Electronic Supplementary Information (ESI)

Negative Ion Photoelectron Spectroscopy of $P_2N_3^-$: Electron Affinity and Electronic Structures of $P_2N_3^{\bullet}$

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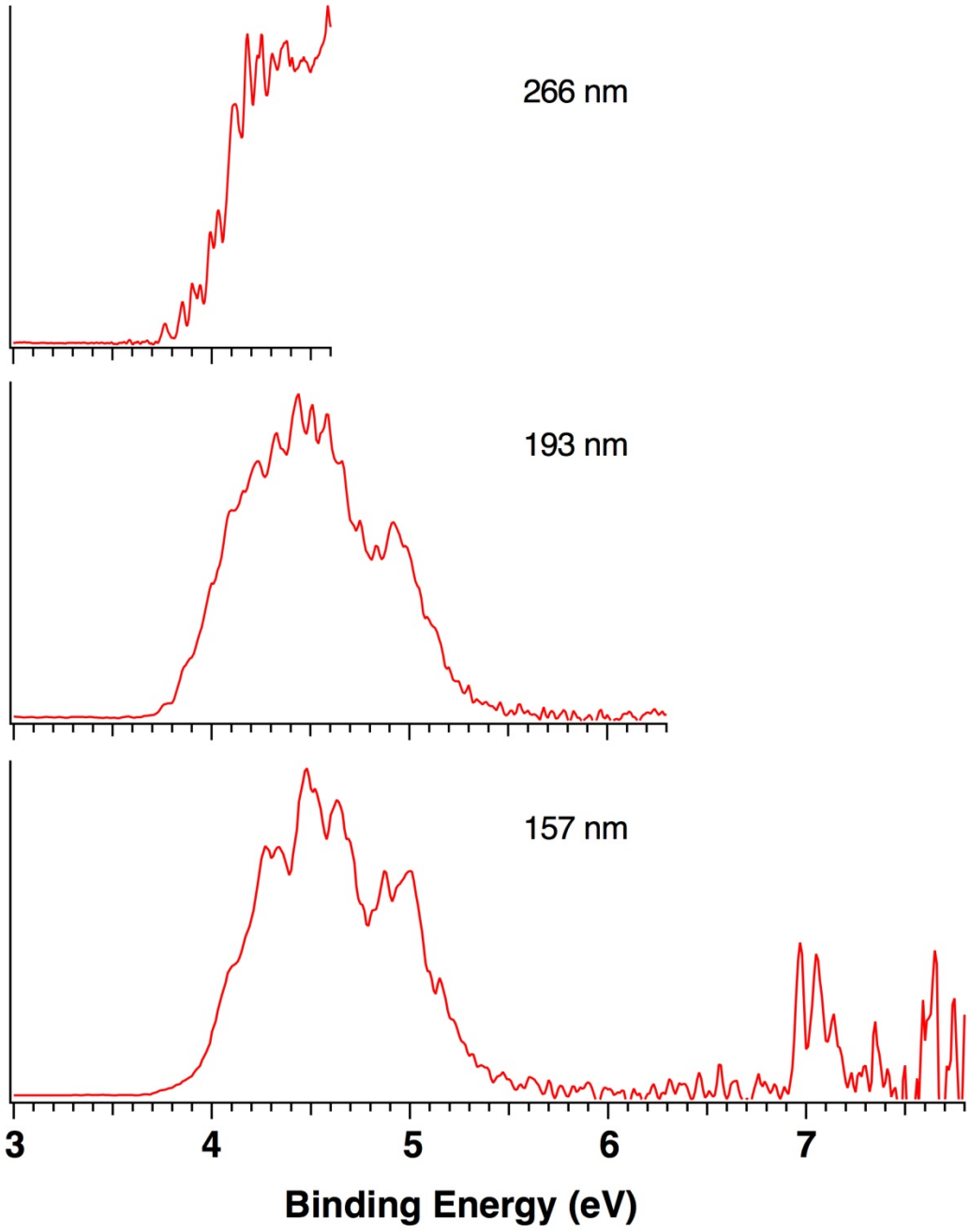

Figure S1. The 20 K NIPE spectra of $P_2N_3^-$ at 266, 193, and 157 nm, respectively.

