Performance of DFT Methods for Describing the $X^- + CH_3ONO_2$ Gas-Phase Reactions with X = F, OH, CH_2CN

Yaicel G. Proenza,[a] Miguel A. F. de Souza,[a,b] Elizete Ventura,[b] Silmar A. do Monte[b] and Ricardo L. Longo[a,*]

[a] *Y. G. Proenza, M. A. F. de Souza, R. L. Longo, Departamento de Química Fundamental, CCEN, Universidade Federal de Pernambuco, 50.740-560, Recife, PE, Brazil*
[b] *E. Ventura, S. A. do Monte, M. A. F. de Souza, Departamento de Química, CCEN, Universidade Federal da Paraíba, 58.059-900, João Pessoa, PB, Brazil*
[*] *Fax: +55 83 21268000, e-mail: longo@ufpe.br*

Electronic Supplementary Information (ESI)

All geometry optimizations and frequency calculations have been performed with the Gaussian 09 program using the MP2/6-311+G(3df,2p) method. All single point calculations were based in these optimized geometries. The benchmark PEPs have been calculated with the ACES-III package using the CCSD(T)/CBS method and for the DFT calculations the aug-cc-pVTZ basis set has been used. In order to gain in clarity and consistency the following notation has been used for the systems and their respective reaction pathways.
(**1**) $F^- + CH_3ONO_2$ system (**2**) $OH^- + CH_3ONO_2$ system (**3**) $CH_2CN^- + CH_3ONO_2$ system
(**a**) $E_{CO}2$ pathway (**b**) S_N2@C pathway (**c**) S_N2@N pathway

Contents

Table S1. The optimized geometry of the reactants and products of the $X^- + CH_3ONO_2$ (X = F, OH, CH_2CN) gas-phase reactions along with the main results of their vibrational analysis, calculated with the MP2/6-311+G(3df,2p) method.

Table S2. The optimized geometry of the reactant complex (RC), transition state (TS) and product complex (PC) for the $E_{CO}2$, S_N2@C and S_N2@N reaction pathways of the $X^- + CH_3ONO_2$ (X = F, OH, CH_2CN) gas-phase reactions along with the main results of their vibrational analysis, calculated with the MP2/6-311+G(3df,2p) method.

Table S3. The absolute energies (in Hartree) of all stationary points for the $E_{CO}2$, $S_N2@C$ and $S_N2@N$ reaction pathways of the $X^- + CH_3ONO_2$ (X = F, OH, CH_2CN) gas-phase reactions, calculated with the CCSD(T)/CBS method, using the aug-cc-pVXZ (X = D, T) basis sets for extrapolation.

Table S4. The absolute energies (in Hartree) of all stationary points for the $E_{CO}2$ and $S_N2@C$ reaction pathways of the $F^- + CH_3ONO_2$ gas-phase reaction, calculated with the nineteen DFT methods using the DFT/aug-cc-pVTZ method.

Table S5. The absolute energies (in Hartree) of all stationary points for the $E_{CO}2$, $S_N2@C$ and $S_N2@N$ reaction pathways of the $OH^- + CH_3ONO_2$ gas-phase reaction, calculated with the nineteen DFT methods using the DFT/aug-cc-pVTZ method.

Table S6. The absolute energies (in Hartree) of all stationary points for the $E_{CO}2$, $S_N2@C$ and $S_N2@N$ reaction pathways of the $CH_2CN^- + CH_3ONO_2$ gas-phase reaction, calculated with the nineteen DFT methods using the DFT/aug-cc-pVTZ method.

Table S7. Barrier heights (in kcal mol^{-1}) for the $E_{CO}2$, $S_N2@C$ and $S_N2@N$ reaction pathways of the $X^- + CH_3ONO_2$ (X = F, OH, CH_2CN) gas-phase reactions obtained from the PEP calculated with the CCSD(T)/CBS and DFT/aug-cc-pVTZ methods at the MP2 geometries. The ZPE corrections are included. The calculated barrier heights are related to the most stable RC found for each one of the systems.

Table S8. Relative barrier heights (in kcal mol^{-1}) between the $E_{CO}2$, $S_N2@C$ and $S_N2@N$ reaction pathways of the $X^- + CH_3ONO_2$ (X = F, OH, CH_2CN) gas-phase reactions, obtained from the PEP calculated with the CCSD(T)/CBS and DFT/aug-cc-pVTZ methods at the MP2 geometries. All differences (in kcal mol^{-1}) are related to the $E_{CO}2$ channel.

Table S9. Energies relative to the reactants (in kcal mol^{-1}) of all stationary points for the $E_{CO}2$, $S_N2@C$ and $S_N2@N$ reaction pathways of the $X^- + CH_3ONO_2$ (X = F, OH) gas-phase reactions, calculated with the CCSD(T)/CBS method using the aug-cc-pVXZ (X = T, Q) basis sets for extrapolation. The errors (in kcal mol^{-1}) related to the PEP calculated with X = D, T for extrapolations are presented in parenthesis.

Table S10. Energies relative to reactants (in kcal mol^{-1}) of all stationary points for the $E_{CO}2$ and $S_N2@C$ reaction pathways of the $F^- + CH_3ONO_2$ gas-phase reaction, calculated with the functionals M08-SO, CAM-B3LYP, B2PLYP and B2GPPLYP using the DFT/aug-cc-pVQZ method. The errors (in kcal mol^{-1}) related to the results obtained with the aug-cc-pVTZ basis sets are presented in parenthesis.

Table S11. Energies relative to reactants (in kcal mol^{-1}) of all stationary points for the $E_{CO}2$, $S_N2@C$ and $S_N2@N$ reaction pathways of the $OH^- + CH_3ONO_2$ gas-phase reaction, calculated with the functionals M08-SO, CAM-B3LYP, B2PLYP and B2GPPLYP using the DFT/aug-cc-pVQZ method. The errors (in kcal mol^{-1}) related to the results obtained with the aug-cc-pVTZ basis sets are presented in parenthesis.

Table S1. The optimized geometry of the reactants and products of the $X^- + CH_3ONO_2$ (X = F, OH, CH_2CN) gas-phase reactions along with the main results of their vibrational analysis, calculated with the MP2/6-311+g(3df,2p) method. Geometries from Cartesian coordinates in Å, Electronic energies in Hartree particle^{-1} and Frequencies in cm^{-1}.

