

**Trajectory based nonadiabatic molecular dynamics without calculating
nonadiabatic coupling in the avoided crossing case: Trans $\leftrightarrow$ cis
Photoisomerization in azobenzene**

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S1. A typical resonance trajectory

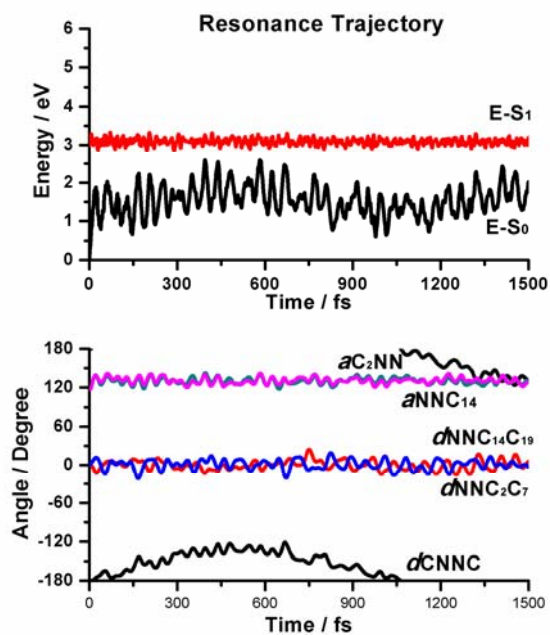


Fig. S1. Potential energies and five important angles evolve along typical resonance trajectory starting from *trans*-azobenzene.

