Exploring the Effect of External Electric Field on the Hydrogen Bonding of Methanol Dimer and Fluorinated Methanol Dimer: A Quantum Chemical Investigation

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Electronic Supplementary Information

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S1 Optimized Geometry of Methanol Dimer Under the Presence of External Electric Filed

The *ab-initio* calculations are performed using the density function theory (DFT) and coupled-cluster singles with doubles (CCSD) as implemented in orca quantum chemistry package[1]. Here, we project the Cartesian component (x, y, z) of EEFs along the dipole moment vector of the free methanol dimer system. The structure and energetics of the methanol dimer (M_2) are done at different classes of the DFT functionals. To explore the dispersion effect, some D3-variants are also used. These results are benchmarked against CCSD calculation. During the energy and geometry optimizations, no symmetry constraint is imposed. Harmonic frequency calculations are carried out at the same level of theory to characterize the stationary points. Harmonic frequency calculations are done at the B3LYP/cc-PVTZ level of theory to characterize the stationary points and vibrational spectra. The numerical Hessian calculation is done here. For the DFT methods, the geometry optimizations are carried out by using VeryTightSCF criteria on the self-consistent field part of the calculation, VeryTightOPT criteria on the geometry optimization, and the Defgrid3 keyword to define a very fine numerical grid. In CCSD geometry optimizations only TightOPT criteria are used. The bonding nature were performed by QTAIM[2–4]. The AIM picture is drawn from AIMUC package.[5]

This Supporting Information contains:

- Optimized Cartesian geometry at CCSD/cc-PVTZ level of thoery. The DFT optimized geometries at different functionals can found at other suplymentary files.
- Root mean square deviation of optimized structures with CCSD optimized ones.
- AIM picture of QTAIM analysis
- B3LYP/cc-PVTZ optimized structures of fluorinated substituted methanol dimers (FM and F_2)
- Optimized Cartesian corrdinates of FM and F_2.
- Sample input file for Orca quantum chemistry for optimization under EEFs.

S1.1 Cartesian coordinates (in Å) of the CCSD/cc-pVTZ optimized structure of free M_2

Atomic Type	X	Y	Z
C	-1.97752389054012	-0.44377809745643	0.19116867918405
H	-1.25466670737129	-1.11390477033425	0.64807854366714
H	-2.40765056946977	-0.94211942552475	-0.67936811119090
H	-2.76798085566819	-0.22599669423694	0.91123225417306
O	-1.26672105830085	0.73421987621292	-0.17438431807335
H	-1.85318716657345	1.29892836100818	-0.67735886556793
C	2.11576352102986	0.07282063915701	0.41260868978585
H	2.43938842565369	1.09820985998678	0.21071931685108
H	3.00181089422645	-0.55749959117164	0.46161360679329
H	1.62970808592543	0.05346838622094	1.39280753884307
O	1.28371241542905	-0.43756447532641	-0.60722739800532
H	0.48243790565917	0.09457893146460	-0.61457693646005

S1.2 Cartesian coordinates of the CCSD/cc-pVTZ optimized structure of M_2 (in Å) in the presence of electric field at the strength of 0.01 V/Å

Atomic Type	X	Y	Z
C	-1.97734445878687	-0.44381385393226	0.19120227501456
H	-1.25478146257168	-1.11411842078558	0.64834599749715
H	-2.40757008972452	-0.94205798108423	-0.67931699404571
H	-2.76777823236989	-0.22569247450415	0.91105309159449
O	-1.26605043854227	0.73394658714762	-0.17449776337572
H	-1.85248193701289	1.29920021696214	-0.67695914252311
C	2.11540458110091	0.07284863009102	0.41249244049427
H	2.43846674137453	1.09844039985358	0.21075051345058
H	3.00184766528799	-0.55706942071224	0.46158101472540
H	1.62925577905787	0.05322697096109	1.39258203700937
O	1.28380909249324	-0.43786582990004	-0.60738344961019
H	0.48231375969356	0.09431817590305	-0.61453702023110

S1.3 Cartesian coordinates of the CCSD/cc-pVTZ optimized structure of M_2 (in Å) in the presence of electric field at the strength of 0.02 V/Å

Atomic Type	X	Y	Z
C	-1.97734445878687	-0.44381385393226	0.19120227501456
H	-1.25478146257168	-1.11411842078558	0.64834599749715
H	-2.40757008972452	-0.94205798108423	-0.67931699404571
H	-2.76777823236989	-0.22569247450415	0.91105309159449
O	-1.26605043854227	0.73394658714762	-0.17449776337572
H	-1.85248193701289	1.29920021696214	-0.67695914252311
C	2.11540458110091	0.07284863009102	0.41249244049427
H	2.43846674137453	1.09844039985358	0.21075051345058
H	3.00184766528799	-0.55706942071224	0.46158101472540
H	1.62925577905787	0.05322697096109	1.39258203700937
O	1.28380909249324	-0.43786582990004	-0.60738344961019
H	0.48231375969356	0.09431817590305	-0.61453702023110

S1.4 Cartesian coordinates of the CCSD/cc-pVTZ optimized structure of M_2 (in Å) in the presence of electric field at the strength of 0.05 V/Å