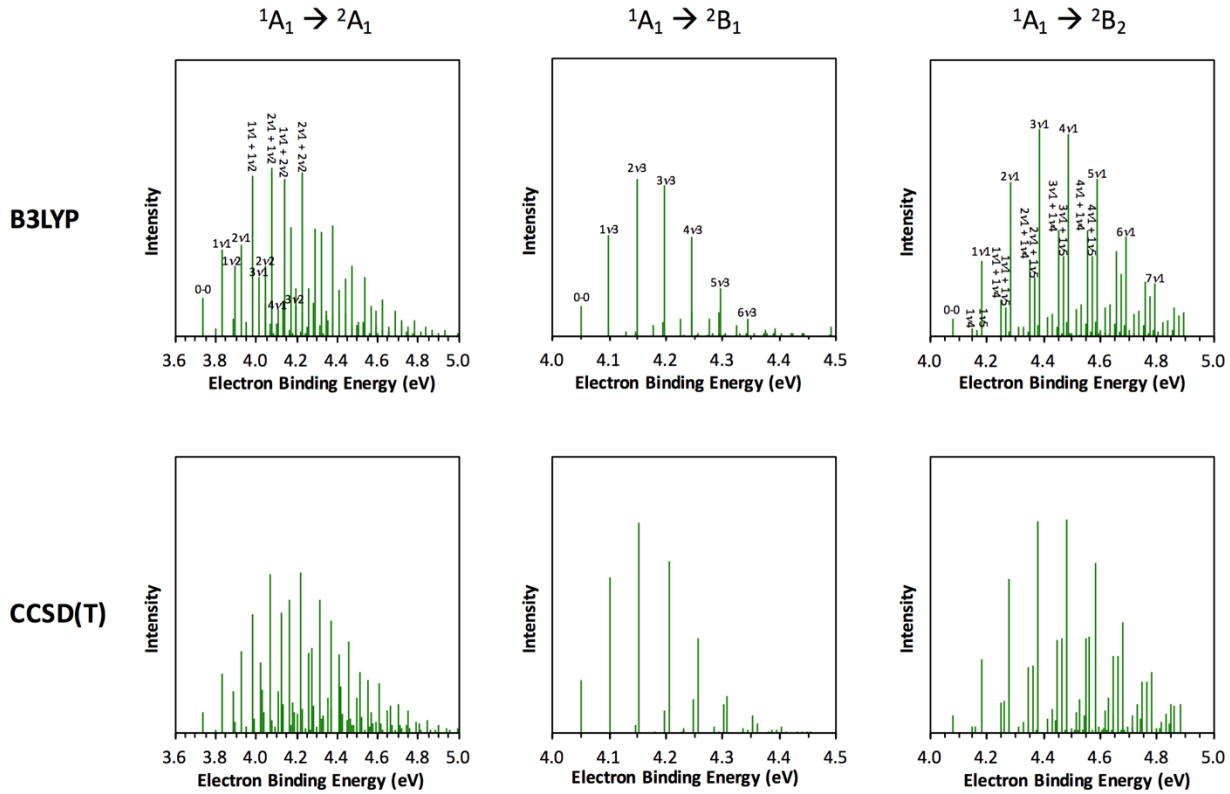

Figure S2. Comparison of B3LYP and CCSD(T) simulations of vibrational progressions (stick spectra) for the $^2A_1$, $^2B_1$, and $^2B_2$ states of $P_2N_3^{\bullet}$. The CCSD(T) frequency analyses were not successful for the other two low-lying state of $P_2N_3^{\bullet}$ ($^2A_2$ and 2^2A_1); therefore, no CCSD(T) stick spectra for the two states were obtained.

