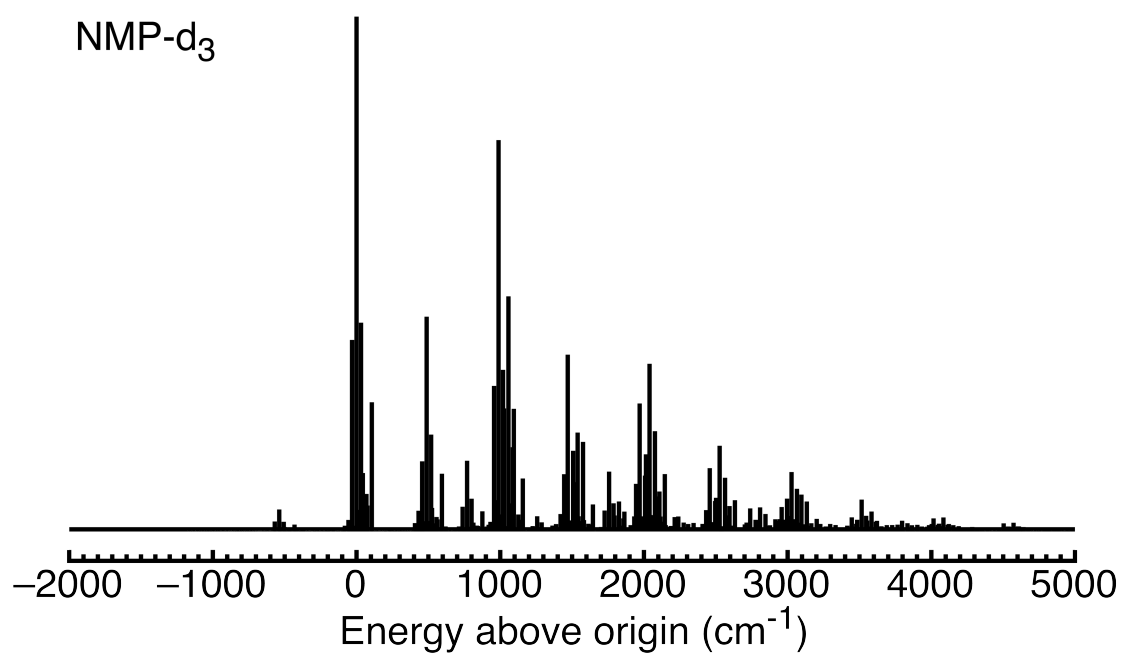


Figure S2 Simulated absorption spectra for N-methylpyridinium-d₃ and N-methylpyridinium-d₅ ion.



CASSCF(6,6)/aug-cc-pVDZ optimized geometries.

NMP-d₀

S₀

		x	y	z
1	C	1.899454	-0.008693	0.000187
2	C	1.179929	-1.208061	0.00013
3	C	-0.20366	-1.164905	-0.000136
4	C	-0.188136	1.176818	-0.000229
5	C	1.20108	1.197685	0.000014
6	H	2.97847	-0.017687	0.000332
7	H	1.675104	-2.165517	0.00023
8	H	-0.815165	-2.051838	-0.000168
9	H	-0.779278	2.076452	-0.000354
10	H	1.709585	2.148093	0.000013
11	C	-2.339975	0.000376	0.00031
12	H	-2.682344	-0.520171	-0.887923
13	H	-2.681697	-0.508608	0.895511
14	H	-2.700933	1.020928	-0.006326
15	N	-0.857989	0.013828	-0.000347

S₁

		x	y	z
1	C	1.973816	-0.010102	0.007544
2	C	1.213772	-1.225127	-0.028893
3	C	-0.211444	-1.188902	-0.047771
4	C	-0.201307	1.188554	0.013005
5	C	1.224168	1.211634	0.033405
6	H	3.04875	-0.015043	0.021372
7	H	1.687332	-2.192544	-0.045644
8	H	-0.810376	-2.082565	-0.06785
9	H	-0.792609	2.087142	0.038731
10	H	1.705953	2.174574	0.06601
11	C	-2.373516	0.008576	0.005521
12	H	-2.742886	-0.864666	-0.519671
13	H	-2.68935	-0.015473	1.045858
14	H	-2.735227	0.909573	-0.476348
15	N	-0.902631	0.003416	-0.041716