CH_3ONO_2				
Geometry (x, y, z)				Frequencies
C	-1.010721	-0.134056	0.000014	146.2759
H	-1.721897	-0.953458	0.000247	230.0050
H	-1.129003	0.475709	-0.891369	354.2980
H	-1.129026	0.476241	0.891028	594.4990
O	0.256273	-0.799414	0.000221	687.7712
N	1.335862	0.092947	0.000042	782.9660
O	1.075723	1.274336	-0.000319	872.2084
O	2.401519	-0.466269	0.000123	1065.5725
				1190.0076
Zero-point correction			0.055363	1209.4102
Sum of electronic and zero-point Energies			-319.642243	…

NO_2CHCN^-				
Geometry (x, y, z)				Frequencies
N	0.891106	0.041667	-0.000088	135.0804
O	2.032267	-0.497761	0.000346	174.4451
O	0.754954	1.291188	-0.000178	443.4495
C	-0.209182	-0.767402	-0.000381	515.5659
H	-0.026177	-1.826175	-0.000273	536.3920
C	-1.494555	-0.222171	-0.000366	545.4295
N	-2.611513	0.160354	0.000440	745.1005
				768.2377
				1015.0884
Zero-point correction			0.036000	1115.1894
Sum of electronic and zero-point Energies			-336.126406	…

OH^-				
Geometry (x, y, z)				Frequencies
O	-3.369439	0.041091	0.000379	3836.1453
H	-3.749287	0.926825	0.000468	
Zero-point correction			0.008739	
Sum of electronic and zero-point Energies			-75.679622	

HF				
Geometry (x, y, z)				Frequencies
F	0.328899	0.309971	-0.012175	4163.7408
H	-0.589009	0.309971	-0.012175	
Zero-point correction			0.009486	
Sum of electronic and zero-point Energies			-100.319952	

H_2O				
Geometry (x, y, z)				Frequencies
H	-2.355177	-0.246882	-0.235168	1623.5176
O	-2.288501	-1.090234	0.216307	3857.8047
H	-1.347287	-1.271032	0.247084	3985.8918
Zero-point correction			0.021568	
Sum of electronic and zero-point Energies			-76.296717	

NO_2^-				
Geometry (x, y, z)				Frequencies
N	0.684536	-0.998246	0.154399	800.3849
O	1.108809	0.169505	-0.058305	1323.8665
O	1.549051	-1.915582	0.156232	1386.9049
Zero-point correction			0.007999	
Sum of electronic and zero-point Energies			-204.849430	

Table S1. Continue…

CH_2CN^-					CH_3F				
Geometry (x, y, z)				Frequencies	Geometry (x, y, z)				Frequencies
C	-0.014072	-1.215388	-0.018161	383.6248	F	0.332304	0.309957	-0.012175	1080.9983
H	0.335266	-1.711832	0.879516	424.6477	C	-1.050942	0.309976	-0.012175	1220.5090
H	0.233306	-1.697904	-0.956320	545.2378	H	-1.400553	0.793096	0.896461	1220.5136
C	0.000262	0.178366	-0.008361	1045.5715	H	-1.400553	0.855302	-0.884896	1511.6227
N	-0.047613	1.368258	0.003326	1047.4834	H	-1.400531	-0.718476	-0.048089	1528.3899
Zero-point correction			0.030418	1432.6367	Zero-point correction			0.040031	1528.3945
Sum of electronic and zero-point Energies			-131.849122	2094.8948	Sum of electronic and zero-point Energies			-139.485186	3092.2707
				…					…

CH_2O					ONO_2^-				
Geometry (x, y, z)				Frequencies	Geometry (x, y, z)				Frequencies
C	-0.758634	1.632500	0.281142	1199.6858	O	0.498379	-0.964949	0.009262	714.7561
H	0.085143	2.338741	0.282022	1275.3763	N	1.095316	0.141403	-0.001420	714.7608
H	-0.821441	0.937427	1.131826	1547.1719	O	0.435608	1.211547	-0.007797	850.4948
O	-1.575874	1.620815	-0.609970	1768.2253	O	2.351952	0.177612	-0.005755	1082.0945
Zero-point correction			0.026933	2977.4792	Zero-point correction			0.014453	1490.9423
Sum of electronic and zero-point Energies			-114.279462	3054.1574	Sum of electronic and zero-point Energies			-279.952168	1490.9436

CH_3OH					CH_3CN				
Geometry (x, y, z)				Frequencies	Geometry (x, y, z)				Frequencies
C	-2.536875	-0.813559	-0.000514	288.7855	C	1.182164	-0.000175	-0.000162	361.4040
H	-3.614423	-0.944572	-0.006079	1067.4787	H	1.553288	-0.495885	0.893338	361.4168
H	-2.124678	-1.295375	-0.888454	1096.2297	H	1.553519	-0.526192	-0.876048	933.1098
H	-2.133300	-1.299878	0.888933	1192.9502	H	1.553664	1.021329	-0.017598	1064.9052
O	-2.298394	0.584548	0.004195	1375.2210	C	-0.275008	-0.000137	-0.000507	1064.9611
H	-1.351130	0.730823	0.008665	1499.9796	N	-1.443228	0.000260	0.000577	1421.6294
Zero-point correction			0.052098	1528.3100	Zero-point correction			0.045342	1497.9443
Sum of electronic and zero-point Energies			-115.461777	1538.3986	Sum of electronic and zero-point Energies			-132.440312	1497.9599
				…					…

Table S1. Continue…

CH_3CH_2CN				
Geometry (x, y, z)				Frequencies
C	-1.53840	-0.45780	0.00000	205.4384
H	-1.43080	-1.08560	0.88160	228.1613
H	-2.53800	-0.02880	0.00000	379.2225
H	-1.43080	-1.08560	-0.88160	537.4738
C	-0.49270	0.65810	0.00000	791.5178
H	-0.60770	1.29470	-0.87740	851.9561
H	-0.60770	1.29470	0.87740	1037.1906
C	0.86630	0.12280	0.00000	1103.1056
N	1.94350	-0.33260	0.00000	1120.3093
				1300.0880
Zero-point correction			0.074665	1355.8285
Sum of electronic and zero-point Energies			-171.629350	…

Table S2. The optimized geometry of the reactant complex (RC), transition state (TS) and product complex (PC) for the $E_{CO}2$, $S_N2@C$ and $S_N2@N$ reaction pathways of the $X^- + CH_3ONO_2$ (X = F, OH, CH_2CN) gas-phase reactions along with the main results of their vibrational analysis, calculated with the MP2/6-311+g(3df,2p) method. Geometries from Cartesian coordinates in Å, Electronic energies in Hartree particle^{-1} and Frequencies in cm^{-1}.

