Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information:

Dissociative ionization dynamics of C_3F_7CN

M. Rankovič[1], J. Chalabala[2], M. Zawadzki[1,3], J. Kočíšek[1], P. Slavíček[1,2*], J. Fedor[1*]

[1]*J. Heyrovský Institute of Physical Chemistry, Czech Academy of Sciences, Dolejškova 3,* 18223, *Prague, Czech Republic*

[2]*Department of Physical Chemistry, University of Chemistry and Technology, Technicka 5, 16628 Prague, Czech Republic*

[3]*Department of Atomic, Molecular, and Optical Physics, Faculty of Applied Physics and Mathematics, Gdańsk University of Technology, ul. G. Narutowicza 11/12, 80-233 Gdańsk, Poland*

*Corresponding author: petr.slavicek@vscht.cz, juraj.fedor@jh-inst.cas.cz

1. Optimized geometries

All geometries were optimized in Gaussian 09 package with BhandhLYP/6-31g* method. A frequency analysis was always performed for each geometry to confirm stationary point.

Neutral C_3F_7CN

12
scf done: -905.706684

C	0.016305	0.021353	-0.042137
C	0.049406	-0.053531	1.503481
C	1.386305	-0.003559	-0.570445
F	-0.661020	-1.071928	-0.474632
C	-0.733814	1.259656	-0.589473
F	-0.735842	1.210814	-1.910911
F	-1.983177	1.271774	-0.165632
F	-0.134816	2.373958	-0.202858
F	-1.174925	-0.083353	1.994216
F	0.677619	-1.159119	1.866265
F	0.691556	0.988447	2.005341
N	2.454181	-0.018833	-0.979647

Ionized C_3F_7CN

12

scf done: -905.210080

C	0.071285	-0.055495	1.777921
C	0.001004	-0.000962	-0.447418
C	-0.762114	1.307640	-0.727667
F	-0.023715	2.312968	-0.316985
C	1.381461	-0.077710	-0.696596
N	2.531348	-0.111746	-0.814919
F	-0.699059	-1.078585	-0.604227
F	-1.158837	-0.219678	1.974775
F	0.813652	-1.059624	1.933186
F	0.559934	1.073159	2.038542
F	-0.966825	1.379187	-2.017330
F	-1.905291	1.286734	-0.082850

C_3F_4N neutral fragment (Table II in manuscript)

8

scf done: -567.736346

C	-0.057544	0.003316	0.014767
F	0.061002	-0.155187	1.308290
C	1.410382	0.028672	-0.507113
F	1.960457	1.135106	-0.617139
C	2.130614	-1.128299	-0.802639
N	2.679212	-2.116631	-1.041106
F	-0.613258	1.136219	-0.286426
F	-0.662087	-1.006228	-0.540334

C_3F_5N neutral fragment (Table II in manuscript)

9

scf done: -667.962933

C	0.117296	0.106309	1.470603
F	0.102709	-0.091293	0.165115
C	-0.649218	1.391832	1.806151
F	-0.599445	1.574852	3.127004
F	1.363686	0.218553	1.882284
F	-0.452959	-0.920744	2.073566

F -0.038564 2.412132 1.200577
C -2.055576 1.328497 1.369162
N -3.144806 1.270037 1.026622

C_3F_4N cation fragment (Table II in manuscript)

8
scf done: -567.736346
C -0.057544 0.003316 0.014767
F 0.061002 -0.155187 1.308290
C 1.410382 0.028672 -0.507113
F 1.960457 1.135106 -0.617139
C 2.130614 -1.128299 -0.802639
N 2.679212 -2.116631 -1.041106
F -0.613258 1.136219 -0.286426
F -0.662087 -1.006228 -0.540334

C_3F_6N cation fragment (Table II in manuscript, reaction n. 5)

11
scf done: -805.446620
C 0.112229 0.047209 1.474882
C -0.023013 -0.187476 -0.075167
C -0.892796 0.939217 -0.616169
C 1.261089 -0.141536 -0.768482
N 2.260198 -0.087321 -1.324524
F -0.692068 -1.319234 -0.293002
F -1.115876 0.224173 1.932001
F 0.669550 -0.991280 2.009347
F 0.816224 1.135976 1.671142
F -0.535425 2.117982 -0.566028
F -1.993554 0.705210 -1.110584

C_3F_6N cation fragment (Table II in manuscript, reaction n. 6)

11
scf done: -805.428257
C 0.024891 -0.353709 0.046274
F 0.848161 -0.166894 1.035708
F 0.646678 -0.363925 -1.110361