NMP-d3

S₀

		x	y	z
1	C	1.899454	-0.008693	0.000189
2	C	1.17993	-1.208061	0.000121
3	C	-0.203659	-1.164905	-0.000149
4	C	-0.188136	1.176818	-0.00022
5	C	1.20108	1.197685	0.000026
6	H	2.97847	-0.017686	0.000337

7	H	1.675105	-2.165517	0.00021
8	H	-0.815164	-2.051839	-0.000198
9	H	-0.779279	2.07645	-0.000339
10	H	1.709583	2.148094	0.000033
11	C	-2.339975	0.000376	0.000311
12	H	-2.682349	-0.520234	-0.887883
13	H	-2.681693	-0.508543	0.895552
14	H	-2.700932	1.020929	-0.006397
15	N	-0.857989	0.013827	-0.000349

NMP-d₃

S_1

		x	y	z
1	C	1.973818	-0.010121	0.00734
2	C	1.213765	-1.225145	-0.029023
3	C	-0.21145	-1.188919	-0.04771
4	C	-0.201302	1.188539	0.01304
5	C	1.224178	1.211619	0.033235
6	H	3.048753	-0.015069	0.021066
7	H	1.687323	-2.192561	-0.045884
8	H	-0.810382	-2.082581	-0.067764
9	H	-0.792606	2.087126	0.038825
10	H	1.705968	2.174563	0.065674
11	C	-2.37352	0.008614	0.005739
12	H	-2.742903	-0.864894	-0.519002
13	H	-2.689347	-0.014905	1.046085
14	H	-2.73522	0.909381	-0.476577
15	N	-0.902634	0.003401	-0.041493

NMP-d₅

S_0

		x	y	z
1	C	1.899453	-0.008692	0.000183
2	C	1.179931	-1.208061	0.000134
3	C	-0.203656	-1.164906	-0.00012
4	C	-0.188135	1.176813	-0.000235
5	C	1.201079	1.197684	0.000007
6	H	2.97847	-0.017683	0.000327
7	H	1.675107	-2.165518	0.000239
8	H	-0.815167	-2.051836	-0.000147
9	H	-0.779286	2.076442	-0.000363
10	H	1.70958	2.148095	0.000001
11	C	-2.339975	0.000377	0.000307
12	H	-2.682343	-0.520127	-0.887952
13	H	-2.681707	-0.508644	0.895484
14	H	-2.700922	1.020934	-0.006283
15	N	-0.857986	0.013824	-0.000338

NMP-d₅

S₁

		x	y	z
1	C	1.97382	-0.010124	0.007323
2	C	1.21373	-1.225134	-0.028616
3	C	-0.211491	-1.188853	-0.047269
4	C	-0.201258	1.188626	0.012682
5	C	1.224217	1.211651	0.032823
6	H	3.048755	-0.015099	0.021008
7	H	1.687252	-2.192573	-0.045171
8	H	-0.810469	-2.082497	-0.067008
9	H	-0.792515	2.087246	0.038176
10	H	1.706043	2.174588	0.064925
11	C	-2.373523	0.008543	0.005718
12	H	-2.74281	-0.863646	-0.521307
13	H	-2.68943	-0.017682	1.045973
14	H	-2.735246	0.910516	-0.474295
15	N	-0.902633	0.003487	-0.041409

**CASSCF(6,6)/aug-cc-pVDZ excited state normal modes used
for absorption spectrum simulation**

NMP-d₀

Mode 1

Freq 49.1672 cm⁻¹

	x	y	z
1	0	0	0
2	0.01	0	-0.03
3	0.01	-0.01	-0.02
4	-0.01	-0.01	0.02
5	-0.01	0	0.03
6	0	0.01	0
7	0.01	0	-0.05
8	0.02	-0.01	-0.04
9	-0.02	-0.02	0.04
10	-0.01	0	0.05
11	0	0.02	0
12	-0.02	-0.26	0.49
13	0	0.61	0.01
14	0.01	-0.24	-0.5
15	0	-0.01	0

