

## Supporting Information:

# Ultrafast Conformational Dynamics of Rydberg-excited N-Methyl Piperidine

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## Supporting information

S1. The time-resolved photoelectron spectra of NMP at various excitation wavelengths.

S2. The definition of the nitrogen inversion angle.

S3. The binding energy oscillations in the 3p excited state.

S4. Vibrational energy of NMP in the 3s Rydberg states.

S5. Calculated structures of NMP.

## S1. The time-resolved photoelectron spectra of NMP at various excitation wavelengths.

Probe wavelength: 400 nm

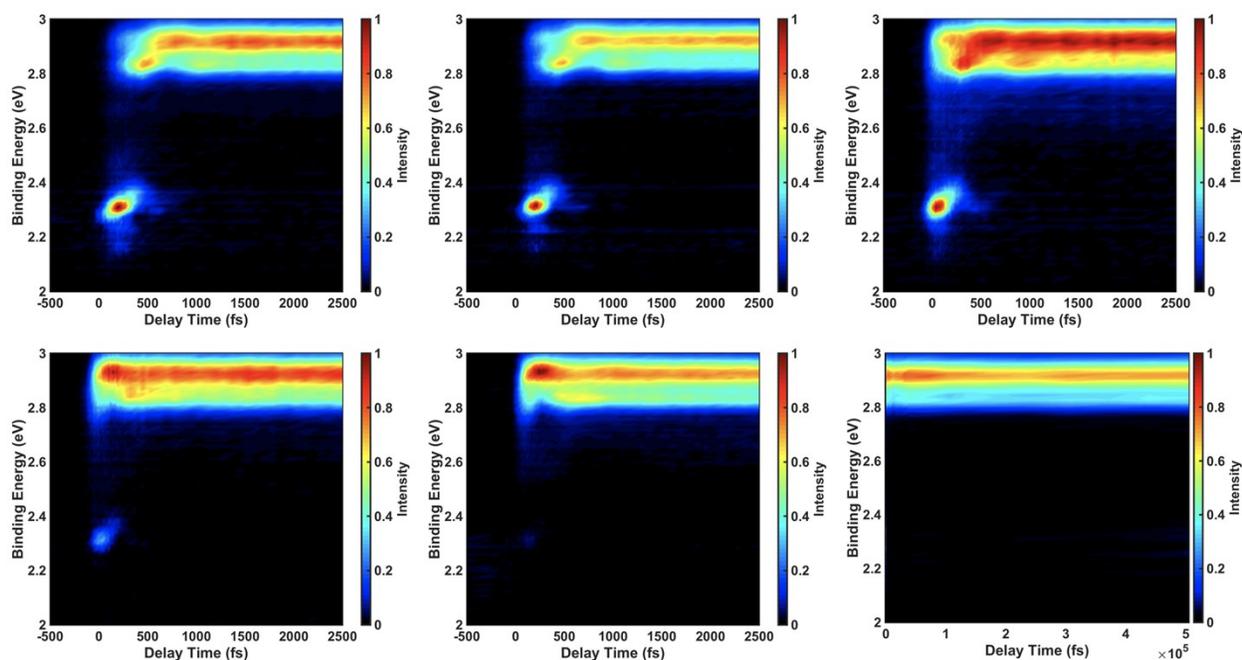


Figure S1. The time-resolved photoelectron spectra of NMP (top left) excited at 212 nm, (top center) excited at 216 nm, (top right) excited at 220 nm, (bottom left) excited at 225 nm, (bottom center) excited at 229 nm, (bottom right) excited at 212 nm with 500 ps time range.

## S2. The definition of the nitrogen inversion angle.

Molecular geometries are obtained by scanning the dihedral angle N1-C2-C6-C7 in Figure S2 (left), from  $-40^\circ$  to  $40^\circ$  while relaxing all other atoms positions. Then the nitrogen inversion angle as shown in Figure S2 (right) is obtained from the results of the scan.

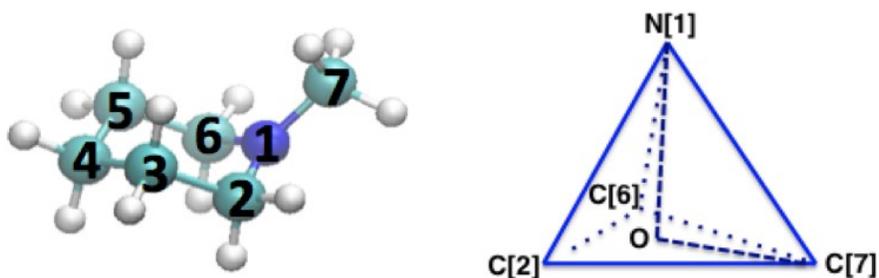


Figure S2. (Left) The molecular model of NMP ion structure. (Right) The definition of the nitrogen projection of N atom position to the plane spanned by atoms C[2], C[6] and C[7]. The N[1]-C[7]-O is the angle of the nitrogen inversion coordinate.