1ab-RC

Geometry (x, y, z)				Frequencies
N	1.35914	-0.08147	-0.00001	71.5970
O	0.05681	-0.47359	0.00007	77.9170
O	1.61573	1.10939	-0.00003	154.5328
O	2.15200	-1.00599	-0.00003	226.2499
C	-0.90789	0.61115	0.00003	395.7411
H	-0.74798	1.21804	-0.88923	401.8236
H	-1.92883	0.12762	0.00000	602.2572
H	-0.74805	1.21804	0.88931	716.3509
F	-3.47089	-0.29986	-0.00004	802.5522
Zero-point correction			0.055296	932.3465
Sum of electronic and zero-point Energies			-419.411646	994.2254
				…

1a-TS

Geometry (x, y, z)				Frequencies
N	1.40569	-0.25006	0.00000	-703.0446
F	-3.21318	1.05379	0.00000	73.2998
O	0.00000	0.45921	0.00000	82.0870
O	1.40098	-1.45802	0.00000	163.8899
O	2.34940	0.51087	0.00000	230.5747
C	-1.06204	-0.38758	0.00000	383.5976
H	-1.12435	-1.00825	0.90163	440.6119
H	-2.30333	0.51181	0.00000	581.5082
H	-1.12435	-1.00825	-0.90163	731.9489
Zero-point correction			0.049226	734.7711
Sum of electronic and zero-point Energies			-419.401095	924.8027
				…

1b-TS

Geometry (x, y, z)				Frequencies
N	1.31616	0.06486	-0.00001	-568.0413
O	0.38811	-0.85773	-0.00017	67.6299
O	0.98470	1.25103	0.00022	135.8556
O	2.48412	-0.33030	-0.00010	170.0622
C	-1.25363	-0.28707	-0.00004	307.8394
H	-1.22301	0.26260	-0.91889	345.7449
H	-1.62699	-1.29174	-0.00022	395.0517
H	-1.22298	0.26226	0.91903	723.3298
F	-3.16376	0.17014	0.00008	756.1566
Zero-point correction			0.055173	827.0892
Sum of electronic and zero-point Energies			-419.398630	1033.7694
				…

1a-PC

Geometry (x, y, z)				Frequencies
N	-1.88986	0.21610	-0.15151	46.7739
O	1.16989	0.58583	-0.59979	71.9112
O	-0.83075	-0.30872	0.42840	118.2120
O	-2.83400	-0.54981	-0.20731	202.4167
C	0.37669	0.75942	0.40035	293.5315
H	0.77502	0.52353	1.39956	338.5142
H	2.28221	-0.14908	-0.26362	435.1941
H	-0.21130	1.68834	0.40653	593.9389
F	3.12020	-0.66115	0.01617	827.8606
Zero-point correction			0.052526	1051.3395
Sum of electronic and zero-point Energies			-419.494722	1180.1620
				…

Table S2. Continue….

1b-PC				
Geometry (x, y, z)				Frequencies
N	-1.52298	0.01883	0.00024	16.1139
O	-0.78136	-0.99975	0.00193	68.7811
O	-1.00423	1.16552	0.00202	74.6329
O	-2.76837	-0.11027	-0.00328	108.0333
C	1.99374	-0.20574	0.00131	122.8911
H	1.36249	0.67459	-0.00030	127.2542
H	1.80653	-0.79540	0.89170	717.1392
H	1.80312	-0.80103	-0.88458	718.6147
F	3.35089	0.17561	-0.00242	850.0533
				997.7418
				1082.9641
Zero-point correction			0.055474	1176.5434
Sum of electronic and zero-point Energies			-419.451786	…

2ab-RC				
Geometry (x, y, z)				Frequencies
C	0.88467	0.58101	0.00089	39.0387
H	1.88305	0.07884	0.00152	61.7404
H	0.73724	1.18755	0.89141	79.6681
H	0.73821	1.18707	-0.89012	154.3579
O	-0.09132	-0.49396	0.00064	191.1901
N	-1.38802	-0.08687	-0.00014	224.3204
O	-1.63000	1.10683	-0.00062	366.6625
O	-2.19136	-1.00223	-0.00025	386.0298
O	3.56893	-0.19202	0.00108	604.6193
H	4.23956	-0.88102	0.00364	716.2522
				802.4143
Zero-point correction			0.064904	935.5945
Sum of electronic and zero-point Energies			-395.357034	…

2c-RC				
Geometry (x, y, z)				Frequencies
C	1.47732	0.01972	-0.07096	36.8356
H	1.65789	-0.39774	-1.05992	67.8928
H	2.38367	-0.01578	0.52718	158.7613
H	1.08428	1.06668	-0.09683	169.8640
O	0.60550	-0.88648	0.67000	191.3245
N	-0.59483	-1.10279	0.07238	277.2198
O	-1.35899	-1.77471	0.74349	339.6621
O	-0.78199	-0.65068	-1.03852	365.1124
O	1.03378	2.77359	0.10425	603.6883
H	0.44173	3.48296	-0.16341	710.4600
				792.6098
Zero-point correction			0.065069	929.2276
Sum of electronic and zero-point Energies			-395.353543	…

2a-TS				
Geometry (x, y, z)				Frequencies
C	-0.95675	0.47375	0.00508	-1052.2445
H	-2.16795	-0.23792	0.01866	57.4754
H	-0.81480	1.09035	-0.88768	67.0027
H	-0.80641	1.10984	0.88267	77.3871
O	0.08451	-0.53849	0.01129	158.5872
N	1.38622	-0.09928	0.00029	294.4694
O	1.60855	1.09753	-0.01395	427.9902
O	2.21359	-0.99883	0.00627	523.4520
O	-3.25014	-0.80784	0.03007	592.2866
H	-3.03501	-1.74476	0.03936	616.0502
				709.8605
Zero-point correction			0.060359	801.4538
Sum of electronic and zero-point Energies			-395.355532	…

Table S2. Continue….

2b-TS					**2c-TS**				
Geometry (x, y, z)				Frequencies	Geometry (x, y, z)				Frequencies
C	1.19391	-0.30554	-0.00019	-555.4854	C	1.62158	-0.29051	-0.33157	-282.3855
H	1.61579	-1.29221	-0.00020	68.8961	H	1.74254	-0.96873	-1.17785	149.2516
H	1.20588	0.24657	0.91833	100.6318	H	2.49539	-0.34453	0.31723	203.2843
H	1.20572	0.24653	-0.91874	128.9857	H	1.42378	0.73788	-0.64699	222.0726
O	-0.40407	-0.85678	-0.00001	186.9867	O	0.54157	-0.68337	0.49879	251.4172
N	-1.32509	0.08118	0.00004	294.8653	N	-0.71485	-0.40691	-0.16712	275.9695
O	-0.97987	1.26154	-0.00004	318.3116	O	-1.64152	-0.42086	0.61651	364.7267
O	-2.49330	-0.30681	0.00018	362.7171	O	-0.73004	-0.61825	-1.36176	501.9810
O	3.29801	0.06209	-0.00038	545.1424	O	-0.26715	1.77293	-0.28228	523.5835
H	3.49313	1.00522	-0.00060	724.3560	H	-0.66312	1.95556	0.57707	609.8758
Zero-point correction			0.065044	754.7872	Zero-point correction			0.065265	654.6779
Sum of electronic and zero-point Energies			-395.346509	822.7419	Sum of electronic and zero-point Energies			-395.346139	825.7144
				…					…