Mode 7

Freq 502.3043 cm⁻¹

	x	y	z
1	0.33	0	0.01

2	0.11	0.16	0
3	0.05	0.15	0.01
4	0.05	-0.15	0
5	0.11	-0.16	-0.01
6	0.33	0	0.06
7	-0.07	0.06	0.01
8	0.25	0.01	0.04
9	0.25	-0.02	0.04
10	-0.08	-0.06	0
11	-0.36	0	0.01
12	-0.33	-0.01	0.01
13	-0.33	0	0.02
14	-0.33	0.01	0.01
15	-0.23	0	-0.03

Mode 14

Freq 791.7436 cm⁻¹

	x	y	z
1	0.13	0	0
2	-0.15	0.2	0
3	-0.08	0.2	0
4	-0.08	-0.2	-0.01
5	-0.15	-0.2	-0.01
6	0.13	0	-0.01
7	-0.41	0.09	0
8	0.01	0.15	0.01
9	0.01	-0.15	0
10	-0.41	-0.08	0
11	0.32	0	-0.01
12	0.3	0.01	-0.01
13	0.26	0	-0.03
14	0.3	-0.02	-0.01
15	-0.01	0	0.02

Mode 15

Freq 986.6543 cm⁻¹

	x	y	z
1	0.28	0	0
2	0	-0.21	-0.01
3	-0.11	0	0
4	-0.11	0	0
5	0	0.21	0.01
6	0.31	0	0
7	-0.31	-0.38	-0.01
8	-0.31	0.13	-0.01
9	-0.31	-0.12	-0.01
10	-0.31	0.38	0.01
11	0.02	0	0

12	0.01	0.01	0
13	0.03	0	0
14	0.01	-0.01	0
15	0.01	0	0

Mode 17

Freq 1054.9536 cm⁻¹

	x	y	z
1	0.22	0	0
2	0.01	0.16	0
3	-0.15	-0.31	-0.01
4	-0.14	0.32	0.01
5	0.01	-0.16	0
6	0.23	0	0
7	0.25	0.28	0.01
8	-0.12	-0.36	0
9	-0.12	0.36	0.02
10	0.25	-0.28	-0.01
11	0.09	0	-0.02
12	-0.01	0	0.04
13	0.12	0	0
14	-0.01	-0.01	0.04
15	-0.07	0	0.01

NMP-d₃

Mode 1

Freq 35.4025 cm⁻¹

	x	y	z
1	0	0.01	0
2	0.01	0	-0.05
3	0.01	-0.01	-0.05
4	-0.01	-0.01	0.05
5	-0.01	0	0.05
6	0	0.01	0
7	0.02	0.01	-0.09
8	0.02	-0.02	-0.08
9	-0.02	-0.02	0.08
10	-0.02	0	0.09
11	0	0.02	0
12	-0.01	-0.26	0.48
13	0	0.6	0.01
14	0.01	-0.24	-0.49
15	0	-0.02	0

Mode 7

Freq 486.8401 cm⁻¹

	x	y	z
1	0.32	0	0.02
2	0.12	0.14	-0.01
3	0.06	0.14	0.02
4	0.06	-0.14	0.01
5	0.12	-0.15	-0.01
6	0.32	0	0.02
7	-0.05	0.06	-0.01
8	0.25	0.01	0.06
9	0.25	-0.01	0.06
10	-0.05	-0.06	-0.02
11	-0.34	0	0.01
12	-0.36	0	0.01
13	-0.34	0	0.01
14	-0.36	0	0.01
15	-0.2	0	-0.04

Mode 13

Freq 769.5717 cm⁻¹

	x	y	z
1	0.15	0	0
2	-0.14	0.21	0
3	-0.08	0.2	0
4	-0.08	-0.2	-0.01
5	-0.14	-0.21	-0.01
6	0.15	0	-0.01
7	-0.4	0.09	0
8	0.03	0.14	0.01
9	0.03	-0.14	0
10	-0.4	-0.08	0
11	0.25	0	0
12	0.33	-0.01	-0.02
13	0.27	0	0
14	0.33	0.01	-0.02
15	-0.05	0	0.02