F	-0.939678	0.520121	0.058106
C	-0.555625	-1.787403	0.135445
C	0.354724	-2.945684	0.614985
F	-0.130886	-4.087256	0.220862
C	-1.857924	-2.028344	-0.205650
N	-2.966221	-2.233328	-0.495862
F	0.306138	-2.831053	1.922146
F	1.557706	-2.757328	0.157846

C_3F_3N cation fragment (Table II in manuscript, reaction n. 7)

7

scf done: -467.931986

C	0.176957	-0.290443	0.101192
F	0.209129	-0.117584	1.339697
F	0.878646	0.464186	-0.604077
C	-0.620093	-1.298450	-0.484796
C	-1.409682	-2.149990	0.279773
N	-2.059933	-2.848322	0.936752
F	-0.579872	-1.390208	-1.760997

C_3F_3N cation fragment (Table II in manuscript, reaction n. 8)

7

scf done: -467.849469

C	0.025049	0.145520	0.065556
F	0.197303	0.410237	1.326544
F	1.114932	-0.307085	-0.499115
C	-0.928498	-1.058911	-0.033735
C	-1.337731	-2.245876	0.325348
N	-1.785654	-3.314968	0.580613
F	-0.469789	1.154989	-0.572597

CF_3 cation fragment (Table II in manuscript)

4

scf done: -337.098317

C	0.000000	0.000000	0.090716
F	-0.000001	0.000000	1.317877
F	1.062781	0.000000	-0.522793

F -1.062779 0.000000 -0.522796

CF_3 neutral fragment (Table II in manuscript)

4
scf done: -337.427735
C 0.000564 -0.296402 0.090383
F -0.000216 0.097222 1.339167
F 1.080870 0.101638 -0.533246
F -1.081216 0.097542 -0.533300

CF_4 neutral fragment (Table II in manuscript)

5
scf done: -437.321028
C 0.339992 0.180001 0.360011
F 0.174605 1.481113 0.336837
F 1.415573 -0.111810 1.051919
F -0.704989 -0.383773 0.917631
F 0.474818 -0.265531 -0.866398

2. Potential energy surface

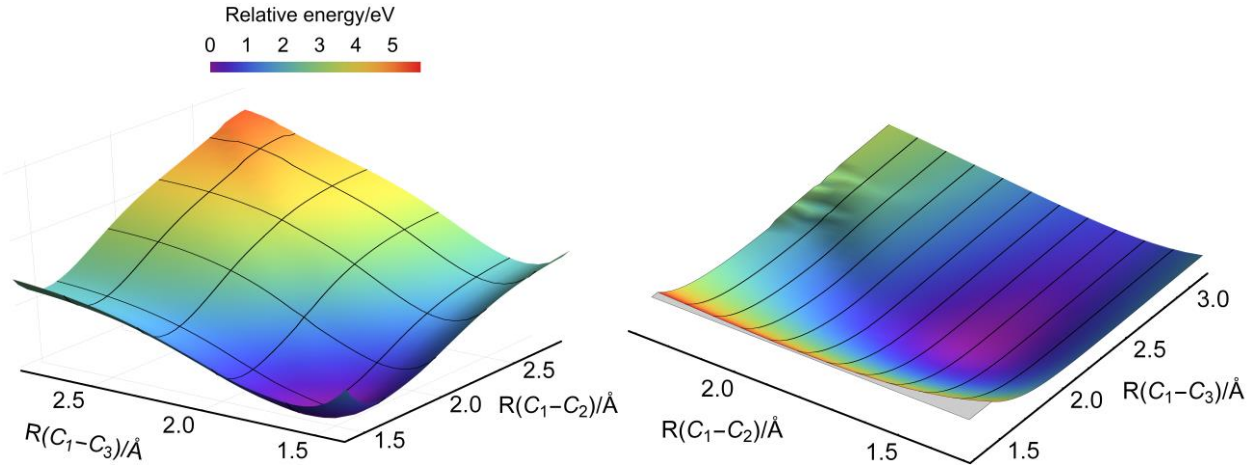

Fig. S1: Ground state, constrained PESs of ionized C_3F_7CN along the C-CF_3 bonds calculated at the FOMO-CASCI(13,8)/6-31g* level using the geometry of a) neutral and b) ionized molecule optimized at the BHandHLYP/6-31g* level.