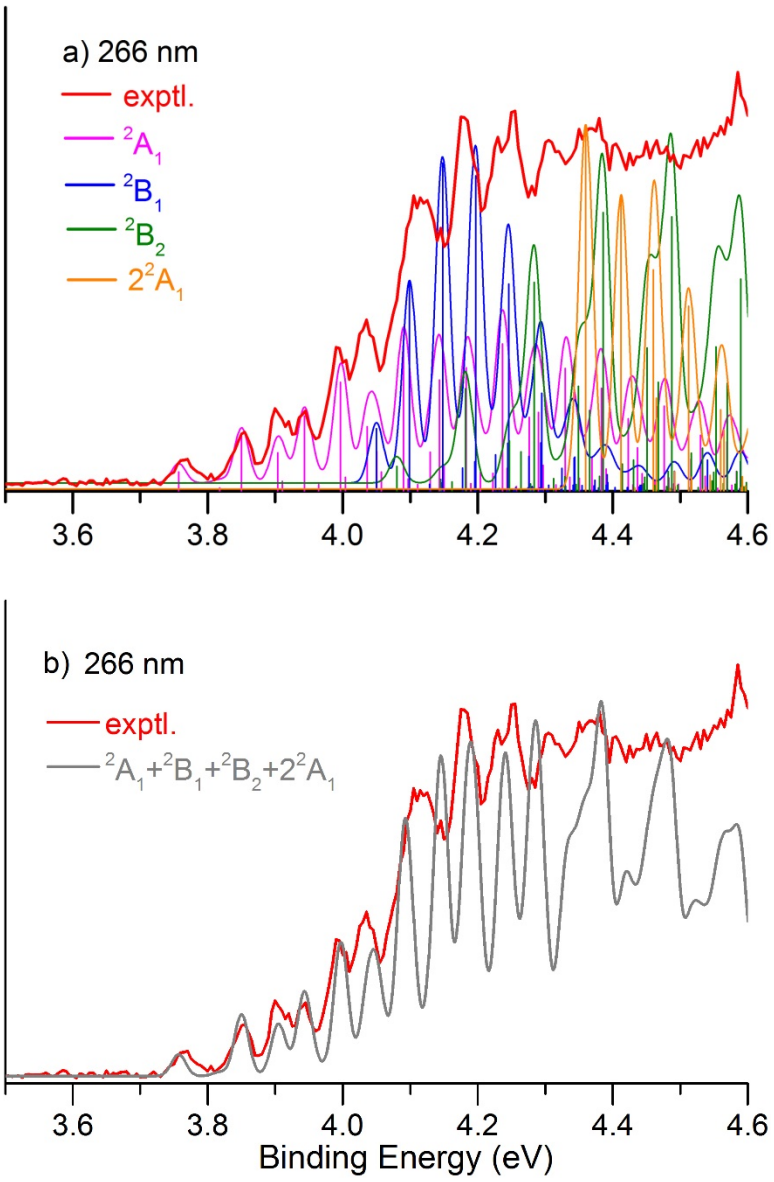

Figure S3. (a) UB3LYP/aug-cc-pVTZ simulated vibrational progressions (stick spectrum) and the convoluted spectra, superimposed onto the experimental 266 nm NIPE spectrum (red). The UCCSD(T) predicted 0-0 band position of the ground state ($^2A_1$) has been slightly adjusted, i.e., + 0.02 eV (3.74→3.76 eV); and the UCCSD(T) predicted 0-0 band positions for the excited states ($^2B_1$, $^2B_2$, 2^2A_1) are used without any adjustments. The convoluted spectrum, using Gaussian line shapes with 25 meV full widths at half maxima for each stick in $^2A_1$, $^2B_1$, $^2B_2$, and 2^2A_1 is also shown. (b) The computed NIPE spectrum (grey), calculated from the sum of the convoluted contributions of the four doublets in Figure S3(a), superimposed on the experimental 266 spectrum (red).

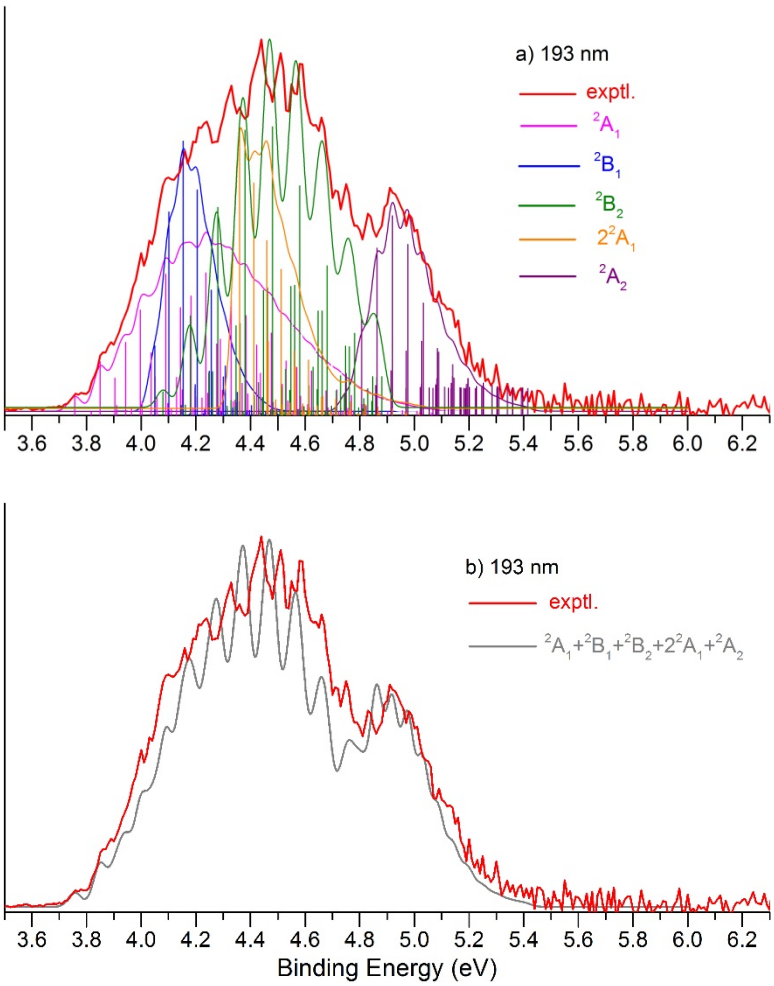

Figure S4. (a) UB3LYP/aug-cc-pVTZ simulated vibrational progressions (stick spectrum) and the convoluted spectra, superimposed onto the experimental 193 nm NIPE spectrum (red). The UCCSD(T) predicted 0-0 band positions for the ground state ($^2A_1$) and the highest excited state ($^2A_2$) have been slightly adjusted, i.e., +0.02 eV (3.74→3.76 eV) for $^2A_2$ and +0.13 eV (4.62→4.75 eV) for $^2A_2$; all other 0-0 band positions are kept the same as UCCSD(T) predictions. The convoluted spectrum, using Gaussian line shapes with 55 meV full widths at half maxima for each stick in $^2A_1$, $^2B_1$, $^2B_2$, 2^2A_1 and $^2A_2$, is also shown. (b) The computed NIPE spectrum (grey), calculated from the sum of the convoluted contributions of the five doublets in Figure S4(a), superimposed on the experimental 193 spectrum (red).