2a-PC					**2bc-PC**				
Geometry (x, y, z)				Frequencies	Geometry (x, y, z)				Frequencies
C	-0.73304	1.63675	0.28571	68.0774	C	-2.55643	-0.79012	-0.02895	25.6031
H	-2.34470	-0.26201	-0.21305	88.4213	H	-3.63499	-0.94155	0.04707	47.4800
H	0.11015	2.33948	0.25576	118.5416	H	-2.22427	-1.16187	-1.00374	80.1621
H	-0.79809	0.98981	1.16842	141.7125	H	-2.05711	-1.38972	0.73536	111.6607
O	-1.61781	1.66326	-0.55919	161.9053	O	0.58754	-0.96749	0.34752	153.9267
N	0.65914	-1.01750	0.17648	175.7190	N	1.11779	0.11978	0.02181	211.6479
O	1.05306	0.15323	-0.12477	186.4835	O	0.37874	1.12300	-0.20993	719.6276
O	1.53407	-1.90898	0.22074	314.4285	O	2.35653	0.22864	-0.07943	726.9727
O	-2.27600	-1.15247	0.15268	515.3184	O	-2.30754	0.58477	0.12789	846.3164
H	-1.30614	-1.26455	0.20279	545.7532	H	-1.33780	0.72216	0.04343	862.5748
Zero-point correction			0.063992	591.7385	Zero-point correction			0.068482	1086.0068
Sum of electronic and zero-point Energies			-395.461227	772.7732	Sum of electronic and zero-point Energies			-395.437491	1108.4327
				…					…

Table S2. Continue….

3a-RC

Geometry (x, y, z)				Frequencies
C	0.09250	0.10850	0.00000	37.4387
H	0.90910	-0.61160	0.00000	50.6624
H	0.11540	0.72820	0.88940	54.0547
H	0.11540	0.72820	-0.88930	101.1293
O	-1.09810	-0.72580	0.00000	120.3063
N	-2.26910	-0.02480	0.00000	166.8248
O	-3.25860	-0.73060	0.00000	172.9936
O	-2.21770	1.18940	0.00000	288.6250
C	3.40890	-1.14920	0.00000	366.7386
H	3.80300	-1.56910	-0.91800	420.4473
H	3.80300	-1.56910	0.91800	465.7411
C	3.16200	0.21950	0.00000	554.0459
N	2.82180	1.36140	0.00000	602.9392
				711.2810
Zero-point correction			0.087326	798.3902
Sum of electronic and zero-point Energies			-451.514484	…

3b-RC

Geometry (x, y, z)				Frequencies
C	-0.08530	0.09700	-0.00020	36.6459
H	-0.88090	-0.64290	-0.00030	47.5083
H	-0.12510	0.71630	-0.88890	51.1763
H	-0.12540	0.71640	0.88850	97.1955
O	1.12890	-0.70470	0.00000	110.6317
N	2.27890	0.03070	-0.00010	160.7802
O	3.28880	-0.64530	0.00020	188.9710
O	2.19150	1.24290	-0.00040	269.1792
C	-3.18190	1.17520	0.00020	364.8371
H	-3.48590	1.66430	0.91860	421.8685
H	-3.49040	1.66470	-0.91640	466.2543
C	-3.21440	-0.21490	0.00010	556.5051
N	-3.11840	-1.40300	0.00010	601.1030
				709.3666
Zero-point correction			0.087265	798.4036
Sum of electronic and zero-point Energies			-451.513728	…

3c-RC

Geometry (x, y, z)				Frequencies
C	-0.05670	-0.74650	-0.07500	35.9086
H	-0.54800	-1.46460	-0.71910	45.9485
H	-0.55690	0.21700	-0.14220	48.1313
H	-0.02330	-1.11150	0.94530	97.2887
O	1.28850	-0.67370	-0.62660	127.8069
N	2.12470	0.15560	0.06630	157.2873
O	3.23680	0.23600	-0.41800	195.7096
O	1.69920	0.70230	1.06240	253.7930
C	-2.98040	1.29410	-0.46290	354.7905
H	-3.13090	2.10800	0.23610	421.6979
H	-3.39430	1.43390	-1.45420	443.7619
C	-3.02690	0.00690	0.05780	554.4348
N	-2.94740	-1.10240	0.48700	601.8904
				705.0682
Zero-point correction			0.087220	794.7878
Sum of electronic and zero-point Energies			-451.513322	…

3a-TS

Geometry (x, y, z)				Frequencies
C	-0.06750	0.69210	-0.00010	-1118.7060
H	1.26490	-0.10780	0.00010	15.3913
H	-0.22350	1.31170	0.88950	38.8075
H	-0.22340	1.31140	-0.88990	48.9488
O	-1.02220	-0.37520	0.00000	88.8012
N	-2.38280	-0.02750	-0.00010	161.3040
O	-3.13460	-0.98740	0.00000	278.4114
O	-2.68330	1.14880	-0.00020	311.0619
C	2.33420	-0.89050	0.00020	392.2095
H	2.26970	-1.51280	-0.89230	446.9695
H	2.26970	-1.51260	0.89280	479.8425
C	3.53330	-0.11260	0.00010	480.9017
N	4.46320	0.61130	0.00000	562.0666
				651.8345
Zero-point correction			0.080750	761.0729
Sum of electronic and zero-point Energies			-451.492648	…

Table S2. Continue….

