Supporting information for

Photoinduced Curtius rearrangements of fluorocarbonyl azide, $FC(O)N_3$: a QM/MM nonadiabatic dynamics simulation

Bin-Bin Xie[1,2*], Cheng-Xing Cui[3], Wei-Hai Fang[1,2*], Ganglong Cui[2]

1) Hangzhou Institute of Advanced Studies, Zhejiang Normal University, 1108 Gengwen Road, Hangzhou 311231, Zhejiang, P. R. China;

2) Key Laboratory of Theoretical and Computational Photochemistry, Ministry of Education College of Chemistry, Beijing Normal University, Beijing 100875, China

3) School of Chemistry and Chemical Engineering, Henan Institute of Science and Technology, Xinxiang 453003, People's Republic of China

E-mail: binbinxie@mail.bnu.edu.cn;fangwh@bnu.edu.cn

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1. Zhu-Nakamura method

Trajectory-based nonadiabatic dynamics simulations involved the lowest four singlet states and are carried out using the recently developed surface-hopping method proposed by Zhu et al.[1] In this dynamics simulation approach, the system is merely propagated in an electronic state at any time; however, near quasi-degenerate regions, it can jump between different potential energy surfaces. The nonadiabatic transition probability is computed according to the Landau-Zener formula improved by Zhu and Nakamura,[2-4]

$$p = \exp(-(\frac{\pi}{4\sqrt{a^2}}\sqrt{\frac{2}{b^2+\sqrt{|b^4 \pm 1|}}})) \quad (1)$$

in which two unitless parameters, i.e., effective coupling and collision energy, are written as

$$a^2 = \frac{\mathbf{h}^2}{2\mu}\frac{\sqrt{|F_2F_1|}\,|F_2 - F_1|}{(2V_{12})^3} \quad (2)$$

and

$$b^2 = (E_t - E_x)\frac{|F_2 - F_1|}{\sqrt{|F_2F_1|}(2V_{12})} \quad (3)$$

where F_1 and F_2 are two mass-scaled one-dimensional diabatic forces, V_{12} is diabatic coupling, □ is the reduced mass of the diatomic molecule, E_x is the energy at the crossing point, and E_t is the potential energy plus kinetic energy component along the hopping vector direction. Finally, the mass-scaled one-dimensional diabatic forces in Eqs. (2) and (3) are converted from mass-scaled multi-dimensional diabatic forces based on

$$\frac{\sqrt{|F_2 F_1|}}{\sqrt{\mu}} = \sqrt{|\sum_i^N \frac{1}{m_i} \sum_{\alpha=x,y,z} F_2^{i\alpha} F_1^{i\alpha}|} \quad (4)$$

and

$$\frac{|F_2 - F_1|}{\sqrt{\mu}} = \sqrt{\sum_i^N \frac{1}{m_i} \sum_{\alpha=x,y,z} (F_2^{i\alpha} - F_1^{i\alpha})^2} \quad (5)$$

in which N is the number of nuclei in a system, m_i is the i-th atomic mass, $F_1^{i\alpha}$ and $F_2^{i\alpha}$ are multi-dimensional diabatic forces of the ith atom (α: x, y, and z) related to the involved two states. These diabatic forces can be further converted from multi-dimensional adiabatic forces, which are directly calculated by the electronic structure packages available. The detailed description on definitions of the hopping direction and the momentum change at a hopping region can be found in recent works by Zhu and co-workers.[1,5] This Zhu-Nakamura nonadiabatic dynamics method has been recently coded, as a module, into our own generalized trajectory-based surface hopping (GTSH) package.[6-7] Compared with the fewest switches surface-hopping method developed by Tully and Preston,[8-10] the largest advantage of the Zhu-Nakamura method is that it does not need to compute expensive nondiabetic coupling vectors, in particular for those electronic structure methods incapable of efficiently computing these vectors.

2. The simulated absorption spectrum for the FC(O)N_3 system in gas phase

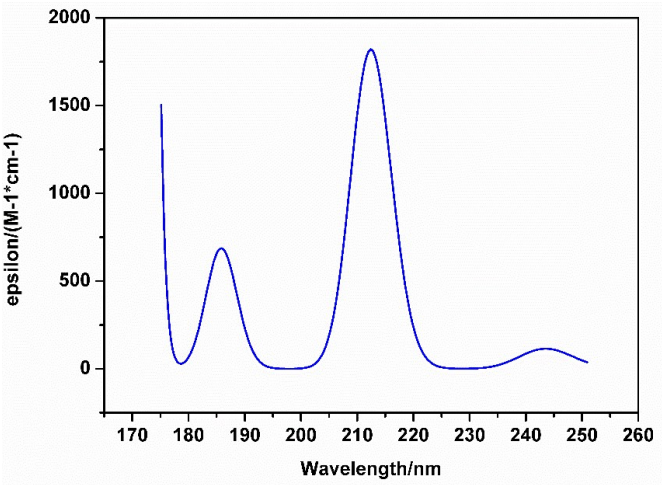


Figure S1. The simulated absorption spectrum for the $FC(O)N_3$ system in gas phase.