### S3. The binding energy oscillations in the 3p excited state.

3p states have much shorter lifetimes than 3s states. The signal between 2.2 eV and 2.45 eV at each time slice is fitted with a Gaussian function and the peak center is plotted as the red curves in Figure S3. The period of the oscillation is about 400 fs.

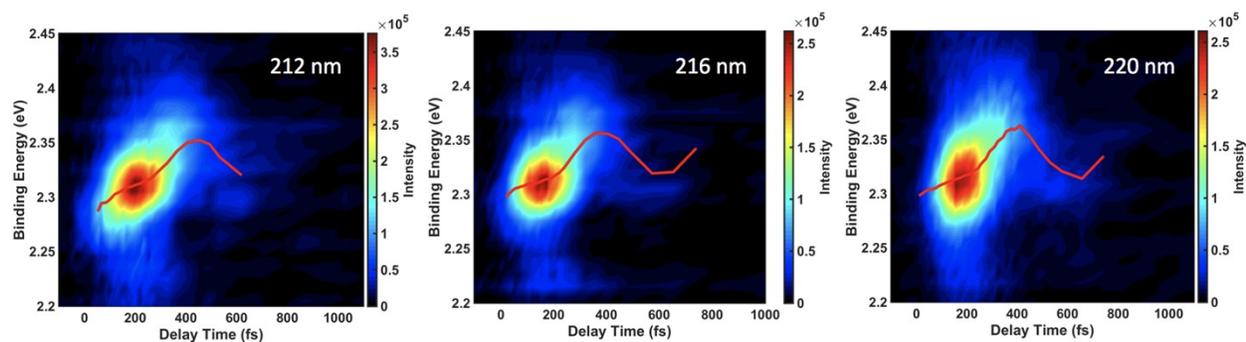


Figure S3. The time-resolved photoelectron spectra of NMP excited at 212 nm, 216 nm and 200 nm, respectively, in the vicinity of the 3p peak. The red curves represent the fitted peak centers of the oscillatory 3p state.

#### **S4. Vibrational energy of NMP in the 3s Rydberg states.**

The internal vibrational energy of NMP in the 3s Rydberg states is calculated as

$$E_{\text{vib}} = h\nu_{\text{pump}} + E_{\text{b}} - IP_{\text{a}}$$

Where  $h\nu_{\text{pump}}$  is the energy of the pump photon,  $E_{\text{b}}$  is the binding energy of 3s state (2.83 V) obtained from the spectral information, and  $IP_{\text{a}}$  is the adiabatic ionization potential, which was estimated by subtracting the minimum energy of the ground state from the minimum energy of the ion state. An adiabatic ionization energy of 7.43 eV is obtained from a B3LYP/6-311++G(d,p) calculation and is used in the calculation of the internal vibrational energy. Thus, the 3s state of NMP has internal energies 1.25, 1.14, 1.04, 0.91 and 0.82 eV with the excitation wavelengths of 212 nm, 216 nm, 220 nm, 225 nm and 229 nm.

Assuming the energy is distributed across all vibrational modes in accordance with the quantum harmonic oscillator partition functions and with the set of vibrational frequencies calculated by MP2/Aug-cc-pVDZ using the NMP ion chair structure and scaled by the factor of 0.959 from NIST<sup>i</sup>. The effective vibrational temperatures are estimated as 829K, 791K, 755K, 707K and 669K. A detailed description of the vibrational energy and effective vibrational temperature estimation can be found in the literature.<sup>ii</sup>

## S5. Calculated structures of NMP

The NMP ground chair-equatorial structure optimized with B3LYP/6-311++G(d,p):

Element	Cartesian coordinates (Angstroms)		
	x	y	z
N	-0.55801	0.85153	0.00000
C	0.09650	-1.17336	1.25859
C	0.09650	-1.17336	-1.25859
C	0.09650	0.35618	-1.21091
C	0.74581	-1.76127	0.00000
C	0.09650	0.35618	1.21091
C	-0.66983	2.30140	0.00000
H	0.66709	-2.85291	0.00000
H	0.62280	-1.50872	-2.15816
H	-0.93871	-1.52326	-1.33771
H	-0.93871	-1.52326	1.33771
H	0.62280	-1.50872	2.15816
H	-0.43640	0.76038	2.07682
H	-0.43640	0.76038	-2.07682
H	-1.22068	2.63109	-0.88469
H	-1.22068	2.63109	0.88469
H	1.81739	-1.52292	0.00000
H	1.14113	0.72586	1.27417
H	0.31340	2.80980	0.00000

H	1.14113	0.72586	-1.27417
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The NMP ion chair structure optimized with B3LYP/6-311++G(d,p):

