

Supplementary Information

Theoretical Insight into the Wavelength-Dependent Photodissociation Mechanism of Nitric Acid

Hongyan Xiao,^{*ab} Satoshi Maeda^{*c} and Keiji Morokuma^{*bd}

^a *Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing 100190, People's Republic of China*

^b *Fukui Institute for Fundamental Chemistry, Kyoto University, 34-4 Takano Nishihiraki-cho, Sakyo, Kyoto 606-8103, Japan*

^c *Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060-0810, Japan*

^d *Cherry L. Emerson Center for Scientific Computation and Department of Chemistry, Emory University, Atlanta, Georgia 30322, United States*

***Corresponding Authors:** hyxiao@mail.ipc.ac.cn; smaeda@mail.sci.hokudai.ac.jp; morokuma@fukui.kyoto-u.ac.jp

CONTENTS

S1. Fig. S1. Molecular orbitals in the active space (16e,12o)

S2. Fig. S2. Molecular orbitals in the active space (12e,8o)

S3. Cartesian coordinates (Å) of structures in Fig. 1

S4. Cartesian coordinates (Å) of structures in Fig. 6

S1. Molecular orbitals in the active space (16e,12o)

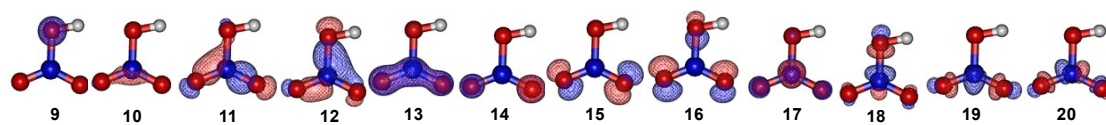


Fig. S1 Molecular orbitals in the active space (16e,12o) in the Franck-Condon region.

S2. Molecular orbitals in the active space (12e,8o)

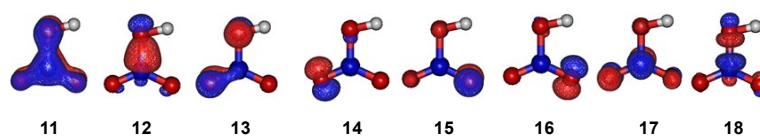


Fig. S2 Molecular orbitals in the active space (12e,8o) in the Franck-Condon region

S3. Cartesian coordinates (Å) of structures in Fig. 1

[The imaginary frequencies (cm^{-1}) of transition states were listed in parentheses.]

SA2-CAS (12e,8o) PT2/6-31+G*

S ₀			
N	-0.006523420002	-0.001013868079	-0.000003786767
O	1.226083566613	0.001971331632	0.000112438938
O	-0.784764574004	0.927595473349	-0.000118057528
O	-0.616500217805	-1.259568671898	0.000174184236
H	0.149495645202	-1.877955265006	-0.000164778877
S ₁			
N	-0.283163841688	0.050413174984	0.080857879071
O	-0.754691266893	1.023306353149	-0.656438183994
O	-0.800617904520	-1.049407589637	-0.339437070958
O	1.082597243728	0.004922187228	0.373072929586
H	1.315503388658	0.952749584841	0.514447162685
S ₁ -TS1 (284.9i)			
N	-0.441680716369	0.082475456664	0.101345246083
O	-0.864144792009	-1.016638579371	-0.373892813630
O	-0.834539443449	0.971386656596	-0.722717292362
O	1.361744855273	0.035670111528	0.422408131246
H	1.329183246295	0.293840873932	1.370333051285
S ₁ /S ₀ -1			
N	0.000308644922	-0.006271277961	0.001213573161
O	-0.568054329296	-0.413622179569	-1.047713270207
O	-0.581072234664	1.260573959928	0.004736271011
O	1.401248841320	-0.009458740619	-0.005338241897
H	1.637569537715	-0.456411181773	0.835377497944
S ₁ /S ₀ -2			
N	0.022707733904	0.009865100618	-0.079412827938
O	-0.145003719135	1.253746404813	0.065308467078
O	1.416608106459	0.019999999300	0.028311454777
O	-0.467308203187	-0.626554357301	-1.202581205154
H	-0.068943362245	-0.118650368127	-1.952471946028