S2. Average population distribution in terms of sampling trajectories

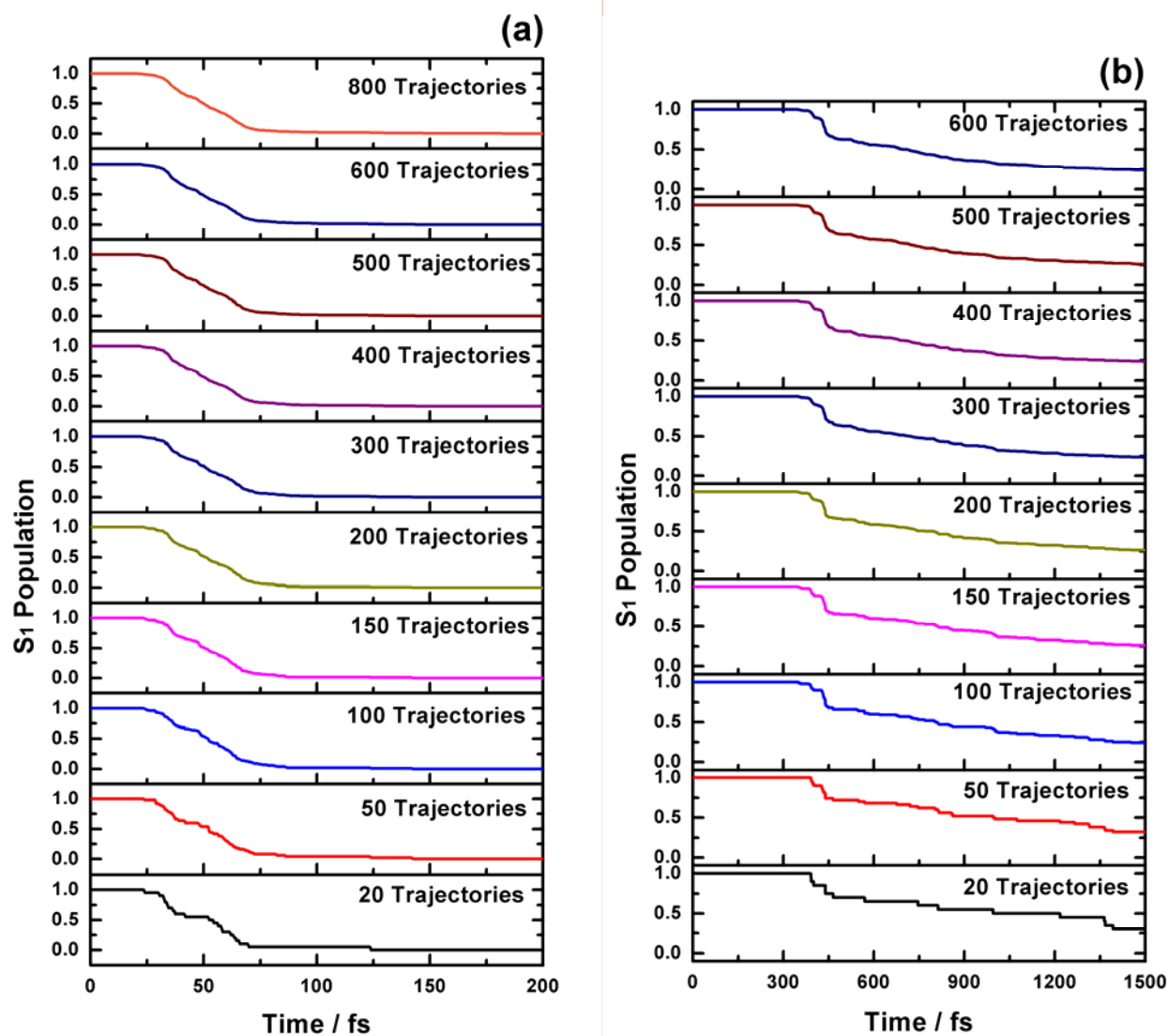


Fig. S2. Average population distribution in S₁ state with respect to number of sampling trajectories. (a) Starting from cis-isomer. (b) Starting from trans-isomer.

S3. The potential energy surfaces near vicinity of the two conical intersections.

Around CI-rot, CNNC and NNCC dihedral angles are good variable to show structure of conical intersection and Fig.S3(a) shows that there is potential well in S_1 state. This structure can attract trajectory moving around conical intersection and enhance chance to visit the seam. On the contrary, CNN and NNC angles are good variable to show structure of CI-inv and Fig.S3(b) shows conical seam between two plane-shaped potential energy surfaces and this kind shape of seam does not help trajectory to visit seam unless trajectory with very high excitation energy. However, potential energy at CI-inv is 0.42eV higher than that at CI-rot, and thus trajectory quickly moves to CI-rot although geometry of CI-inv is close to trans-isomer geometry.

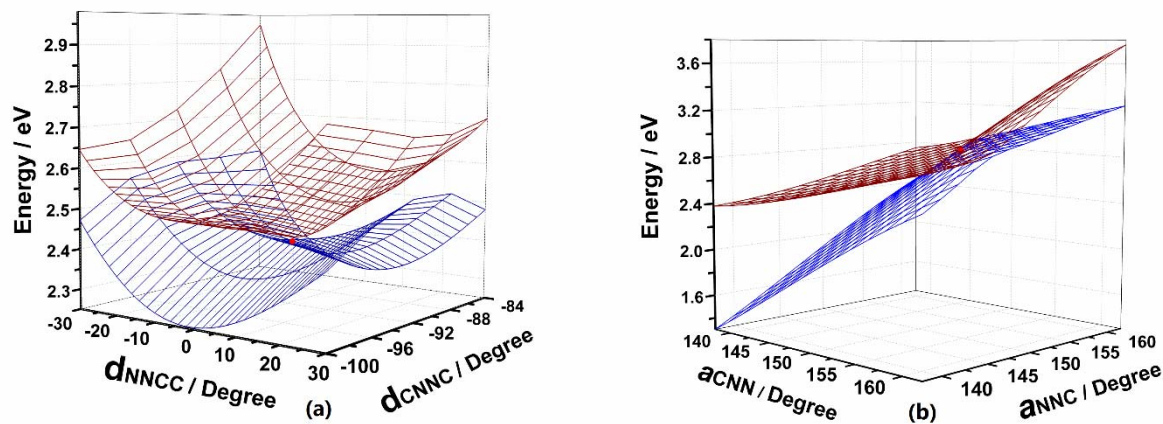


Fig. S3. Two-dimensional potential energy surfaces in vicinity of conical intersections. (a) CI-rot in terms of NNCC and CNNC dihedral angles. (b) CI-inv in terms of CNN and NNC bond angles.