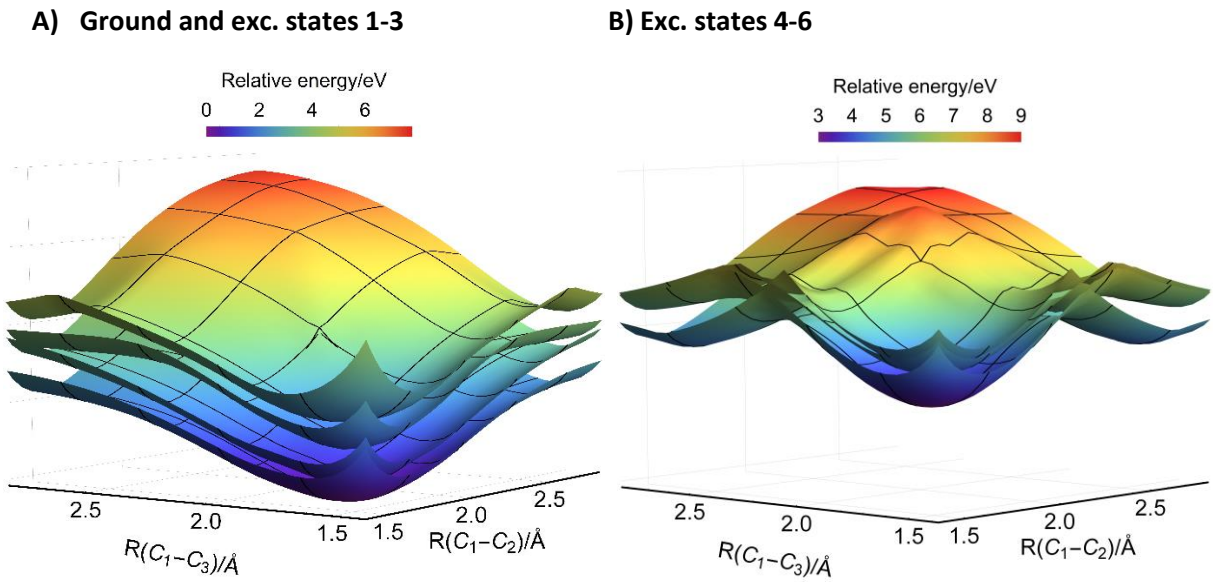

Fig. S2: Constrained PESs of ionized C_3F_7CN along the C-CF_3 bonds calculated at the FOMO-CASCI(13,8)/6-31g* level using the geometry of neutral molecule optimized at the BHandHLYP/6-31g* level. Panel A shows PES of ground and excited state 1-3 and panel B shows PES of excited states 4-6.

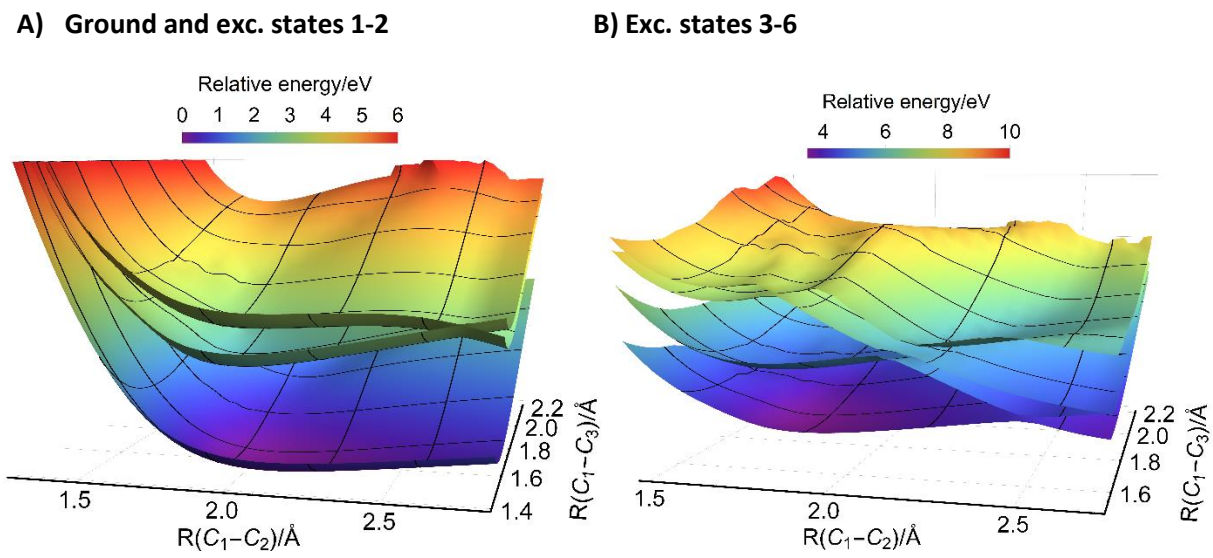

Fig. S3: Constrained PESs of ionized C_3F_7CN along the C-CF_3 bonds calculated at the FOMO-CASCI(13,8)/6-31g* level using the geometry of ionized molecule optimized at the BHandHLYP/6-31g* level. Panel A shows PES of ground and excited states 1-2 and panel B shows PES of excited states 3-6.