SA3-CAS (12e,8o) PT2/6-31+G*

S ₀			
N	0.207800016102	0.168963269176	0.032241324635
O	1.378589933601	-0.219761605018	-0.057121411335
O	-0.254651908045	1.291104439487	-0.038145660706
O	-0.755867476242	-0.836322313125	0.250393135539
H	-0.212594624994	-1.657430379707	0.278838587261
S ₂ -1			
N	-0.007963303305	0.355741267613	-0.358280601855

O	-0.416615965202	1.490992748499	-0.324770564799
O	1.298102405122	0.156919752421	-0.009439954712
O	-0.818069863947	-0.735398757587	0.456825998949
H	1.327706155902	-0.818495140501	0.132134188066
S ₂ -1-TS1	(706.6i)		
N	0.275417309360	0.227712907840	0.073848394110
O	0.817550571181	-1.163976611464	0.430531347792
O	1.089961398427	0.935893579087	-0.391300607475
O	-1.200017809735	0.075995843919	-0.874332285544
H	-1.650998949234	-0.574667449381	-0.290615608883
S ₂ -1-TS2a	(767.6i)		
N	-0.139299416548	-0.165452854088	0.165351609610
O	-0.641292727254	1.819265455855	-0.201497644807
O	-0.663976590144	-1.191370672308	-0.086474846896
O	1.234688875067	-0.250817027119	0.111113548019
H	1.494626528882	0.694054727658	0.197223084074
S ₂ -1-TS2b	(424.3i)		
N	-0.067107152778	-0.257862076323	0.276102204663
O	-0.837017224977	1.894484545345	-0.298016030438
O	-0.657796753717	-1.234721706218	-0.057050461862
O	1.319164044600	-0.386724246320	0.030471533197
H	1.677881926880	0.470108623520	0.346344794443
S ₂ -1-TS3	(3024.8i)		
N	0.064335187299	0.431460631063	-0.427231611284
O	-0.570996544890	-0.867799974631	0.452126734259
O	-0.404279112476	1.520707468846	-0.267930839457
O	1.334405929967	0.136241990865	-0.160787575235
H	0.959693970105	-0.770850246139	0.300292351716
S ₂ -2			
N	0.169147592326	0.017710625533	0.374769147506
O	-0.604028278034	1.023005425895	-0.142947746139
O	-0.611736259286	-0.992832485249	-0.120648806409
O	1.397354084594	0.004831769638	-0.363845435052
H	2.062486864516	0.010167602866	0.353949214163
S ₂ -2-TS1	(1196.0i)		
N	0.039188619980	0.018708580478	0.424798430305
O	-0.633675280139	0.990136464678	-0.133219617915
O	-0.641298811560	-0.959517642512	-0.111683234771
O	1.564293697210	0.003437095967	-0.426568807830
H	2.163210214511	0.010005121384	0.353956780211
S ₂ -3			
N	-0.024918990993	0.004357769173	0.465876983438
O	0.810111537207	-0.934308586127	-0.094230927045
O	0.585722332294	1.092774064904	-0.112531536446

O	-1.311588281850	-0.143202729326	-0.102577289829
H	-1.166901032954	-0.136011696034	-1.079236795028
S ₂ -3-TS1	(1140.4i)		
N	0.108847858911	0.019497290448	0.511414143158
O	0.836845382247	-0.886493934385	-0.091472087016
O	0.623107953421	1.052214139617	-0.107829395855
O	-1.491864903279	-0.162779128260	-0.148512657246
H	-1.237897401300	-0.142512297418	-1.103747423040
S ₂ -4			
N	0.117019767829	-0.066926210377	0.183811578930
O	1.115651333520	-1.242592246013	0.010226849603
O	0.515922391289	1.028916250551	-0.173151931101
O	-1.078498503544	-0.508975324545	-0.300028748041
H	-1.444874783696	0.250760457057	-0.815682600864
S ₂ -4-TS1	(704.9i)		
N	0.254290726004	-0.019786291025	0.185521924708
O	1.247541059279	-1.144161189491	0.193156838369
O	0.721185254416	1.004204523431	-0.184936009427
O	-1.189054697125	-0.589479430090	-0.601931982017
H	-1.702049822590	0.250180657177	-0.643679541649
S ₂ -4-TS2a	(462.2i)		
N	0.048138978651	-0.012406715207	0.118351807276
O	1.440071613584	-1.525397610979	0.068282129212
O	0.385587302917	1.094628000834	-0.172079768493
O	-1.206141817396	-0.350721845879	-0.302611972356
H	-1.564475907755	0.444035251230	-0.772962105640
S ₂ -4-TS2b	(454.2i)		
N	0.000209559263	0.080807748808	0.184134092014
O	1.526822947042	-1.682775910685	0.058808660390
O	0.331913297432	1.171833957687	-0.202969264159
O	-1.208890273199	-0.350975052781	-0.317040757689
H	-1.531133170888	0.376796218746	-0.908353731250
S ₂ -5			
N	0.036589910899	0.033876852625	0.134668209918
O	1.480391079789	-1.612146439225	0.069313432439
O	0.353867381794	1.147643672397	-0.180237637179
O	-1.203151331998	-0.357046790705	-0.309231395999
H	-1.573810456261	0.418789480186	-0.801819094349
S ₂ -TS14	(453.0i)		
N	0.005124155124	0.197300668616	-0.082488051513
O	1.541265250345	-0.078487799589	-0.107177515939
O	-0.310100897783	1.332195126442	0.192013927028
O	-0.549172579273	-0.372274771741	-1.222376736111
H	-0.142232521850	0.123262415038	-1.975519979219