S4. Cartesian coordinates for all optimized geometries (in Table 2).

trans-azobenzene (S_0)

N	-0.0000075939	0.4724502032	0.3962961271
C	-0.0001262444	0.1698048384	1.7857523126
C	0.0018771616	1.2817675641	2.6449059578
C	0.0020904351	1.0941575993	4.0132333476
C	0.0001060812	-0.2098822605	4.5376720905
C	-0.0018849384	-1.2919639313	3.6892113910
C	-0.0020702778	-1.1056237506	2.3014396426
H	0.0032681865	2.2623172339	2.2123329723
H	0.0037337931	1.9386389651	4.6745476445
H	0.0000807009	-0.3572860864	5.6005195459
H	-0.0032726478	-2.2886352331	4.0862567250
H	-0.0036668663	-1.9455517524	1.6377026829
N	-0.0000010953	-0.4724501937	-0.3962961290
C	-0.0001258050	-0.1698048388	-1.7857523100
C	0.0018785017	-1.2817675650	-2.6449059601
C	0.0020875852	-1.0941576071	-4.0132333491
C	0.0001068720	0.2098822621	-4.5376720892
C	-0.0018867035	1.2919639246	-3.6892113918
C	-0.0020669683	1.1056237539	-2.3014396399
H	0.0032730392	-2.2623172285	-2.2123329715
H	0.0037255533	-1.9386389792	-4.6745476508
H	0.0000870174	0.3572860958	-5.6005195405
H	-0.0032798806	2.2886352161	-4.0862567238
H	-0.0036577374	1.9455517680	-1.6377026814

cis-azobenzene (S_0)

N	1.8626860656	-0.0121406221	0.6167035421
C	0.6999105646	-0.0832958764	1.4553395680
C	0.6775399950	0.8006777008	2.5502979881
C	-0.3548652757	0.7325933762	3.4638805497
C	-1.3572436332	-0.2446734202	3.3198085917
C	-1.3050125312	-1.1250575447	2.2687198323
C	-0.2703294892	-1.0458837553	1.3238093672
H	1.4740710324	1.5099199914	2.6593540468
H	-0.3824443376	1.4103376770	4.2948564611
H	-2.1504979013	-0.3063502214	4.0392821999
H	-2.0556920967	-1.8835963454	2.1599178125
H	-0.2381909238	-1.7437796913	0.5109976195
N	1.8649132228	0.0015708492	-0.6141669326
C	0.7043228824	0.0796520715	-1.4552994857
C	0.6653847475	-0.8190665415	-2.5377829312
C	-0.3661982543	-0.7445394564	-3.4517806054
C	-1.3508391542	0.2525307384	-3.3207160074

C	-1.2817232311	1.1464323455	-2.2821598613
C	-0.2477062599	1.0616440205	-1.3368551945
H	1.4479953293	-1.5451309988	-2.6368633509
H	-0.4074537058	-1.4339185393	-4.2725744894
H	-2.1434750176	0.3183350755	-4.0404924476
H	-2.0182917670	1.9200652725	-2.1836310401
H	-0.2016113447	1.7697561974	-0.5334671523

TS-inv-rot (S_0)