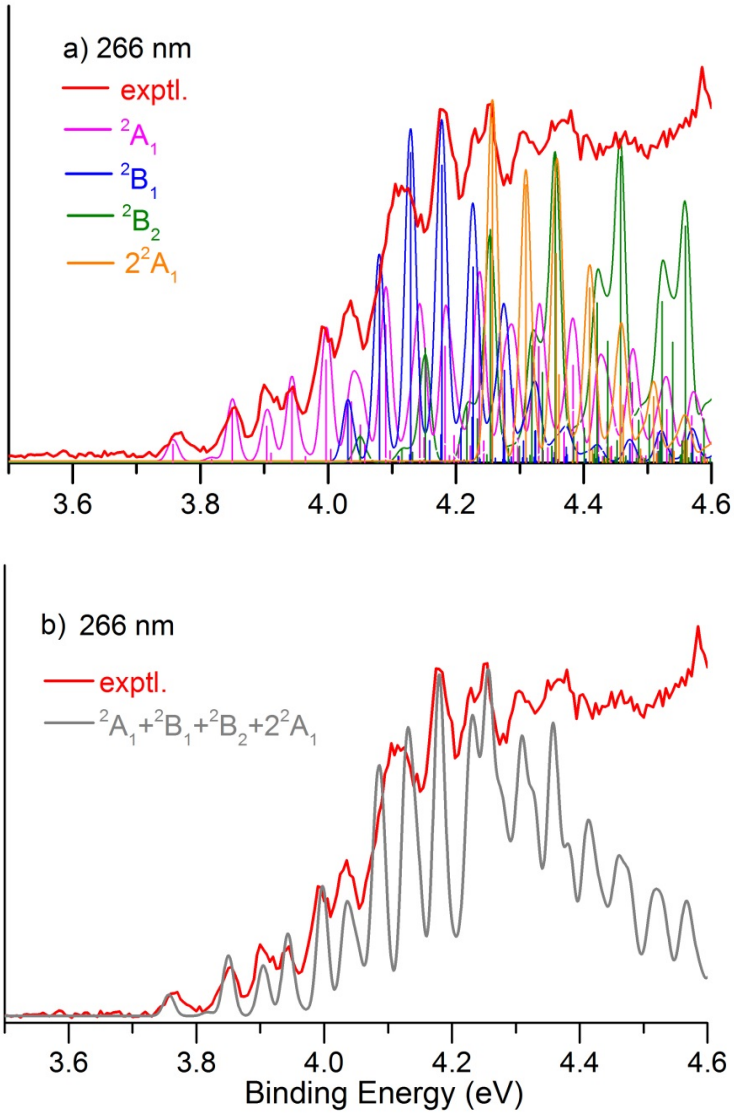

Fig. S5 (a) UB3LYP/aug-cc-pVTZ simulated vibrational progressions (sticks) in the NIPE spectrum and the convoluted spectra, superimposed onto the experimental 266 nm NIPE spectrum (red). The UCCSD(T) predicted positions of the 0-0 bands have been slightly adjusted – 3.74 → 3.76 eV for $^2A_1$ (pink), 4.05 → 4.03 eV for $^2B_1$(blue), 4.08 → 4.05 eV for $^2B_2$ (green), 4.36 → 4.26 eV for 2^2A_1 (orange) – to give a better match to the experimental spectrum. The convoluted spectrum, using Gaussian line shapes with 20 meV full widths at half maxima for each stick in the $^2A_1$, $^2B_1$, $^2B_2$, and 2^2A_1 states is also shown. (b) The computed NIPE spectrum (grey), calculated from the sum of the convoluted contributions of the four doublet states in Fig. 5a, superimposed on the experimental 266 spectrum (red).