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Element	Cartesian coordinates (Angstroms)		
	x	y	z
N	-0.98230	-0.00010	0.20370
C	-0.27960	1.23520	0.49760
C	1.05090	-1.26530	-0.31240
C	1.87170	0.00010	-0.05190
C	1.05080	1.26540	-0.31240
C	-0.27950	-1.23520	0.49750
C	-2.27270	-0.00000	-0.45170
H	2.75330	0.00010	-0.69900
H	1.58920	2.16710	-0.01300
H	0.81300	1.36540	-1.37570
H	0.81320	-1.36540	-1.37570
H	1.58940	-2.16700	-0.01300
H	-0.92200	-2.08240	0.26330
H	-0.92220	2.08230	0.26330
H	-2.38910	0.89890	-1.05740
H	-2.38980	-0.89960	-1.05630
H	2.24100	0.00010	0.97950
H	-0.04620	-1.24260	1.56870
H	-3.05680	0.00080	0.32050
H	-0.04630	1.24260	1.56870

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The NMP ion chair structure optimized with MP2/Aug-cc-pVDZ

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Element	Cartesian coordinates (Angstroms)		
	x	y	z
N	-0.98216	0.02615	0.30166
C	-0.24689	1.24486	0.58130
C	0.96580	-1.27483	-0.32611
C	1.82857	-0.02483	-0.11517
C	1.00659	1.24939	-0.34317
C	-0.29394	-1.22148	0.58558
C	-2.15174	0.01475	-0.55599
H	2.68240	-0.04380	-0.81031
H	1.57998	2.15829	-0.10433
H	0.67922	1.32601	-1.39379
H	0.64457	-1.35617	-1.37838
H	1.51015	-2.19758	-0.07305
H	-0.97819	-2.06056	0.40141
H	-0.89820	2.11145	0.41030
H	-2.49147	1.03791	-0.74973
H	-1.89242	-0.49499	-1.50138
H	2.24277	-0.02387	0.90814
H	0.01240	-1.20570	1.64421
H	-2.94144	-0.57163	-0.05836
H	0.07506	1.21057	1.63498

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Frequencies (cm<sup>-1</sup>):

62.9499, 92.7303, 193.4928, 294.9263, 410.124, 423.2976, 436.52, 458.5236, 566.4851, 749.3785, 792.0106, 845.3662, 854.5086, 880.1798, 954.351, 975.6588, 1001.8753, 1015.886, 1037.6659, 1084.4291, 1095.4472, 1134.6604, 1147.6474, 1179.3182, 1250.4339, 1272.2832, 1287.3432, 1311.9918, 1321.7511, 1343.6205, 1350.409, 1376.727, 1388.8634, 1423.0874, 1456.6442, 1466.0814, 1471.4536, 1475.9378, 1478.1712, 1484.7604, 1514.1325, 3047.1993, 3070.6097, 3079.3563, 3081.1457, 3087.1572, 3091.9704, 3134.2342, 3141.1051, 3151.6888, 3153.971, 3181.0419, 3187.6762, 3219.9047.

The NMP ion twist structure optimized with MP2/Aug-cc-pVDZ

Element	Cartesian coordinates (Angstroms)		
	x	y	z
N	0.96749	0.05786	0.09976
C	0.25496	1.33055	0.06467
C	-1.03824	-1.34912	-0.17185
C	-1.75018	-0.02125	-0.53491
C	-1.23672	1.13687	0.33616
C	0.27494	-1.10550	0.62167
C	2.33806	-0.03881	-0.36238
H	-2.83763	-0.13233	-0.42224
H	-1.74974	2.07875	0.09144
H	-1.41743	0.94324	1.40595
H	-1.67087	-1.97934	0.47075
H	-0.80609	-1.93159	-1.07523
H	0.03585	-0.87135	1.67553
H	0.75657	1.99292	0.79885
H	2.95508	-0.46291	0.44661
H	2.36747	-0.73457	-1.21939
H	-1.56333	0.22738	-1.59307
H	0.95481	-1.96698	0.59507
H	2.70663	0.95038	-0.65776
H	0.43935	1.76496	-0.93501

Frequencies (cm<sup>-1</sup>):

57.2084, 82.1841, 112.4532, 292.1493, 324.1677, 373.9127, 424.7632, 485.3979, 569.9745, 725.1314, 780.977, 827.7138, 857.6675, 906.2308, 942.7721, 969.289, 1025.3545, 1035.8807, 1053.8359, 1106.3217, 1109.8668, 1136.66, 1168.381, 1182.7664, 1247.1284, 1284.147, 1297.0865, 1297.6231, 1326.4345, 1335.5376, 1367.6918, 1371.4952, 1397.8365, 1424.0101, 1435.2929, 1458.7442, 1468.2849, 1479.6692, 1486.731, 1494.7028, 1501.8995, 3025.0017, 3049.8473, 3051.2902, 3078.9375, 3084.6687, 3095.7213, 3102.326, 3138.5594, 3153.3526, 3156.531, 3167.5861, 3177.4229, 3213.781.

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<sup>i</sup> <http://cccbdb.nist.gov/vibscalejust.asp>

<sup>ii</sup> Minitti, M. P.; Cardoza, J. D.; Weber, P. M. Rydberg fingerprint spectroscopy of hot molecules: structural dispersion in flexible hydrocarbons. *J. Phys. Chem. A* 2006, 110, 10212-8.