N	0.1748670130	1.4034601557	0.6766415176
C	0.0627473135	0.5027295695	1.8081916605
C	0.1041621813	1.0992865789	3.0507249572
C	0.0008629294	0.3028134051	4.2051283816
C	-0.1387172900	-1.0568133489	4.0860940649
C	-0.1788855057	-1.6572136459	2.8139470350
C	-0.0799869036	-0.8905908900	1.6824771181
H	0.2141568338	2.1637578220	3.1143594834
H	0.0320098578	0.7635396666	5.1730971793
H	-0.2173752960	-1.6704862076	4.9626356609
H	-0.2868049649	-2.7216063077	2.7333396721
H	-0.1080908524	-1.3400763110	0.7096687681
N	0.1282360261	0.9509498221	-0.4441203698
C	0.0770536850	0.4190745068	-1.6893213899
C	1.2096604230	-0.0827670646	-2.3057737166
C	1.1147060847	-0.6105450276	-3.5998565147
C	-0.0801572327	-0.6535142260	-4.2720061144
C	-1.2296351419	-0.1464547487	-3.6399911444
C	-1.1680522914	0.3886169997	-2.3714057557
H	2.1511022095	-0.0568907600	-1.7962699219
H	2.0062768364	-0.9886082185	-4.0621313374
H	-0.1419780305	-1.0618876241	-5.2610247505
H	-2.1729610791	-0.1671633932	-4.1506557003
H	-2.0390710902	0.7867646485	-1.8921017686

TS-rot (S_0)

N	1.4588049216	0.3754725219	0.5451132893
C	0.5860124522	0.0877849950	1.5775132925
C	0.6407839870	0.9596150760	2.6939474589
C	-0.1885069465	0.7531353312	3.7747576313
C	-1.0862257375	-0.3344784091	3.7761384567
C	-1.1287119544	-1.1874075821	2.7005541462
C	-0.2935552174	-0.9847912357	1.5955371923
H	1.3407190297	1.7702885094	2.6657623458
H	-0.1488728897	1.4148896321	4.6180043392
H	-1.7279648667	-0.4957370277	4.6205099480
H	-1.8021227475	-2.0226329346	2.7011609533

H	-0.3243799934	-1.6684356035	0.7712847466
N	1.4689304712	-0.3611385782	-0.5551095227
C	0.5902672812	-0.0813392400	-1.5843832467
C	0.6570894569	-0.9459116395	-2.7041048098
C	-0.1839943798	-0.7506211435	-3.7785864170
C	-1.0990566238	0.3206568657	-3.7658246010
C	-1.1516570629	1.1709681403	-2.6862027087
C	-0.3072124241	0.9777589151	-1.5892570775
H	1.3732353508	-1.7425896186	-2.6840985482
H	-0.1390717498	-1.4059714879	-4.6262031651
H	-1.7488986902	0.4753129645	-4.6053023926
H	-1.8394991009	1.9938994308	-2.6813205732
H	-0.3387139762	1.6561222737	-0.7611145444

TS-planar-inv (S₀)

N	0.0000000000	1.3706122728	0.6560470168
C	0.0000000000	0.5047183497	1.8152098271
C	0.0000000000	1.1842700316	3.0327633187
C	0.0000000000	0.4711786257	4.2317521204
C	0.0000000000	-0.9231310590	4.2092844505
C	0.0000000000	-1.5944981555	2.9828586162
C	0.0000000000	-0.8853418088	1.7974487050
H	0.0000000000	2.2559931978	3.0175099750
H	0.0000000000	0.9958952015	5.1676741099
H	0.0000000000	-1.4796940145	5.1265955585
H	0.0000000000	-2.6676983610	2.9622685480
H	0.0000000000	-1.4067377267	0.8647917371
N	0.0000000000	0.9160642908	-0.4842629174
C	0.0000000000	0.3391092060	-1.7407336225
C	0.0000000000	1.1922527484	-2.8480503440
C	0.0000000000	0.6801575449	-4.1337170660
C	0.0000000000	-0.6945987294	-4.3292703542
C	0.0000000000	-1.5530278149	-3.2385921197
C	0.0000000000	-1.0413921340	-1.9510621543
H	0.0000000000	2.2480318409	-2.6693997021
H	0.0000000000	1.3448061231	-4.9751992908
H	0.0000000000	-1.0947088810	-5.3248257788
H	0.0000000000	-2.6148175223	-3.3899160692
H	0.0000000000	-1.7079335062	-1.1157608471