S ₂ -TS23	(427.8i)		
N	-0.004058009954	-0.004700478847	0.506372049036
O	-0.518691297839	-1.069735458063	-0.197578756814
O	-0.845101637539	0.921564993516	-0.100619732237
O	1.327932640670	0.194708248730	-0.001806876341
H	1.359583604664	1.153744044666	-0.214695553643
S ₂ /S ₁ -1			
N	-0.156759672868	-0.254519996037	0.163113321805
O	-0.579582451017	1.780898789695	-0.230974272082
O	-0.635321323996	-1.322942333632	-0.008928598020
O	1.218370022543	-0.250907558442	0.049222365349
H	1.406308548778	0.712683622171	0.133439000040
S ₂ /S ₁ -2			
N	0.067394468127	0.449354025286	-0.424669589904
O	-0.402209337263	1.539042488670	-0.286780045383
O	1.332612029355	0.139307790157	-0.148100347812
O	-0.546297256305	-0.897373482362	0.470699364667
H	0.938549566503	-0.775763361801	0.310471807646
S ₂ /S ₁ -3			
N	0.240198388534	0.055887410300	-0.489680937347
O	-0.634508787962	0.981172973131	0.047492761270
O	-0.291022871611	-1.108386308764	0.117077358535
O	1.331855271877	0.399379828146	0.413041043679
H	-0.511448280142	-1.673720553249	-0.652983114432
S ₂ /S ₁ -4			
N	-0.047662494165	0.075550132665	-0.551296140040
O	1.226986013684	-0.100109799417	0.000686356772
O	-0.746598680841	0.836092773351	0.481368865496
O	-0.595687190800	-1.160184289770	-0.233880033709
H	1.060362389635	-0.181891966957	0.974999148257
SA4-CAS (12e,8o) PT2/6-31+G*			
S ₀			
N	0.201632653675	0.174887504213	0.032285666688
O	1.383149681329	-0.229081698063	-0.056618651841
O	-0.256496952637	1.290621370036	-0.037881101952
O	-0.758368180433	-0.836500978034	0.250688339733
H	-0.206641261513	-1.653372787341	0.277731722766
S ₃ -1			
N	-0.003642776448	0.407830183155	0.181629309030
O	-0.485201152702	1.426261972275	-0.512781899335
O	1.301909127561	0.108940962637	-0.131594357101
O	-0.815026585306	-0.645780254647	0.252099586331
H	1.385120815470	-0.847492992983	0.107116426722