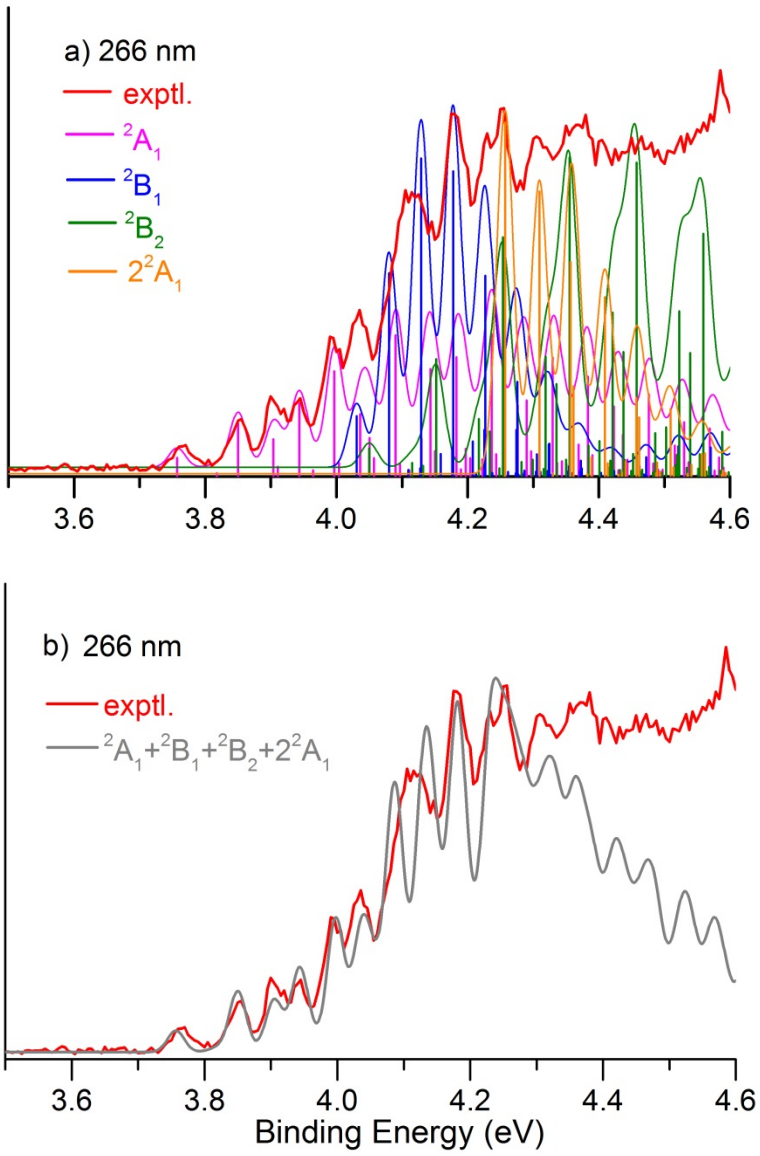

Fig. S6 (a) UB3LYP/aug-cc-pVTZ simulated vibrational progressions (sticks) in the NIPE spectrum and the convoluted spectra, superimposed onto the experimental 266 nm NIPE spectrum (red). The UCCSD(T) predicted positions of the 0-0 bands have been slightly adjusted – 3.74 → 3.76 eV for $^2A_1$ (pink), 4.05 → 4.03 eV for $^2B_1$(blue), 4.08 → 4.05 eV for $^2B_2$ (green), 4.36 → 4.26 eV for 2^2A_1 (orange) – to give a better match to the experimental spectrum. The convoluted spectrum, using Gaussian line shapes with 30 meV full widths at half maxima for each stick in the $^2A_1$, $^2B_1$, $^2B_2$, and 2^2A_1 states is also shown. (b) The computed NIPE spectrum (grey), calculated from the sum of the convoluted contributions of the four doublet states in Fig. 5a, superimposed on the experimental 266 spectrum (red).

Table S1. Coordinates and energies of calculated structures.

$P_2N_3^-$, $^1A_1$ state						
UB3LYP/aug-cc-pVTZ geometry				UCCSD(T)/aug-cc-pVTZ geometry		
N	0.000000	0.000000	1.566609	N	0.000000	0.000000	1.575092
N	0.000000	-1.134574	0.909852	N	0.000000	-1.144472	0.911056
N	0.000000	1.134574	0.909852	N	0.000000	1.144472	0.911056
P	0.000000	-1.050800	-0.790140	P	0.000000	-1.049702	-0.795586
P	0.000000	1.050800	-0.790140	P	0.000000	1.049702	-0.795586
UB3LYP/aug-cc-pVTZ energy = -847.121388557				UCCSD(T)/aug-cc-pVTZ energy = -845.88545933		
UB3LYP/aug-cc-pVTZ ZPE correction= 0.014879				UCCSD(T)/aug-cc-pVTZ ZPE correction=0.01470034		

$P_2N_3^{\bullet}$, $^2A_1$ state						
UB3LYP/aug-cc-pVTZ geometry				UCCSD(T)/aug-cc-pVTZ geometry		
N	0.000000	0.000000	1.437593	N	0.000000	0.000000	1.435489
N	0.000000	-1.140905	0.947571	N	0.000000	-1.155647	0.953700
N	0.000000	1.140905	0.947571	N	0.000000	1.155647	0.953700
P	0.000000	-1.073576	-0.777638	P	0.000000	-1.069094	-0.782715
P	0.000000	1.073576	-0.777638	P	0.000000	1.069094	-0.782715
UB3LYP/aug-cc-pVTZ energy = -846.989342529				UCCSD(T)/aug-cc-pVTZ energy = -845.74777734		
UB3LYP/aug-cc-pVTZ ZPE correction= 0.014566				UCCSD(T)/aug-cc-pVTZ ZPE correction=0.01439744		

$P_2N_3^{\bullet}$, $^2B_1$ state						
UB3LYP/aug-cc-pVTZ geometry				UCCSD(T)/aug-cc-pVTZ geometry		
N	0.000000	0.000000	1.547833	N	0.000000	0.000000	1.557798
N	0.000000	-1.143913	0.880553	N	0.000000	-1.154604	0.882842
N	0.000000	1.143913	0.880553	N	0.000000	1.154604	0.882842
P	0.000000	-1.133769	-0.772086	P	0.000000	-1.125725	-0.779358
P	0.000000	1.133769	-0.772086	P	0.000000	1.125725	-0.779358
UB3LYP/aug-cc-pVTZ energy = -846.972511846				UCCSD(T)/aug-cc-pVTZ energy = -845.73490611		
UB3LYP/aug-cc-pVTZ ZPE correction= 0.011603				UCCSD(T)/aug-cc-pVTZ ZPE correction=0.01285665		

$P_2N_3^{\bullet}$, $^2B_2$ state						
UB3LYP/aug-cc-pVTZ geometry				UCCSD(T)/aug-cc-pVTZ geometry		
N	0.000000	0.000000	1.676220	N	0.000000	0.000000	1.686993
N	0.000000	-1.057542	0.923277	N	0.000000	-1.064652	0.922816
N	0.000000	1.057542	0.923277	N	0.000000	1.064652	0.922816
P	0.000000	-1.034960	-0.821981	P	0.000000	-1.036584	-0.826907
P	0.000000	1.034960	-0.821981	P	0.000000	1.036584	-0.826907
UB3LYP/aug-cc-pVTZ energy = -846.970269560				UCCSD(T)/aug-cc-pVTZ energy = -845.73178216		
UB3LYP/aug-cc-pVTZ ZPE correction= 0.011568				UCCSD(T)/aug-cc-pVTZ ZPE correction=0.01079250		