3b-TS				
Geometry (x, y, z)				Frequencies
C	0.30400	0.09180	0.32880	-618.9478
H	0.83780	-0.71310	0.80190	22.1410
H	0.04910	0.96300	0.90130	51.7769
H	0.40250	0.20330	-0.73460	72.1536
O	-1.20790	-0.73360	0.39940	116.1811
N	-2.22870	-0.05010	-0.07300	185.6453
O	-3.32630	-0.60090	-0.01270	249.2867
O	-2.03320	1.07350	-0.53610	292.9802
C	2.45290	1.04040	0.30510	360.1533
H	2.43080	1.85750	-0.41120	403.3972
H	2.68620	1.36790	1.31530	470.8576
C	3.19970	-0.07500	-0.11690	542.3493
N	3.71350	-1.08330	-0.46690	708.9986
Zero-point correction			0.086544	722.9788
Sum of electronic and zero-point Energies			-451.499744	749.4590
				…

3c-TS				
Geometry (x, y, z)				Frequencies
C	-0.29690	1.79940	-0.10630	-331.2208
H	-0.08710	2.51910	-0.89460	43.2219
H	0.62690	1.32910	0.23100	70.8681
H	-0.81320	2.28250	0.72270	152.5346
O	-1.11840	0.82580	-0.73160	189.5710
N	-1.27480	-0.31730	0.12280	228.4630
O	-1.77690	-1.25670	-0.46460	254.2121
O	-1.26190	-0.09450	1.32260	334.0931
C	1.05610	-1.07810	-0.25930	382.3426
H	0.80090	-1.86720	0.43840	400.2783
H	0.80300	-1.26940	-1.29510	450.9273
C	2.26920	-0.41880	-0.03020	548.2731
N	3.24010	0.23080	0.18590	574.6983
Zero-point correction			0.086715	635.8603
Sum of electronic and zero-point Energies			-451.505091	656.2020
				…

3a-PC				
Geometry (x, y, z)				Frequencies
C	-2.03160	1.61980	-0.09750	35.0143
H	0.90160	0.91860	-0.21020	38.7275
H	-2.69990	1.60960	0.77380	50.7082
H	-2.30370	0.95330	-0.92250	66.6614
O	-1.09060	2.39190	-0.16680	75.0986
N	-1.53400	-1.29880	-0.29320	83.6785
O	-0.97790	-2.41770	-0.23300	95.0925
O	-1.46210	-0.58580	0.75620	115.1508
C	1.38140	-0.04630	-0.05900	131.0180
H	1.10790	-0.71190	-0.87410	141.3797
H	0.98100	-0.48330	0.85290	285.6902
C	2.82790	0.10650	0.01030	386.2369
N	3.98990	0.23110	0.06550	391.4718
Zero-point correction			0.083869	495.6381
Sum of electronic and zero-point Energies			-451.607803	807.8719
				…

3b-PC				
Geometry (x, y, z)				Frequencies
C	1.20250	1.27740	0.03630	7.7956
H	1.61810	1.82600	-0.80870	19.8133
H	0.11430	1.33160	0.00900	49.1503
H	1.56950	1.73770	0.95340	71.6730
O	-2.14360	1.11020	-0.04660	76.4168
N	-2.27740	-0.14080	-0.00720	120.4316
O	-3.41430	-0.65320	0.07370	229.3191
O	-1.25180	-0.87400	-0.04960	270.2820
C	1.60660	-0.19530	-0.02600	394.5053
H	1.16210	-0.74210	0.80390	550.9787
H	1.20420	-0.65760	-0.92590	716.5236
C	3.05700	-0.37330	-0.00080	720.2316
N	4.22200	-0.48950	0.02030	789.0280
Zero-point correction			0.089879	850.3357
Sum of electronic and zero-point Energies			-451.604478	850.8935
				…

Table S2. Continue….

3c-PC				
Geometry (x, y, z)				Frequencies
C	2.32320	-0.67020	0.55770	35.8602
H	2.36390	0.39050	0.30510	49.1102
H	3.32910	-1.02750	0.77400	70.2054
H	1.70720	-0.78330	1.45160	109.1568
O	1.82850	-1.44730	-0.52230	119.7632
N	-0.27770	1.09970	-0.04230	134.5342
O	0.45180	1.92010	-0.65790	165.1827
O	-0.43600	1.15890	1.20000	173.8636
C	-0.87980	0.09650	-0.76390	438.6210
H	-0.79730	0.17270	-1.83400	510.3542
H	0.93850	-1.10820	-0.70740	531.8802
C	-1.80920	-0.74620	-0.14110	546.9655
N	-2.59390	-1.49660	0.31900	613.3226
				750.2493
				770.4494
				…
Zero-point correction			0.089620	
Sum of electronic and zero-point Energies			-451.603402	

Table S3. The absolute energies (in Hartree) of all stationary points for the $E_{CO}2$, S_N2@C and S_N2@N reaction pathways of the $X^- + CH_3ONO_2$ (X = F, OH, CH_2CN) gas-phase reactions, calculated with the CCSD(T)/CBS method, using the aug-cc-pVXZ (X = D, T) basis sets for the extrapolation.

	X = F		X = OH			X = CH_2CN		
	a	b	a	b	c	a	b	c
R	-419.7030		-395.6555			-451.8977		
RC	-419.7408		-395.6910		-395.6877	-451.9227	-451.9221	-451.9214
TS	-419.7260	-419.7296	-395.6863	-395.6828	-395.6794	-451.8947	-451.9090	-451.9101
PC	-419.8249	-419.7830	-395.7969	-395.7768		-452.0140	-452.0143	-452.0109
P	-419.7689	-419.7674	-395.7536	-395.7504		-451.9721	-451.9905	-451.9937

Table S4. The absolute energies (in Hartree) of all stationary points for the $E_{CO}2$ and $S_N2@C$ reaction pathways of the F^- + CH_3ONO_2 gas-phase reaction, calculated with the nineteen DFT methods using the DFT/aug-cc-pVTZ method.

Method	R	ab-RC	a-TS	b-TS	a-PC	b-PC	a-P	b-P
B3LYP	-420.0339	-420.0704	-420.0598	-420.0615	-420.1490	-420.1115	-420.0975	-420.0992
PBE0	-419.7730	-419.8116	-419.7996	-419.8003	-419.8877	-419.8526	-419.8269	-419.8395
BMK	-419.9923	-420.0300	-420.0120	-420.0190	-420.1131	-420.0760	-420.0599	-420.0630
B97-K	-420.0631	-420.0998	-420.0809	-420.0895	-420.1805	-420.1460	-420.1306	-420.1323
B97-3	-420.0845	-420.1200	-420.1066	-420.1085	-420.1979	-420.1640	-420.1479	-420.1521
M05	-420.0215	-420.0586	-420.0423	-420.0452	-420.1344	-420.1001	-420.0791	-420.0862
M05-2X	-420.1556	-420.1938	-420.1768	-420.1867	-420.2803	-420.2426	-420.2169	-420.2266
M06	-419.9955	-420.0337	-420.0199	-420.0211	-420.1113	-420.0744	-420.0558	-420.0600
M06-2X	-420.0462	-420.0851	-420.0713	-420.0743	-420.1716	-420.1330	-420.1113	-420.1171
M08-HX	-420.0523	-420.0911	-420.0733	-420.0790	-420.1707	-420.1360	-420.1152	-420.1199
M08-SO	-419.9228	-419.9614	-419.9429	-419.9499	-420.0422	-420.0068	-419.9888	-419.9909
MPW1K	-420.0375	-420.0758	-420.0565	-420.0632	-420.1547	-420.1214	-420.0962	-420.1091
BB1K	-420.0220	-420.0585	-420.0396	-420.0468	-420.1375	-420.1047	-420.0839	-420.0923
MPW1B95	-420.0615	-420.0987	-420.0843	-420.0881	-420.1764	-420.1421	-420.1206	-420.1287
CAM-B3LYP	-420.0809	-420.1189	-420.1018	-420.1080	-420.1987	-420.1608	-420.1409	-420.1471
ωB97X	-420.1066	-420.1452	-420.1232	-420.1332	-420.2219	-420.1878	-420.1636	-420.1721
ωB97X-D	-420.0769	-420.1143	-420.0970	-420.1020	-420.1913	-420.1566	-420.1362	-420.1424
B2PLYP	-419.9581	-419.9945	-419.9820	-419.9853	-420.0746	-420.0350	-420.0217	-420.0212
B2GPPLYP	-419.8810	-419.9178	-419.9025	-420.0615	-419.9986	-419.9594	-419.9445	-419.9450