S₀/S₁ CI-rot

N	-0.0233907999	-1.3708088557	0.6014715397
C	-0.0576865575	-0.5156364503	1.7258814114
C	-0.6437005383	0.7444935586	1.7245564298
C	-0.6066325147	1.5210622086	2.8929459433
C	-0.0017195838	1.0370918643	4.0264372895

C	0.5804242878	-0.2445532740	4.0267578331
C	0.5489167116	-1.0146558698	2.8970267345
H	-1.1292440863	1.1109370696	0.8424028706
H	-1.0585382618	2.4938697458	2.8934503769
H	0.0244161001	1.6313063222	4.9192563244
H	1.0453389020	-0.6166263457	4.9187940731
H	0.9775136557	-1.9964508990	2.8699976240
N	-0.5238029529	-1.0408951892	-0.4886171141
C	-0.1806632151	-0.4444321745	-1.6751018847
C	-1.1648254291	-0.3494128066	-2.6885116888
C	-0.8499233033	0.2477682223	-3.8899779341
C	0.4440151043	0.7552645529	-4.1195282316
C	1.3924723382	0.6511073119	-3.1330303255
C	1.0910620611	0.0543224637	-1.9016903752
H	-2.1401920439	-0.7503523505	-2.4995235233
H	-1.5960357303	0.3201122486	-4.6576363895
H	0.6818257469	1.2142312371	-5.0590105285
H	2.3839270891	1.0285285476	-3.2953117548
H	1.8402535368	-0.0264507223	-1.1394194103

S₀/S₁ CI-inv

N	0.0000000000	-0.2826934380	0.5450392600
C	0.0000000000	-0.1270566778	1.9041891841
C	0.0000000000	1.1495150878	2.4739587399
C	0.0000000000	1.2751352406	3.8529088573
C	0.0000000000	0.1599923829	4.6780763533
C	0.0000000000	-1.1018869048	4.0974323560
C	0.0000000000	-1.2584042643	2.7236493746
H	0.0000000000	2.0159252798	1.8437683345
H	0.0000000000	2.2592938541	4.2812106104
H	0.0000000000	0.2700748261	5.7441842013
H	0.0000000000	-1.9772001868	4.7185031843
H	0.0000000000	-2.2343958644	2.2820735768
N	0.0000000000	0.1773727447	-0.5714057207
C	0.0000000000	0.0963786773	-1.8645467109
C	0.0000000000	1.2926980465	-2.6787224119
C	0.0000000000	1.1748038115	-4.0609554371
C	0.0000000000	-0.0807038340	-4.6869760496
C	0.0000000000	-1.2684945343	-3.8727782161
C	0.0000000000	-1.2036739620	-2.5334273688
H	0.0000000000	2.2505398333	-2.1988100934
H	0.0000000000	2.0660951084	-4.6588763438
H	0.0000000000	-0.1625124539	-5.7549978225
H	0.0000000000	-2.2271479862	-4.3553376481
H	0.0000000000	-2.0876787902	-1.9262808108

trans-azobenzene (S₁)