$P_2N_3^{\bullet}$, $^2A_2$ state						
UB3LYP/aug-cc-pVTZ geometry				UCCSD(T)/aug-cc-pVTZ geometry		
N	0.000000	0.000000	1.634662	N	0.000000	0.000000	1.64166437
N	0.000000	-1.121935	0.990300	N	0.000000	-1.13096781	0.98665937
N	0.000000	1.121935	0.990300	N	0.000000	1.13096781	0.98665937
P	0.000000	-1.015926	-0.843561	P	0.000000	-1.02094292	-0.84342156
P	0.000000	1.015926	-0.843561	P	0.000000	1.02094292	-0.84342156
UB3LYP/aug-cc-pVTZ energy = -846.952784459				UCCSD(T)/aug-cc-pVTZ energy = -845.71574313		
UB3LYP/aug-cc-pVTZ ZPE correction= 0.013481						

$P_2N_3^{\bullet}$, 2^2A_1 state						
UB3LYP/aug-cc-pVTZ geometry				TD-UB3LYP/aug-cc-pVTZ geometry		
N	0.000000	0.000000	1.538110	N	0.000000	0.000000	1.536429
N	0.000000	1.148446	0.872565	N	0.000000	-1.146708	0.872431
N	0.000000	-1.148446	0.872565	N	0.000000	1.146708	0.872431
P	0.000000	1.087657	-0.766089	P	0.000000	-1.079845	-0.765634
P	0.000000	-1.087657	-0.766089	P	0.000000	1.079845	-0.765634

UB3LYP/aug-cc-pVTZ energy = -846.959080003 UB3LYP/aug-cc-pVTZ ZPE correction= 0.014348 UCCSD(T)/aug-cc-pVTZ energy = -845.72541483	TD-UB3LYP/aug-cc-pVTZ energy = -846.959640532

Table S2. Calculated Franck-Condon Factors.