As the gaseous precursor $FC(O)N_3$ shows moderate UV absorptions, we firstly explored the electronic structures and vertical excitation energies of several of the lowest excited singlet states (i.e. S_1, S_2, and S_3 states) at the Frank-Condon point at the most stable S_0 conformer S0-syn in gas phase. According to the vertical excitation energies and corresponding oscillator strengths, we have simulated absorption spectrum for the $FC(O)N_3$ system in gas phase (see Fig. S1 and Table S1). It is clear that the absorption spectrum calculated by using CASPT2 method well agrees with the experimental spectrum (205 nm [1840 $mol^{-1}•cm^{-1}$] and 195 nm [1300 $mol^{-1}•cm^{-1}$]), which is computed to be 211.1 nm [1800 $mol^{-1}•cm^{-1}$] and 184.6 nm [800 $mol^{-1}•cm^{-1}$].

Table S1. The CASPT2 computed vertical excitation energies (nm) and fitted molar extinction coefficients [($mol^{-1}•cm^{-1}$)] of the lowest three excited singlet states.

States	Energies[a]	Exp[b]
S_1-FC	242.2	—
S_2-FC	211.1 [1800]	205 [1840]
S_3-FC	184.6 [800]	195 [1300]

[a] calculated in gas phase; [b] measured in gas phase[11].

3. The choice of the active space

Prior to production dynamics simulations, we have done a lot of benchmarks on different active spaces including CASPT2 (10, 8), CASPT2 (12, 9), and CASPT2 (14, 10) (see Table S2). It is clear that molecular orbitals located on the carbonyl group are not significantly involved in the S_1, S_2, and S_3 states. Moreover, we have found that adding more n, π, and π* orbitals of the carbonyl group into the active space do not improve the results of absorption spectra (see Table S3). Taken together, the CASPT2 (10, 8) method is finally adopted concerning a balanced accuracy and efficiency.

Table S2. CASPT2(14,10) with molecular orbitals of the carbonyl group

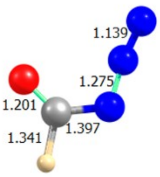
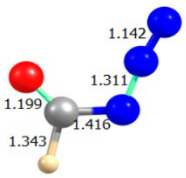
					
16	17	18	19	20	21
					
22H	23L	24	25		
S0-syn	energy(kcal/mol)	energy(nm)	orbital	weight	
root1	0.0		2222222000	0.828377	
root2	118.6	241.2	222222u0d0	0.920955	
root3	136.2	210.0	222222ud00 22222u20d0	0.498482 0.414735	
root4	155.1	184.4	22222u2d00	0.915229	

Table S3. CASPT2(10,8) with molecular orbitals of the carbonyl group

				
18	19	20	21	
				
22H	23L	24	25	
S0-syn	energy(kcal/mol)	energy(nm)	orbital	weight
root1	0.00		22222000	0.851619
root2	122.50	233.48	222u2d00	0.849762
root3	123.57	231.45	222u20d0	0.662684
root4	144.78	197.54	2u2220d0	0.81271
root5	164.47	173.89	2u222d00	0.747846

4. The choice of QM and MM regions

Table S4 gives the detailed energies of QM and MM subsystems of S0-anti and the ΔE_{QM} and ΔE_{MM} between S0-syn and S0-anti are estimated to be 11.79 and 3.23 kcal/mol, respectively. In our opinion, the steric and cage effects of the Ar matrix are more significant than the van der Waals interaction. Therefore, it is a safe treatment without including argon atoms in the QM region in the present work.

Previously, we have performed the nonadiabatic dynamics modelling about the photodissociation dynamics of $CH_3C(O)SH$ in the argon matrix at 15 K (*J. Chem. Phys. 2015, 143, 194303*). More recently, Martínez et al. studied the photochemistry of the sulfine in the Ar matrix at 11 K (*Angew. Chem. Int. Ed. 2016, 55, 14993*). Both of these theoretical calculations provide dependable calculation results, where the QM region merely contains the $CH_3C(O)SH$ or the sulfine molecules and the MM region the argon atoms.