Mode 17

Freq 986.5530 cm⁻¹

	x	y	z
1	0.28	0	0
2	0	-0.21	-0.01
3	-0.11	0	0
4	-0.11	0	0
5	0	0.21	0.01
6	0.3	0	0
7	-0.31	-0.38	-0.01
8	-0.31	0.12	-0.01
9	-0.31	-0.12	-0.02

10	-0.31	0.38	0.01
11	0.01	0	0.01
12	0.03	0.02	-0.02
13	-0.01	0	0.01
14	0.03	-0.02	-0.02
15	0	0	-0.01

Mode 18

Freq 1055.3208 cm⁻¹

	x	y	z
1	0.21	0	0
2	0.01	0.15	0
3	-0.15	-0.31	-0.01
4	-0.14	0.31	0.01
5	0.01	-0.16	0
6	0.22	0.01	0
7	0.27	0.28	0.01
8	-0.12	-0.36	-0.01
9	-0.11	0.37	0.01
10	0.26	-0.28	-0.01
11	0.07	0	0.02
12	0.09	0.02	-0.02
13	-0.01	0	0
14	0.1	-0.02	-0.02
15	-0.08	0	-0.01

NMP-d₅

Mode 1

Freq 48.6971 cm⁻¹

	x	y	z
1	0	0	0
2	0.01	0	-0.02
3	0.01	-0.01	-0.02
4	-0.01	-0.01	0.02
5	-0.01	0	0.02
6	0	0.01	0
7	0.01	0	-0.04
8	0.02	-0.01	-0.04
9	-0.02	-0.02	0.03
10	-0.01	0	0.04
11	0	0.02	0
12	-0.02	-0.26	0.49
13	0	0.61	0.02
14	0.01	-0.23	-0.5
15	0	-0.01	0

Mode 8

Freq 490.5531 cm⁻¹

	x	y	z
1	0.32	0	0.02
2	0.1	0.16	0
3	0.04	0.15	0
4	0.04	-0.15	-0.01
5	0.09	-0.16	-0.01
6	0.32	0	-0.03
7	-0.1	0.06	0.02
8	0.27	0	0.03
9	0.27	0	0.03
10	-0.1	-0.06	0.01
11	-0.35	0	0.01
12	-0.33	-0.01	0
13	-0.33	0	0.02
14	-0.33	0.01	0.01
15	-0.23	0	-0.02

Mode 14

Freq 743.8851 cm⁻¹

	x	y	z
1	-0.14	0	0
2	0.11	-0.11	0
3	0.05	-0.16	0
4	0.05	0.16	0.01
5	0.11	0.1	0
6	-0.14	0	0
7	0.53	0.09	0.01
8	0.04	-0.16	0
9	0.04	0.16	0
10	0.53	-0.09	0
11	-0.26	0	0.01
12	-0.24	-0.01	0.01
13	-0.21	0	0.02
14	-0.24	0.01	0.01
15	-0.03	0	-0.02

Mode 16

Freq 859.7117 cm⁻¹

	x	y	z
1	-0.16	0	0
2	-0.06	0.23	0.01
3	0.02	0.03	0
4	0.02	-0.02	0
5	-0.07	-0.23	-0.01
6	-0.19	0	0
7	0.29	0.44	0.01

8	0.3	-0.16	0.01
9	0.3	0.15	0.01
10	0.28	-0.44	-0.01
11	0.11	0	0
12	0.1	0	0
13	0.08	0	-0.01
14	0.1	0	0
15	-0.04	0	0.01

Mode 19

Freq 1007.2701 cm⁻¹

	x	y	z
1	-0.28	0	0
2	0.03	-0.05	0
3	0.16	0.29	0.01
4	0.16	-0.3	-0.01
5	0.03	0.05	0
6	-0.33	0	0
7	0.07	-0.03	0
8	-0.06	0.51	0
9	-0.06	-0.51	-0.02
10	0.07	0.03	0
11	-0.1	0	0.02
12	-0.03	0	-0.03
13	-0.12	0	0.01
14	-0.03	0.01	-0.03
15	0.06	0	-0.01