B3LYP simulations											
$^1A_1 \rightarrow {}^2A_1$			$^1A_1 \rightarrow {}^2B_1$			$^1A_1 \rightarrow {}^2B_2$			$^1A_1 \rightarrow {}^2A_2$			$^1A_1 \rightarrow 2^2A_1$	
Energy,eV	Intensity		Energy,eV	Intensity		Energy,eV	Intensity		Energy,eV	Intensity		Energy,eV	Intensity
3.7400	0.0136		4.0500	0.0323		4.0800	0.0067		4.6200	0.0155		4.3600	0.2115
3.7976	0.0027		4.0990	0.1086		4.1452	0.0032		4.6765	0.0669		4.4123	0.1704
3.8319	0.0311		4.1287	0.0036		4.1619	0.0025		4.7275	0.0041		4.4329	0.0019
3.8895	0.0065		4.1466	0.0044		4.1819	0.0276		4.7330	0.1342		4.4600	0.1282
3.8925	0.0256		4.1479	0.1696		4.2471	0.0135		4.7840	0.0180		4.4645	0.0539
3.9238	0.0330		4.1777	0.0120		4.2638	0.0106		4.7895	0.1648		4.4852	0.0015
3.9501	0.0050		4.1955	0.0153		4.2783	0.0020		4.8396	0.0012		4.4919	0.0114
3.9814	0.0071		4.1969	0.1629		4.2838	0.0561		4.8405	0.0368		4.5123	0.1071
3.9844	0.0580		4.2266	0.0188		4.3123	0.0034		4.8461	0.1377		4.5168	0.0080
4.0158	0.0215		4.2319	0.0015		4.3290	0.0040		4.8915	0.0023		4.5329	0.0011
4.0420	0.0117		4.2445	0.0249		4.3456	0.0018		4.8962	0.0052		4.5383	0.0026
4.0450	0.0253		4.2459	0.1071		4.3490	0.0282		4.8971	0.0459		4.5441	0.0092
4.0685	0.0014		4.2533	0.0010		4.3656	0.0217		4.9026	0.0821		4.5600	0.0471
4.0733	0.0048		4.2564	0.0020		4.3802	0.0040		4.9241	0.0019		4.5645	0.0354
4.0764	0.0610		4.2743	0.0017		4.3856	0.0749		4.9384	0.0014		4.5906	0.0021
4.0891	0.0011		4.2756	0.0181		4.4142	0.0073		4.9481	0.0048		4.5919	0.0084
4.1026	0.0047		4.2808	0.0025		4.4309	0.0084		4.9527	0.0105		4.5920	0.0015
4.1077	0.0096		4.2921	0.0018		4.4454	0.0020		4.9536	0.0391		4.5964	0.0029
4.1339	0.0127		4.2935	0.0250		4.4475	0.0037		4.9591	0.0356		4.6123	0.0405
4.1370	0.0567		4.2948	0.0506		4.4508	0.0385		4.9806	0.0026		4.6168	0.0056
4.1604	0.0013		4.2961	0.0011		4.4620	0.0015		4.9949	0.0017		4.6383	0.0016
4.1652	0.0023		4.3023	0.0010		4.4675	0.0292		5.0037	0.0014		4.6441	0.0070
4.1683	0.0394		4.3053	0.0031		4.4794	0.0013		5.0046	0.0061		4.6443	0.0012
4.1810	0.0011		4.3232	0.0028		4.4820	0.0053		5.0092	0.0129		4.6600	0.0133
4.1945	0.0110		4.3246	0.0119		4.4875	0.0737		5.0101	0.0239		4.6645	0.0139
4.1976	0.0174		4.3298	0.0026		4.4923	0.0012		5.0156	0.0111		4.6906	0.0013
4.1996	0.0031		4.3411	0.0030		4.4961	0.0016		5.0371	0.0022		4.6919	0.0035
4.2210	0.0014		4.3425	0.0172		4.5127	0.0010		5.0409	0.0016		4.6964	0.0023
4.2259	0.0086		4.3438	0.0176		4.5161	0.0102		5.0514	0.0014		4.7122	0.0118
4.2289	0.0592		4.3450	0.0011		4.5263	0.0010		5.0556	0.0011		4.7168	0.0023
4.2416	0.0010		4.3543	0.0030		4.5327	0.0116		5.0602	0.0029		4.7441	0.0031
4.2551	0.0031		4.3722	0.0028		4.5473	0.0027		5.0611	0.0053		4.7600	0.0032
4.2602	0.0174		4.3735	0.0056		4.5494	0.0051		5.0657	0.0107		4.7645	0.0042
4.2865	0.0120		4.3788	0.0018		4.5527	0.0388		5.0666	0.0106		4.7665	0.0099
4.2895	0.0387		4.3901	0.0031		4.5639	0.0021		5.0721	0.0024		4.7919	0.0011
4.3129	0.0013		4.3914	0.0086		4.5694	0.0290		5.0936	0.0012		4.7964	0.0010
4.3178	0.0040		4.3928	0.0045		4.5813	0.0019		5.0974	0.0032		4.8122	0.0029
4.3208	0.0379		4.4033	0.0020		4.5839	0.0053		5.1167	0.0036		4.8188	0.0080
4.3335	0.0011		4.4212	0.0019		4.5894	0.0570		5.1176	0.0033		4.8645	0.0010
4.3471	0.0073		4.4225	0.0019		4.5941	0.0012		5.1222	0.0064		4.8665	0.0060
4.3501	0.0093		4.439	0.0022		4.5979	0.0023		5.1231	0.0034		4.871	0.0026
4.3521	0.0055		4.4404	0.0032		4.6146	0.0014		5.1539	0.0039		4.9188	0.0051
4.3784	0.0080		4.4424	0.0031		4.6179	0.0105		5.1723	0.0012		4.9665	0.0022
4.3814	0.0401		4.488	0.0011		4.6281	0.0010		5.1732	0.0031		4.971	0.0017
4.4077	0.0016		4.4914	0.0103		4.6346	0.0118		5.1741	0.0015		5.0188	0.0019
4.4097	0.0013		4.5403	0.0161		4.6491	0.0028		5.1787	0.0028			
4.4127	0.0166		4.5701	0.0011		4.6513	0.0051		5.2105	0.0033			
4.4390	0.0079		4.588	0.0015		4.6546	0.0307		5.2288	0.0015			
4.4420	0.0206		4.5893	0.0155		4.6658	0.0021		5.2297	0.0019			
4.4440	0.0013		4.6191	0.0018		4.6713	0.0227		5.2615	0.0011			
4.4703	0.0037		4.6369	0.0024		4.6832	0.0020		5.267	0.0020			

4.4733	0.0255		4.6383	0.0102		4.6858	0.0041		5.2853	0.0013			
4.4996	0.0038		4.668	0.0017		4.6913	0.0360						
4.5026	0.0042		4.6859	0.0024		4.6998	0.0024						
4.5046	0.0052		4.6873	0.0048		4.7165	0.0015						
4.5309	0.0052		4.717	0.0011		4.7198	0.0085						
4.5339	0.0212		4.7349	0.0016		4.7365	0.0095						
4.5622	0.0012		4.7362	0.0017		4.751	0.0022						
4.5652	0.0110		4.8838	0.0015		4.7531	0.0040						
4.5915	0.0040		4.9328	0.0023		4.7565	0.0199						
4.5945	0.0092		4.9817	0.0022		4.7677	0.0016						
4.5966	0.0012		5.0307	0.0015		4.7731	0.0145						
4.6228	0.0024					4.785	0.0016						
4.6258	0.0134					4.7877	0.0026						
4.6521	0.0016					4.7931	0.0192						
4.6551	0.0016					4.8017	0.0020						
4.6572	0.0034					4.8184	0.0012						
4.6834	0.0027					4.8217	0.0057						
4.6865	0.0093					4.8384	0.0063						
4.7178	0.0057					4.855	0.0026						
4.7440	0.0017					4.8583	0.0109						
4.7471	0.0035					4.875	0.0078						
4.7753	0.0012					4.895	0.0087						
4.7784	0.0058												
4.8097	0.0018												
4.8359	0.0011												
4.8390	0.0036												
4.8703	0.0025												
4.8996	0.0012												
4.9309	0.0022												
4.9915	0.0012												