S ₃ -1-TS1	(551.5i)		
N	-0.1331219339	0.3962590767	0.2066261447
O	-0.5742855740	1.4091147177	-0.4093927465
O	1.4445264474	0.0511932508	-0.2833358555
O	-0.9466937875	-0.5723640688	0.2406134784
H	1.5604330180	-0.8274206965	0.1529837489
S ₃ -1-TS2	(2574.6i)		
N	-0.119462452533	0.101645249536	-0.172659349567
O	-0.843990930782	1.070820771289	0.115403959025
O	1.599621224052	-0.045131096079	0.013045036565
O	-0.766906636910	-1.107779662105	-0.048484912303
H	-0.003345742790	-1.727940003025	-0.141296413505
S ₃ -2			
N	-0.129156809161	0.163095647316	0.449858161257
O	-0.950053835843	1.079596629902	-0.217372528442
O	1.089401314965	0.301727046329	-0.290882958533
O	-0.622611689841	-1.036997999629	-0.074781027128
H	1.750121618102	0.451644985208	0.418240199618
S ₃ -2-TS1	(924.0i)		
N	0.178363841535	-0.013798645841	-0.512886229517
O	-1.353509696771	-0.087267515499	0.145817890962
O	0.702388187060	-1.008644925701	0.207740076454
O	0.568230484499	1.091294318161	0.127839220782
H	-1.886567615367	-0.153670151233	-0.682583547522
S ₃ -3			
N	0.036133930031	0.016591889239	0.506887258780
O	0.651844803481	1.071109543224	-0.186290848671
O	-1.251506556173	0.005867698787	-0.076127260844
O	0.637595228704	-1.089333229324	-0.115027509384
H	-1.089742265224	-0.027406983126	-1.052364482276
S ₃ -3-TS1	(753.6i)		
N	0.0730960450	0.0503858593	0.5008325666
O	0.0225551970	1.3028179760	0.1347527395
O	-1.3841646849	-0.4201565274	-0.0642621722
O	0.9124174429	-0.5741217195	-0.4879974243
H	-1.2594495099	-0.2176006583	-1.0247845796
S ₃ -TS23	(509.3i)		
N	-0.032205728155	0.015379807499	0.006313962818
O	1.398310231432	0.022353123327	-0.007242455548
O	-0.312582240131	1.402603007443	-0.000896787945
O	-0.382753032989	-0.242465139356	1.377694011999
H	1.661257849840	-0.622022908914	0.688974968678
S ₃ /S ₂ -1			
N	-0.012576176342	0.377672128683	-0.085594740558

O	-0.442237252594	1.528587474468	-0.413541418830
O	1.320840384880	0.122043135130	-0.129715988795
O	-0.839240463957	-0.759858129392	0.356895639624
H	1.356372936583	-0.818684738450	0.168425574210
S ₃ /S ₂ -2			
N	0.000259883216	0.000035265360	0.000982719690
O	1.312163114618	0.000250214453	-0.001272497531
O	-0.643229731824	1.158297939352	0.001892101655
O	-0.337128025705	-0.973535624988	-0.818318666388
H	-1.514277370309	0.942251325821	-0.430750447426
S ₃ /S ₂ -3			
N	-0.113379582697	0.096333539882	0.488507899180
O	-0.898045360226	1.084748869678	-0.250948686233
O	1.050316065033	0.339372298315	-0.280175911128
O	-0.648626132917	-1.030760412120	-0.073640746110
H	1.747435609029	0.469372013370	0.401319291063
S ₃ /S ₂ -4			
N	0.068135743434	0.000685313340	0.571249485064
O	0.046606454247	1.356600770294	0.116421205473
O	-1.183651732876	-0.378179875123	0.128184658218
O	0.846837523654	-0.585939455830	-0.470383445828
H	-1.192758670861	-0.090599565607	-0.828775460491
S ₃ /S ₂ -5			
N	-0.231304276525	-0.263237004245	0.018696915634
O	1.574500669770	-0.560305410992	0.042588016925
O	-0.880026182752	0.795354564091	-0.356864496306
O	-0.965910794771	-1.175106843004	0.537595482709
H	1.811350378532	0.253207013467	-0.459514674891

S4. Cartesian coordinates (Å) of structures in Fig. 6

[The imaginary frequencies (cm^{-1}) of transition states were listed in parentheses.]

SA4-CAS (16e,12o) PT2/aug-cc-pVDZ

S_0

N	0.214355975730	0.172889672216	0.031008152642
O	1.370318526895	-0.215483914872	-0.056751201138
O	-0.249484033489	1.282161012461	-0.037581882125
O	-0.759676655295	-0.843097733832	0.251247229928
H	-0.212237873842	-1.649915625973	0.278283660694

S_3-1^* * SA5-CAS (16e,12o) PT2/aug-cc-pVDZ

N	-0.049695483240	0.428111294299	0.205908319554
O	-0.498755090141	1.419025224792	-0.498403581834
O	1.375762501321	0.083866252895	-0.180474636304
O	-0.862904146338	-0.639083039776	0.235201539630
H	1.418751646968	-0.842159861775	0.134237424605

S_3-1 -TS1 (497.6i)