N	0.0018174600	0.3953483822	0.4806341096
C	0.0006829396	0.1595195593	1.8434304481
C	0.0015143916	1.2841572460	2.6995940426
C	0.0004815380	1.0989833720	4.0655547063
C	-0.0012666162	-0.2006750930	4.6081030837
C	-0.0021320673	-1.2845401008	3.7657543855
C	-0.0011266213	-1.1159297023	2.3748540416
H	0.0030020429	2.2650193699	2.2682111541
H	0.0010274970	1.9508219765	4.7176926561
H	-0.0019412400	-0.3373667748	5.6717401758
H	-0.0035873461	-2.2798602423	4.1668314411
H	-0.0017200630	-1.9646153574	1.7216543386
N	0.0018167029	-0.3953556471	-0.4806352298
C	0.0006785361	-0.1595243774	-1.8434310870
C	0.0015089259	-1.2841585366	-2.6995994018
C	0.0004907270	-1.0989785855	-4.0655593497
C	-0.0012731694	0.2006823913	-4.6081019672
C	-0.0021267173	1.2845437363	-3.7657486110
C	-0.0011297205	1.1159270607	-2.3748492370
H	0.0029840484	-2.2650224592	-2.2682204886
H	0.0010609058	-1.9508141099	-4.7177014976
H	-0.0019683962	0.3373796469	-5.6717383521
H	-0.0035653988	2.2798658869	-4.1668204793
H	-0.0017286528	1.9646099644	-1.7216459424

cis-azobenzene (S₁)

N	1.1371822280	0.0009216343	0.6058722647
C	0.4300108677	0.0006291866	1.7862929865
C	1.2008777503	-0.0007292170	2.9779432963
C	0.5740385297	-0.0011787153	4.2036220253
C	-0.8331648266	-0.0007228247	4.2851942856
C	-1.5717372148	0.0002956054	3.1298229075
C	-0.9517856931	0.0008526509	1.8723139666
H	2.2685526213	-0.0008310079	2.8939500100
H	1.1621760922	-0.0019357743	5.1008364644
H	-1.3166262086	-0.0010541622	5.2422405943
H	-2.6440172965	0.0006916464	3.1748128071
H	-1.5565882094	0.0019202530	0.9921130223
N	1.1392645191	0.0008602652	-0.6067275600
C	0.4308207637	0.0004457023	-1.7866390351
C	1.2007704630	-0.0000287758	-2.9788593016
C	0.5730449699	-0.0007850131	-4.2040634063
C	-0.8342446460	-0.0009605589	-4.2845497721
C	-1.5719406200	-0.0002834419	-3.1286435781
C	-0.9510009716	0.0007007200	-1.8715780716

H	2.2684980926	-0.0001252389	-2.8955739765
H	1.1604625592	-0.0015968004	-5.1017519534
H	-1.3184104016	-0.0015150603	-5.2412443832
H	-2.6442549729	-0.0004595943	-3.1728159426
H	-1.5550722525	0.0011724406	-0.9908851825

TS-rot (S_I)

N	1.0488354898	0.5619106547	0.5390623003
C	0.4290198830	0.2004787360	1.7455969744
C	0.5183713688	1.0848564655	2.7975320810
C	-0.0902125606	0.7804406971	4.0204887833
C	-0.7720774551	-0.4016403452	4.1823322402
C	-0.8572752918	-1.3122848406	3.1128348885
C	-0.2620145723	-1.0219157641	1.9019518206
H	1.0555625627	2.0021269563	2.6616653682
H	-0.0176196917	1.4783937510	4.8317537815
H	-1.2360179845	-0.6359808107	5.1206296625
H	-1.3840243147	-2.2381926325	3.2402125434
H	-0.3079464384	-1.7104644640	1.0823275932
N	1.0780828715	-0.1312625033	-0.4934586484
C	0.4468279679	-0.0364593056	-1.7298234474
C	0.8194216696	-0.8963930711	-2.7398120058
C	0.1802943348	-0.8295427995	-3.9827628963
C	-0.8099607519	0.0950624871	-4.2140845841
C	-1.1839795595	0.9802148668	-3.1881168691
C	-0.5711002098	0.9199296294	-1.9526421122
H	1.5998060214	-1.6084909944	-2.5607217816
H	0.4776672373	-1.5076615641	-4.7591805883
H	-1.2941687625	0.1469283039	-5.1695804123
H	-1.9527299308	1.7081013242	-3.3632079570
H	-0.8447350538	1.5912746706	-1.1634501602