CCSD(T) simulations													
$^1A_1 \rightarrow {}^2A_1$			$^1A_1 \rightarrow {}^2B_1$			$^1A_1 \rightarrow {}^2B_2$			$^1A_1 \rightarrow {}^2A_2$			$^1A_1 \rightarrow 2^2A_1$	
Energy,eV	Intensity		Energy,eV	Intensity		Energy,eV	Intensity		Energy,eV	Intensity		Energy,eV	Intensity
3.7400	0.0077		4.0500	0.0579		4.0800	0.0063		N.A. Frequency analysis was not successful			N.A. Geometry optimization and frequency analysis were not successful	
3.8005	0.0014		4.1016	0.1691		4.1470	0.0026						
3.8331	0.0219		4.1456	0.0083		4.1616	0.0027						
3.8866	0.0152		4.1532	0.2280		4.1801	0.0268						
3.8936	0.0040		4.1758	0.0011		4.2471	0.0113						
3.9262	0.0297		4.1807	0.0015		4.2617	0.0117						
3.9471	0.0026		4.1972	0.0256		4.2801	0.0560						
3.9797	0.0429		4.2048	0.1874		4.3141	0.0025						
3.9867	0.0055		4.2273	0.0014		4.3287	0.0041						
4.0193	0.0255		4.2323	0.0048		4.3433	0.0023						
4.0333	0.0157		4.2487	0.0366		4.3471	0.0241						
4.0402	0.0076		4.2563	0.1041		4.3617	0.0247						
4.0728	0.0575		4.2789	0.0012		4.3725	0.0011						
4.0798	0.0049		4.2839	0.0069		4.3802	0.0767						
4.0938	0.0026		4.2927	0.0030		4.4142	0.0054						
4.1124	0.0154		4.3003	0.0321		4.4287	0.0088						
4.1264	0.0439		4.3079	0.0410		4.4433	0.0048						
4.1333	0.0104		4.3278	0.0011		4.4472	0.0336						
4.1659	0.0487		4.3354	0.0062		4.4618	0.0342						
4.1729	0.0030		4.3443	0.0045		4.4726	0.0015						
4.1799	0.0113		4.3519	0.0191		4.4803	0.0776						
4.1869	0.0075		4.3595	0.0116		4.4835	0.0013						
4.2055	0.0070		4.3794	0.0017		4.4957	0.0016						
4.2195	0.0581		4.3870	0.0037		4.5067	0.0012						
4.2264	0.0090		4.3959	0.0041		4.5103	0.0013						
4.2404	0.0018		4.4035	0.0081		4.5142	0.0076						
4.2590	0.0291		4.4111	0.0023		4.5224	0.0011						

4.2660	0.0014		4.4310	0.0016		4.5288	0.0124						
4.2730	0.0311		4.4386	0.0016		4.5381	0.0011						
4.2800	0.0102		4.4475	0.0025		4.5434	0.0067						
4.2986	0.0025		4.4551	0.0025		4.5473	0.0346						
4.3126	0.0485		4.4991	0.0011		4.5619	0.0349						
4.3195	0.0056					4.5727	0.0016						
4.3266	0.0063					4.5803	0.0618						
4.3335	0.0052					4.5812	0.0012						
4.3521	0.0131					4.5835	0.0013						
4.3661	0.0407					4.5958	0.0023						
4.3731	0.0088					4.6067	0.0012						
4.4057	0.0286					4.6104	0.0019						
4.4126	0.0026					4.6143	0.0080						
4.4197	0.0171					4.6224	0.0011						
4.4266	0.0070					4.6289	0.0130						
4.4452	0.0045					4.6381	0.0011						
4.4592	0.0335					4.6435	0.0069						
4.4662	0.0053					4.6473	0.0281						
4.4732	0.0029					4.6619	0.0281						
4.4802	0.0028					4.6727	0.0012						
4.4988	0.0126					4.6804	0.0402						
4.5128	0.0221					4.6813	0.0013						
4.5197	0.0059					4.6836	0.0010						
4.5383	0.0012					4.6959	0.0025						
4.5523	0.0195					4.7105	0.0020						
4.5593	0.0024					4.7144	0.0066						
4.5663	0.0078					4.7289	0.0106						
4.5733	0.0037					4.7435	0.0056						
4.5919	0.0043					4.7474	0.0186						
4.6059	0.0180					4.7620	0.0185						
4.6128	0.0035					4.7805	0.0221						
4.6199	0.0011					4.7814	0.0011						
4.6268	0.0012					4.7959	0.0021						
4.6454	0.0085					4.8105	0.0017						
4.6594	0.0100					4.8144	0.0045						
4.6664	0.0031					4.8290	0.0071						
4.685	0.0012					4.8436	0.0037						
4.6990	0.0104					4.8475	0.0104						
4.7059	0.0016					4.8621	0.0102						
4.7130	0.0031					4.8805	0.0104						
4.7199	0.0016												
4.7385	0.0029												
4.7525	0.0080												
4.7595	0.0018												
4.7921	0.0045												
4.8061	0.0039												
4.8130	0.0013												
4.8456	0.0046												
4.8596	0.0011												
4.8852	0.0015												
4.8992	0.0031												
4.9387	0.0019												
4.9527	0.0013												
4.9923	0.0017												
5.0458	0.0011												