N	-0.001525768054	0.385370545998	0.189670121007
O	-0.483510338181	1.388643820007	-0.467331290048
O	1.525414260266	0.064327222671	-0.240605237441
O	-0.794116746324	-0.635310350473	0.248974859555
H	1.577937723235	-0.864322814419	0.054276486465

S_3-1 -TS2 (2702.4i, 33.3i)

N	-0.087723795520	0.089041365784	-0.153204657211
O	-0.817070935173	1.072072666868	0.113184331467
O	1.594761137975	0.015321227810	0.003996713514
O	-0.789715708988	-1.132679963128	-0.070376638568
H	-0.034335237263	-1.752140037722	-0.127591428987

S_3-2

N	0.122162120785	0.452968803788	0.410283057109
O	-0.369241674289	1.331456605361	-0.571914721678
O	1.347514229639	0.026187190293	-0.223453478081
O	-0.680786961252	-0.688719476907	0.164017880640
H	2.001511133439	0.171949177659	0.483637385335

S_3-2 -TS1 (2782.6i)

N	0.198613958867	-0.008806624762	-0.495430289153
O	-1.393823563113	-0.089192253643	0.157465547200
O	0.716242691099	-1.039434297325	0.198988860901
O	0.573028925149	1.114818194237	0.112478897919
H	-1.885156811048	-0.149471938611	-0.687575605712

S_3-2 -TS2 (2153.0i)

N	0.022969612448	-0.081118380965	0.489476216056
O	-1.019091124418	1.182011870350	-0.249311958497
O	1.294890974636	-0.046337929879	-0.126796459302

O	-0.610839388537	-1.037862552103	-0.026193327182
H	1.776491925869	0.573108992602	0.452701528927
S ₃ /S ₂ -1			
N	-0.090369069521	-0.027576276925	0.002306477267
O	1.371265189615	-0.035610153314	-0.002840642835
O	-0.848721861576	0.985747635141	-0.000089253285
O	-0.640173111699	-1.293295915128	-0.002183627326
H	0.172475591103	-1.838758907363	0.002436955986
S ₂ -1			
N	0.171439912898	0.307675912139	0.016643264521
O	0.536384899803	-1.214533059982	0.407379077730
O	1.038336234516	0.962017244406	-0.485622793850
O	-1.007782911678	0.145525796997	-0.696597169136
H	-1.346039741368	-0.663754195293	-0.252238455636
S ₂ -1-TS1 (840.0i)			
N	0.247338099430	0.257575283988	0.093671393797
O	0.558509433278	-1.108013038561	0.376287990523
O	1.083860175948	0.915334930807	-0.461641046441
O	-1.137179007196	0.131549232124	-0.753492439206
H	-1.420616181463	-0.695488138356	-0.306694658682
S ₂ -1-TS2 (137.5i)			
N	-0.108958658629	-0.171641618870	0.259793620523
O	-0.857099545535	1.915844487419	-0.285208945752
O	-0.688075644036	-1.135301843829	-0.099307388638
O	1.304240767925	-0.279697874190	-0.009224333543
H	1.634639750273	0.576476479474	0.319662797409
S ₂ -1-TS3 (2775. 6i)			
N	0.041211894382	0.429486412851	-0.441344356431
O	-0.408125625242	1.517187777018	-0.270014589321
O	1.330871427571	0.124871292180	-0.113866772242
O	-0.625989366765	-0.841817894633	0.467558002269
H	1.005752171176	-0.772967895864	0.273625337340
S ₂ -2			
N	-0.034893463902	0.036083196307	0.463384853249
O	-0.711821650304	-1.119289672629	0.129541248839
O	-0.929748768418	0.860617028114	-0.188214156584
O	1.164365128945	0.040611801243	-0.328865624504
H	1.842682253678	0.222171946962	0.341907879000
S ₂ -2-TS1 (1648.8i)			
N	0.061775387731	0.019097805729	0.436931441620
O	-0.621827351414	1.000699111155	-0.139833972582
O	-0.626071743213	-0.971066996417	-0.120124921865
O	1.534879601939	0.005490074124	-0.416858574111
H	2.142962544958	0.008549625406	0.347169576945

S₂/S₁-2

N	0.048398368122	0.439892218854	-0.437691982643
O	-0.401092579018	1.530737626117	-0.285962279158
O	1.324586536989	0.133423521036	-0.102229667942
O	-0.637972076365	-0.869868925204	0.486679949229
H	1.009800251387	-0.777424749249	0.255161602128