Table S4. The detailed energies of QM and MM subsystems of S0-syn and S0-anti

Structures	QM Energy [$FC(O)N_3$]	MM Energy [Ar matrix]	Total Energy
S0-syn	-376.396869 a.u.	-3.952123456 a.u.	-380.3489924 a.u.
S0-anti	-376.3780651 a.u.	-3.946969371 a.u.	-380.3250344 a.u.
ΔE(anti-syn)	11.79 kcal/mol	3.23 kcal/mol	15.03 kcal/mol

5. Cartesian coordinates of critical structures at QM(CASPT2)/MM level

S0-syn

C	-1.104623700	-0.267117400	-0.166787100
O	-1.552581400	0.808531500	-0.446829900
N	0.230277600	-0.649958400	0.012493100
N	1.028417700	0.316865800	-0.139565900
N	1.866937300	1.083971200	-0.239986700
F	-1.853653600	-1.353769700	0.033145900

S0-anti

C	-1.628667100	0.066412400	-0.172516800
O	-2.204754000	1.029840900	-0.506404400
N	-0.214812900	-0.052669100	-0.107924300

N	0.293845300	-1.165348400	0.084189100
N	0.947609400	-2.093861600	0.241793800
F	-2.213856600	-1.089409800	0.230370600

S0-nitr

C	-1.505176900	-0.605563100	-0.082250300
O	-1.484764600	0.620324000	-0.443758800
N	-0.259844400	-0.856500600	-0.029950300
N	1.567685900	1.725003300	-0.159081400
N	2.455898700	1.045016600	-0.141418000
F	-2.572006200	-1.327859100	0.147885000

S0-cya

C	-3.997285400	1.270932300	1.792404400
O	-4.339321100	1.334563700	2.913627100
N	-3.700710500	1.476020100	0.589086800
N	-1.415877800	-1.804274900	-0.950178600
N	-0.832149000	-2.219810700	-1.816861900
F	-3.203585500	0.303492500	-0.045547500

S1-syn

C	-1.915059400	-0.047520300	-0.210825500
O	-1.521536700	1.042821600	-0.500931400
N	-1.161264400	-1.109555300	0.348307800
N	0.175353300	-1.017960700	-0.207781300
N	1.061094700	-1.597307000	0.338672800
F	-3.189424700	-0.438013700	-0.282376400

S1-syn-iso

C	-1.894769446	-0.037417588	-0.207438237
O	-1.679568046	1.102755831	-0.591360122
N	-1.009697379	-1.066415057	0.172933501
N	0.372619994	-0.692231032	0.410833220
N	0.742239403	0.411898988	-0.064907185
F	-3.118196874	-0.544669964	-0.142714130

S1-anti

C	-1.264062857	0.581371017	-0.439282768
O	-1.117084919	1.742857284	-0.746707442
N	-0.163687999	-0.193798018	-0.088821185
N	-0.570964028	-1.524262081	0.286766384
N	0.279961172	-2.304990795	0.589578691
F	-2.464792687	-0.007938145	-0.426570127

S1-anti-iso

C	-1.823979242	-0.193782343	-0.180216400
O	-2.953934513	-0.608365278	-0.207936620
N	-0.822294939	-1.031899260	0.261791647
N	0.549317450	-0.780451638	-0.143664785
N	0.893375747	0.371750247	-0.043569953
F	-1.490798098	1.032722491	-0.592360069

S1-nitr

C	-1.450862700	-0.464719500	-0.123893800
O	-1.620014600	0.691207900	-0.458146300
N	-0.211570500	-0.994182000	0.018397700
N	1.499863300	1.639051300	-0.163463700
N	2.456630600	1.062986100	-0.138878400
F	-2.463226500	-1.309472800	0.129026500

S2-syn

C	-1.930796452	-0.077871735	-0.215260325
O	-1.572487234	1.014580395	-0.531056311
N	-0.984640323	-1.024366491	0.104634719
N	0.327527479	-0.844438885	-0.230211728
N	0.815670504	-1.737793860	0.466650200
F	-3.184999694	-0.494916397	-0.117878670

S2-syn-iso

C	-1.966184300	-0.086393000	-0.207344200
O	-1.610622000	1.020708800	-0.529614300
N	-0.956865900	-0.948069400	0.106035000
N	0.368997900	-0.766560800	0.189254100
N	0.760822300	0.405524000	-0.052603500
F	-3.199475300	-0.522026500	-0.139787500

S2-anti

C	-1.150578622	0.505015448	-0.386867818
O	-1.239919705	1.778597586	-0.772024298
N	-0.099971606	-0.180037453	-0.062724130
N	-0.577857181	-1.489316645	0.266802110
N	0.136997345	-2.367036450	0.614372263
F	-2.380377316	0.012628582	-0.390220822

S2-anti-iso

C	-1.140921000	0.379191000	-0.351301300
O	-1.082037600	1.655818500	-0.714337200
N	-0.174367600	-0.398062800	-0.015175900
N	-0.578282300	-1.710474500	0.337847000