Table S5. The absolute energies (in Hartree) of all stationary points for the $E_{CO}2$, $S_N2@C$ and $S_N2@N$ reaction pathways of the OH^- + CH_3ONO_2 gas-phase reaction, calculated with the nineteen DFT methods using the DFT/aug-cc-pVTZ method.

Method	R	ab-RC	c-RC	a-TS	b-TS	c-TS	a-PC	bc-PC	a-P	bc-P
B3LYP	-395.9750	-396.0093	-396.0065	-396.0061	-396.0031	-395.9988	-396.1127	-396.0937	-396.0742	-396.0722
PBE0	-395.7265	-395.7629	-395.7599	-395.7623	-395.7549	-395.7522	-395.8580	-395.8500	-395.8159	-395.8265
BMK	-395.9321	-395.9679	-395.9642	-395.9635	-395.9596	-395.9558	-396.0760	-396.0581	-396.0369	-396.0362
B97-K	-396.0075	-396.0427	-396.0394	-396.0376	-396.0348	-396.0282	-396.1500	-396.1322	-396.1118	-396.1102
B97-3	-396.0308	-396.0643	-396.0612	-396.0616	-396.0557	-396.0512	-396.1667	-396.1526	-396.1303	-396.1318
M05	-395.9547	-395.9901	-395.9873	-395.9836	-395.9796	-395.9766	-396.0893	-396.0759	-396.0470	-396.0520
M05-2X	-396.0935	-396.1306	-396.1273	-396.1274	-396.1257	-396.1206	-396.2343	-396.2218	-396.1901	-396.1974
M06	-395.9339	-395.9700	-395.9671	-395.9666	-395.9607	-395.9620	-396.0735	-396.0565	-396.0289	-396.0317
M06-2X	-395.9886	-396.0260	-396.0229	-396.0253	-396.0180	-396.0165	-396.1324	-396.1177	-396.0884	-396.0925
M08-HX	-395.9973	-396.0353	-396.0319	-396.0321	-396.0263	-396.0250	-396.1417	-396.1258	-396.0978	-396.1008
M08-SO	-395.8661	-395.9034	-395.9002	-395.8993	-395.8945	-395.8928	-396.0107	-395.9923	-395.9669	-395.9677
MPW1K	-395.9814	-396.0179	-396.0145	-396.0156	-396.0082	-396.0034	-396.1156	-396.1100	-396.0769	-396.0877
BB1K	-395.9568	-395.9915	-395.9881	-395.9878	-395.9826	-395.9781	-396.0919	-396.0823	-396.0550	-396.0610
MPW1B95	-395.9955	-396.0308	-396.0276	-396.0281	-396.0231	-396.0201	-396.1303	-396.1185	-396.0903	-396.0959
CAM-B3LYP	-396.0172	-396.0535	-396.0502	-396.0494	-396.0448	-396.0411	-396.1553	-396.1402	-396.1141	-396.1166
ωB97X	-396.0477	-396.0846	-396.0812	-396.0786	-396.0746	-396.0712	-396.1859	-396.1721	-396.1412	-396.1468
ωB97X-D	-396.0198	-396.0552	-396.0520	-396.0515	-396.0457	-396.0421	-396.1569	-396.1427	-396.1148	-396.1186
B2PLYP	-395.9013	-395.9357	-395.9325	-395.9308	-395.9291	-395.9253	-396.0399	-396.0189	-395.9991	-395.9957
B2GPPLYP	-395.8261	-395.8610	-395.8577	-395.8555	-395.8535	-395.8495	-395.9652	-395.9456	-395.9238	-395.9218

Table S6. The absolute energies (in Hartree) of all stationary points for the $E_{CO}2$, $S_N2@C$ and $S_N2@N$ reaction pathways of the CH_2CN^- + CH_3ONO_2 gas-phase reaction, calculated with the nineteen DFT methods using the DFT/aug-cc-pVTZ method.

Method	R	a-RC	b-RC	c-RC	a-TS	b-TS	c-TS	a-PC	b-PC	c-PC	a-P	b-P	c-PC
B3LYP	-452.2984	-452.3193	-452.3189	-452.3181	-452.2962	-452.3085	-452.3091	-452.4077	-452.4069	-452.4042	-452.3720	-452.3874	-452.3951
PBE0	-452.0149	-452.0380	-452.0375	-452.0367	-452.0156	-452.0255	-452.0274	-452.1139	-452.1265	-452.1216	-452.0744	-452.1051	-452.1101
BMK	-452.2512	-452.2744	-452.2739	-452.2731	-452.2474	-452.2603	-452.2618	-452.3676	-452.3685	-452.3646	-452.3295	-452.3471	-452.3539
B97-K	-452.3740	-452.3970	-452.3965	-452.3957	-452.3696	-452.3834	-452.3821	-452.4899	-452.4905	-452.4842	-452.4521	-452.4692	-452.4733
B97-3	-452.3852	-452.4063	-452.4059	-452.4051	-452.3821	-452.3927	-452.3932	-452.4922	-452.4971	-452.4921	-452.4570	-452.4775	-452.4828
M05	-452.2615	-452.2844	-452.2841	-452.2834	-452.2562	-452.2686	-452.2713	-452.3678	-452.3724	-452.3648	-452.3273	-452.3503	-452.3522
M05-2X	-452.4572	-452.4830	-452.4830	-452.4827	-452.4510	-452.4708	-452.4715	-452.5686	-452.5758	-452.5729	-452.5246	-452.5513	-452.5588
M06	-452.2448	-452.2687	-452.2685	-452.2679	-452.2427	-452.2540	-452.2605	-452.3540	-452.3549	-452.3541	-452.3112	-452.3317	-452.3402
M06-2X	-452.3350	-452.3610	-452.3612	-452.3611	-452.3328	-452.3465	-452.3502	-452.4480	-452.4516	-452.4500	-452.4042	-452.4263	-452.4350
M08-HX	-452.3588	-452.3853	-452.3851	-452.3845	-452.3569	-452.3689	-452.3736	-452.4729	-452.4774	-452.4736	-452.4291	-452.4528	-452.4589
M08-SO	-452.1790	-452.2042	-452.2054	-452.2052	-452.1753	-452.1896	-452.1937	-452.2956	-452.2963	-452.2920	-452.2520	-452.2715	-452.2774
MPW1K	-452.3309	-452.3537	-452.3531	-452.3523	-452.3268	-452.3383	-452.3385	-452.4321	-452.4463	-452.4402	-452.3949	-452.4256	-452.4300
BB1K	-452.2898	-452.3123	-452.3117	-452.3110	-452.2832	-452.2963	-452.2974	-452.3938	-452.4031	-452.3982	-452.3574	-452.3825	-452.3882
MPW1B95	-452.3285	-452.3516	-452.3510	-452.3504	-452.3252	-452.3377	-452.3400	-452.4326	-452.4400	-452.4364	-452.3939	-452.4185	-452.4251
CAM-B3LYP	-452.3378	-452.3606	-452.3600	-452.3593	-452.3340	-452.3459	-452.3467	-452.4483	-452.4517	-452.4463	-452.4097	-452.4302	-452.4350
ωB97X	-452.3930	-452.4184	-452.4178	-452.4171	-452.3888	-452.4010	-452.4022	-452.5060	-452.5118	-452.5018	-452.4627	-452.4878	-452.4873
ωB97X-D	-452.3595	-452.3837	-452.3832	-452.3825	-452.3575	-452.3684	-452.3699	-452.4694	-452.4752	-452.4690	-452.4285	-452.4524	-452.4548
B2PLYP	-452.2068	-452.2295	-452.2290	-452.2283	-452.2043	-452.2183	-452.2194	-452.3205	-452.3197	-452.3163	-452.2819	-452.2983	-452.3040
B2GPPLYP	-452.1177	-452.1412	-452.1406	-452.1399	-452.1142	-452.1287	-452.1298	-452.2320	-452.2329	-452.2292	-452.1923	-452.2108	-452.2160

Table S7. Barrier heights for the $E_{CO}2$, $S_N2@C$ and $S_N2@N$ reaction pathways of the $X^- + CH_3ONO_2$ (X = F, OH, CH_2CN) gas-phase reactions (in kcal mol^{-1}), obtained from the PEP calculated with the CCSD(T) and DFT methods on the MP2 geometries. The ZPE corrections are included. The calculated barrier heights are related to the most stable RC found for each one of the systems.

Method	X = F		X = OH			X = CH_2CN		
	a	**b**	**a**	**b**	**c**	**a**	**b**	**c**
CCSD(T)	5.48	6.99	0.05	5.18	7.48	13.42	8.10	7.52
B3LYP	2.83	5.52	-0.82	4.01	6.86	10.36	6.30	5.99
PBE0	3.70	7.07	-2.50	5.12	6.93	9.91	7.29	6.27
BMK	7.45	6.83	-0.11	5.32	7.82	12.80	8.37	7.54
B97-K	8.02	6.40	0.36	5.05	9.29	13.05	8.03	8.95
B97-3	4.61	7.19	-1.14	5.50	8.45	11.06	8.04	7.83
M05	6.38	8.32	1.22	6.63	8.71	13.57	9.42	7.83
M05-2X	6.89	4.43	-0.86	3.15	6.48	15.96	7.14	6.82
M06	4.84	7.85	-0.71	5.93	5.23	12.21	8.76	4.77
M06-2X	4.84	6.70	-2.38	5.13	6.20	13.57	8.61	6.38
M08-HX	7.35	7.54	-0.85	5.75	6.68	13.69	9.78	6.94
M08-SO	7.81	7.19	-0.29	5.67	6.90	14.00	8.71	6.22
MPW1K	8.33	7.90	-1.37	6.18	9.36	12.71	9.12	9.15
BB1K	8.03	7.30	-0.53	5.73	8.67	14.10	9.50	8.94
MPW1B95	5.21	6.60	-1.15	4.92	6.95	12.49	8.25	6.93
CAM-B3LYP	6.92	6.77	-0.28	5.55	8.01	12.53	8.71	8.30
ωB97X	9.98	7.49	0.88	6.35	8.61	14.41	10.40	9.74
ωB97X-D	6.98	7.65	-0.47	6.08	8.46	12.33	9.12	8.29
B2PLYP	4.01	5.70	0.18	4.23	6.74	11.70	6.55	6.00
B2GPPLYP	5.72	6.21	0.54	4.78	7.39	12.81	7.37	6.75

Table S8. Relative barrier heights between the $E_{CO}2$, $S_N2@C$ and $S_N2@N$ reaction pathways of the $X^- + CH_3ONO_2$ (X = F, OH, CH_2CN) gas-phase reactions (in kcal mol^{-1}), obtained from the PEP calculated with the CCSD(T) and DFT methods on the MP2 geometries. The ZPE corrections are included. All differences are related to the $E_{CO}2$ barrier heights. In parenthesis (also in kcal mol^{-1}), the deviation as compared with the CCSD(T) results, $\Delta E^*_{DFT} - \Delta E^*_{CCSD(T)}$.