N	-1.690596400	-2.141943000	0.365548700
F	-2.420539700	0.019068600	-0.392319500

S3-syn

C	-1.049134000	-0.319401000	-0.157600000
O	-1.451082000	0.774346000	-0.434707000
N	0.285038000	-0.638429000	0.082579000
N	1.179360000	0.338428000	-0.186630000
N	1.762864000	1.206742000	0.425339000
F	-1.791714000	-1.397457000	0.035513000

S3-syn-iso

C	-1.029388461	-0.311905658	-0.145034483
O	-1.475039402	0.776197039	-0.447471185
N	0.299844989	-0.642948820	-0.013824027
N	1.220762153	0.370146113	-0.035118666
N	1.837488538	0.849071377	-0.951949904
F	-1.780849703	-1.377631031	0.038061875

S3-anti

C	-1.269924000	0.018138600	-0.153968300
O	-1.739376200	1.083840400	-0.416011000
N	0.101329200	-0.217036300	-0.045988900
N	0.544558700	-1.406111900	0.432509700
N	0.938555200	-2.448341800	-0.044689300
F	-1.953033200	-1.120472400	0.058697800

S3-anti-iso

C	-1.040455527	-0.327773139	-0.130359110
O	-1.968898764	-1.070585838	-0.051412907
N	0.303037104	-0.638030157	-0.024783457
N	1.220844689	0.372069289	-0.028575085
N	1.842145842	0.846439912	-0.946126321
F	-1.158474569	1.000465534	-0.331685112

S1S0-syn

C	-1.901684848	-0.058222002	-0.196211044
O	-1.517989116	1.037107483	-0.496754756
N	-1.129628346	-1.118849760	0.347671944
N	0.169100372	-0.998236447	-0.262613547
N	1.013171660	-1.589250103	0.372650074
F	-3.181636497	-0.439377273	-0.279751429

S1S0-syn-iso

C	-1.927884872	-0.021393334	-0.201809454
O	-1.703435740	1.113822081	-0.560370780
N	-1.006696951	-1.064104633	0.104948782
N	0.406805992	-0.745555989	0.222141783
N	0.810530591	0.370945719	-0.068682118
F	-3.177427461	-0.560891653	-0.139936588

S1S0-anti

C	-1.876859982	-0.019431527	-0.210740342
O	-3.049859735	-0.148606810	-0.370568593
N	-1.102251848	-1.062449405	0.264197976
N	0.217211670	-1.089805752	-0.347778777
N	0.907402301	-1.867132587	0.237569007
F	-1.186627842	1.107281492	-0.458782368

S1S0-anti-iso

C	-1.968001704	0.010948961	-0.159961364
O	-3.119100162	-0.196287607	-0.441941851
N	-1.182294565	-1.078140875	0.332783420
N	0.178292933	-1.044438517	-0.140616166
N	0.698520813	-0.256656118	-0.837642547
F	-1.346625545	1.215367471	-0.336718041

S1S0-nitr

C	-1.090249276	-0.496934243	-0.094449044
O	-1.468122870	0.655411973	-0.325048674
N	0.149611899	-0.971017562	0.121264504
N	1.253783249	1.363083765	-0.422135465
N	2.270060144	1.051078032	-0.072757478
F	-1.949338460	-1.587833724	-0.040290935

S2S1-syn

C	-1.919704275	-0.059524755	-0.232833970
O	-1.615370394	1.040910984	-0.549530492
N	-0.971079489	-0.999248282	0.088816751
N	0.330328067	-0.822276816	-0.188645000
N	0.806101342	-1.786950712	0.453148471
F	-3.147394970	-0.528740205	-0.105273753

S2S1-syn-iso

C	-1.958136885	-0.018949081	-0.220944471
O	-1.779075036	1.115401534	-0.547656521
N	-0.972095713	-0.896137591	0.117288369
N	0.384182597	-0.795889273	0.194520576

N	0.899109270	0.275297814	-0.070474988
F	-3.139495690	-0.625511439	-0.153562200

S2S1-anti

C	-1.218500603	0.602669065	-0.451383943
O	-1.028195889	1.750326371	-0.744272618
N	-0.322263832	-0.376625070	-0.063196321
N	-0.708183452	-1.583673438	0.466343803
N	0.385117501	-2.149464539	0.474621789
F	-2.420999599	0.025353321	-0.430720010

S2S1-anti-iso

C	-1.196916317	0.547232507	-0.412955045
O	-0.983063855	1.683667029	-0.716492103
N	-0.337675979	-0.453779755	-0.004424269
N	-0.515008321	-1.752227012	0.353420061
N	-1.650336981	-2.195868048	0.382598354
F	-2.402692582	-0.023108908	-0.371802829

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