Method	**X = F**	**X = OH**		**X = CH_2CN**	
	C – E	**C – E**	**N – E**	**C – E**	**N – E**
CCSD(T)	1.50	5.13	7.43	-5.31	-5.90
B3LYP	2.69 (+1.19)	4.82 (-0.31)	7.68 (+0.25)	-4.07 (+1.25)	-4.37 (+1.52)
PBE0	3.37 (+1.86)	7.63 (+2.50)	9.44 (+2.01)	-2.61 (+2.70)	-3.64 (+2.26)
BMK	-0.61 (-2.12)	5.43 (+0.30)	7.94 (+0.51)	-4.43 (+0.88)	-5.26 (+0.64)
B97-K	-1.62 (-3.13)	4.69 (-0.44)	8.93 (+1.50)	-5.02 (+0.29)	-4.10 (+1.80)
B97-3	2.58 (+1.08)	6.64 (+1.51)	9.59 (+2.16)	-3.02 (+2.30)	-3.23 (+2.67)
M05	1.94 (+0.44)	5.40 (+0.27)	7.48 (+0.06)	-4.14 (+1.17)	-5.74 (+0.16)
M05-2X	-2.46 (-3.97)	4.02 (-1.11)	7.34 (-0.09)	-8.83 (-3.51)	-9.14 (-3.24)
M06	3.02 (+1.51)	6.64 (+1.51)	5.94 (-1.49)	-3.45 (+1.86)	-7.44 (-1.54)
M06-2X	1.86 (+0.35)	7.51 (+2.38)	8.58 (+1.15)	-4.96 (+0.36)	-7.19 (-1.29)
M08-HX	0.19 (-1.31)	6.60 (+1.47)	7.53 (+0.10)	-3.91 (+1.40)	-6.75 (-0.85)
M08-SO	-0.63 (-2.13)	5.95 (+0.82)	7.18 (-0.24)	-5.29 (+0.03)	-7.77 (-1.87)
MPW1K	-0.43 (-1.93)	7.55 (+2.42)	10.73 (+3.30)	-3.59 (+1.72)	-3.56 (+2.34)
BB1K	-0.73 (-2.24)	6.26 (+1.13)	9.20 (+1.77)	-4.59 (+0.72)	-5.15 (+0.75)
MPW1B95	1.39 (-0.11)	6.07 (+0.94)	8.10 (+0.67)	-4.24 (+1.08)	-5.56 (+0.34)
CAM-B3LYP	-0.15 (-1.65)	5.83 (+0.70)	8.29 (+0.86)	-3.82 (+1.49)	-4.23 (+1.67)
ωB97X	-2.50 (-4.00)	5.47 (+0.34)	7.74 (+0.31)	-4.01 (+1.31)	-4.67 (+1.23)
ωB97X-D	0.67 (-0.84)	6.56 (+1.43)	8.93 (+1.50)	-3.22 (+2.10)	-4.04 (+1.86)
B2PLYP	1.69 (+0.18)	4.04 (-1.09)	6.56 (-0.87)	-5.15 (+0.16)	-5.70 (+0.19)
B2GPPLYP	0.49 (-1.02)	4.23 (-0.90)	6.85 (-0.58)	-5.44 (-0.13)	-6.06 (-0.16)

C, **N** and **E** have been used to identify the $S_N2@C$, $S_N2@C$ and $E_{CO}2$ channels respectively.

Table S9. Energies relative to the reactants (in kcal mol^{-1}) of all stationary points for the $E_{CO}2$, $S_N2@C$ and $S_N2@N$ reaction pathways of the $X^- + CH_3ONO_2$ (X = F, OH) reactions, calculated with the CCSD(T)/CBS method using the aug-cc-pVXZ (X = T, Q) basis sets for extrapolation. The differences from the values calculated with the X = D, T extrapolation are in parenthesis.

	X = F		X = OH		
	a	**b**	**a**	**b**	**c**
R	0.00		0.00		
RC	-24.58 (-0.83)		-22.18 (0.05)		-20.09 (0.10)
TS	-14.40 (0.04)	-17.74 (-0.89)	-18.92 (0.40)	-17.13 (0.00)	-14.50 (0.47)
PC	-76.92 (-0.39)	-51.08 (-0.85)	-89.02 (-0.31)	-75.29 (0.81)	
P	-41.12 (0.27)	-41.15 (-0.70)	-62.40 (-0.84)	-60.25 (-0.70)	

Table S10. Energies relative to reactants (in kcal mol^{-1}) of all stationary points for the $E_{CO}2$ and $S_N2@C$ reaction pathways of the $F^- + CH_3ONO_2$ reaction, calculated with the M08-SO, CAM-B3LYP, B2PLYP and B2GPPLYP/aug-cc-pVQZ methods. The differences (in kcal mol^{-1}) from the values obtained with the aug-cc-pVTZ basis sets are in parenthesis.

Method	**R**	**ab-RC**	**a-TS**	**b-TS**	**a-PC**	**b-PC**	**a-P**	**b-P**
M08-SO	0.00	-24.67 (-0.47)	-13.25 (-0.69)	-17.40 (-0.44)	-75.55 (-0.65)	-53.42 (-0.75)	-42.32 (-0.94)	-43.57 (-0.84)
CAM-B3LYP	0.00	-23.88 (0.01)	-13.01 (0.14)	-16.93 (0.13)	-73.72 (0.21)	-50.31 (-0.12)	-37.77 (-0.09)	-41.73 (-0.20)
B2PLYP	0.00	-22.80 (0.04)	-14.76 (0.24)	-16.95 (0.13)	-72.84 (0.30)	-48.42 (-0.12)	-40.06 (-0.12)	-39.84 (-0.22)
B2GPPLYP	0.00	-23.05 (0.02)	-13.28 (0.25)	-16.71 (0.10)	-73.50 (0.29)	-49.34 (-0.15)	-40.04 (-0.16)	-40.46 (-0.27)

Table S11. Energies relative to reactants (in kcal mol^{-1}) of all stationary points for the $E_{CO}2$ and $S_N2@C$ reaction pathways of the OH^- + CH_3ONO_2 reaction, calculated with the M08-SO, CAM-B3LYP, B2PLYP and B2GPPLYP/aug-cc-pVQZ methods. The differences (in kcal mol^{-1}) from the values obtained with the aug-cc-pVTZ basis sets are in parenthesis.

Method	R	ab-RC	c-RC	a-TS	b-TS	c-TS	a-PC	bc-PC	a-P	bc-P
M08-SO	0.00	-23.90	-21.86	-21.54	-18.39	-17.22	-91.69	-80.34	-64.26	-64.88
		(-0.48)	(-0.46)	(-0.69)	(-0.55)	(-0.46)	(-0.91)	(-1.15)	(-1.01)	(-1.14)
CAM-B3LYP	0.00	-22.68	-20.60	-20.10	-17.08	-14.74	-86.39	-77.25	-60.68	-62.50
		(0.08)	(0.09)	(0.09)	(0.22)	(0.24)	(0.23)	(-0.07)	(0.12)	(-0.12)
B2PLYP	0.00	-21.43	-19.42	-18.34	-17.16	-14.67	-86.67	-73.87	-61.30	-59.41
		(0.14)	(0.16)	(0.20)	(0.27)	(0.38)	(0.29)	(-0.06)	(0.08)	(-0.17)
B2GPPLYP	0.00	-21.79	-19.72	-18.34	-16.98	-14.36	-87.07	-75.11	-61.32	-60.30
		(0.11)	(0.13)	(0.17)	(0.23)	(0.37)	(0.26)	(-0.11)	(0.00)	(-0.24)