Atomic Type	X	Y	Z
C	-1.99564501521300	-0.45512797799834	0.17580017222382
H	-1.28977577327483	-1.18143944239652	0.56997015197862
H	-2.50292230695529	-0.89459455018092	-0.68461742750215
H	-2.73112440330390	-0.21814827223732	0.94631535533760
O	-1.23440653864850	0.69132130784913	-0.19011603630696
H	-1.81906976177353	1.32784843472080	-0.60031093254455
C	2.11966269433381	0.09377636692105	0.41529477296057
H	2.43853525501903	1.11059618273005	0.16696122001057
H	3.01041326749164	-0.52376332061822	0.51697900777611
H	1.61162283796785	0.12150928527148	1.38412033910185
O	1.31531317229541	-0.47724873620966	-0.59411670715038
H	0.50248757206130	0.03663372214846	-0.63096691588509

S1.5 Cartesian coordinates of the CCSD/cc-pVTZ optimized structure of M_2 (in Å) in the presence of electric field at the strength of 0.1 V/Å

Atomic Type	X	Y	Z
C	-1.98386910217295	-0.45276803263028	0.17875081549033
H	-1.28894415563517	-1.24739307726946	0.43815865840743
H	-2.67649670513752	-0.82694624810128	-0.57658558164134
H	-2.54289744977110	-0.16585643978584	1.07054902663310
O	-1.19740637583652	0.62604417121912	-0.31532220778251
H	-1.78326092492248	1.32319603928926	-0.60897710599580
C	2.08649341368715	0.10696753150369	0.43875060497382
H	2.35458250462638	1.14799769199514	0.23419208635366
H	3.00686570527275	-0.45722972149392	0.58175906513908
H	1.52036615570452	0.07790795730890	1.37451201086945
O	1.38282883340125	-0.48556944002467	-0.63097866604467
H	0.54682910078369	-0.01498743201066	-0.70949570640257

S1.6 Cartesian coordinates of the CCSD/cc-pVTZ optimized structure of M_2 (in Å) in the presence of electric field at the strength of 0.2 V/Å

Atomic Type	X	Y	Z
C	-2.05995659483111	-0.45877067177316	0.17261879982514
H	-1.43137675326459	-1.29482296078230	0.46901639233706
H	-2.75312659695329	-0.79686478010282	-0.59849181597216
H	-2.62444680922211	-0.11662814800530	1.04053055347793
O	-1.18424969337374	0.55361866204836	-0.31394766591507
H	-1.70977249137073	1.30021334042882	-0.60076489773518
C	2.13956581905690	0.12968490554898	0.43205888752139
H	2.33535957581818	1.18802418600626	0.23528137718014
H	3.09893771740376	-0.37825885753374	0.52718951783087
H	1.61808092391609	0.05288309197701	1.39023347188160
O	1.42864554066711	-0.48911798677854	-0.61711189237463
H	0.56743036215354	-0.05859778103357	-0.66129972805710

S1.7 Cartesian coordinates of the CCSD/cc-pVTZ optimized structure of M_2 (in Å) in the presence of electric field at the strength of 0.5 V/Å

Atomic Type	X	Y	Z
C	-1.98276751474770	-0.39178572758381	0.24164855252874
H	-1.46250058561167	-1.30945689547341	0.50638512038158
H	-2.89326006684282	-0.64604607979934	-0.29956122520782
H	-2.24428743058155	0.14330749799991	1.15411264009266
O	-1.08507725326017	0.36723528447847	-0.57047020261835
H	-1.53563172986205	1.16832771185984	-0.84064987785053
C	1.99617701965915	0.12284125140309	0.47346324600624
H	1.86954963578357	1.20829919185888	0.50155984831816
H	3.05681347785261	-0.09889932461428	0.60704845686017
H	1.45197504270709	-0.30171516782906	1.32205870684797
O	1.59275181782386	-0.43423622293641	-0.75753530538058
H	0.66134858707968	-0.19650851936386	-0.86274695997826

S1.8 Cartesian coordinates of the CCSD/cc-pVTZ optimized structure of M_2 (in Å) in the presence of electric field at the strength of 1.0 V/Å

Atomic Type	X	Y	Z
C	-2.01540818865851	-0.41424262376303	0.14898723488595
H	-1.59689427976808	-1.38993394490057	0.38628999822603
H	-2.90482135608742	-0.54571669823441	-0.46357284044427
H	-2.28773270689872	0.09581552492491	1.07089604075962
O	-0.99547486997942	0.30930237476685	-0.56460726162964
H	-1.37745806329993	1.15209039837795	-0.81828572068224
C	1.97713516854223	0.14850177654689	0.55338396393112
H	1.65208991507156	1.18529307310490	0.65588924315317
H	3.06626991211965	0.11846999028700	0.67432994281859
H	1.52827241036810	-0.42177335345078	1.37144398667150
O	1.66556857131271	-0.39014771193200	-0.71294748979040
H	0.71354448727630	-0.21629580572470	-0.82649409790638

S1.9 Root Mean Square Deviation of Optimized Structures

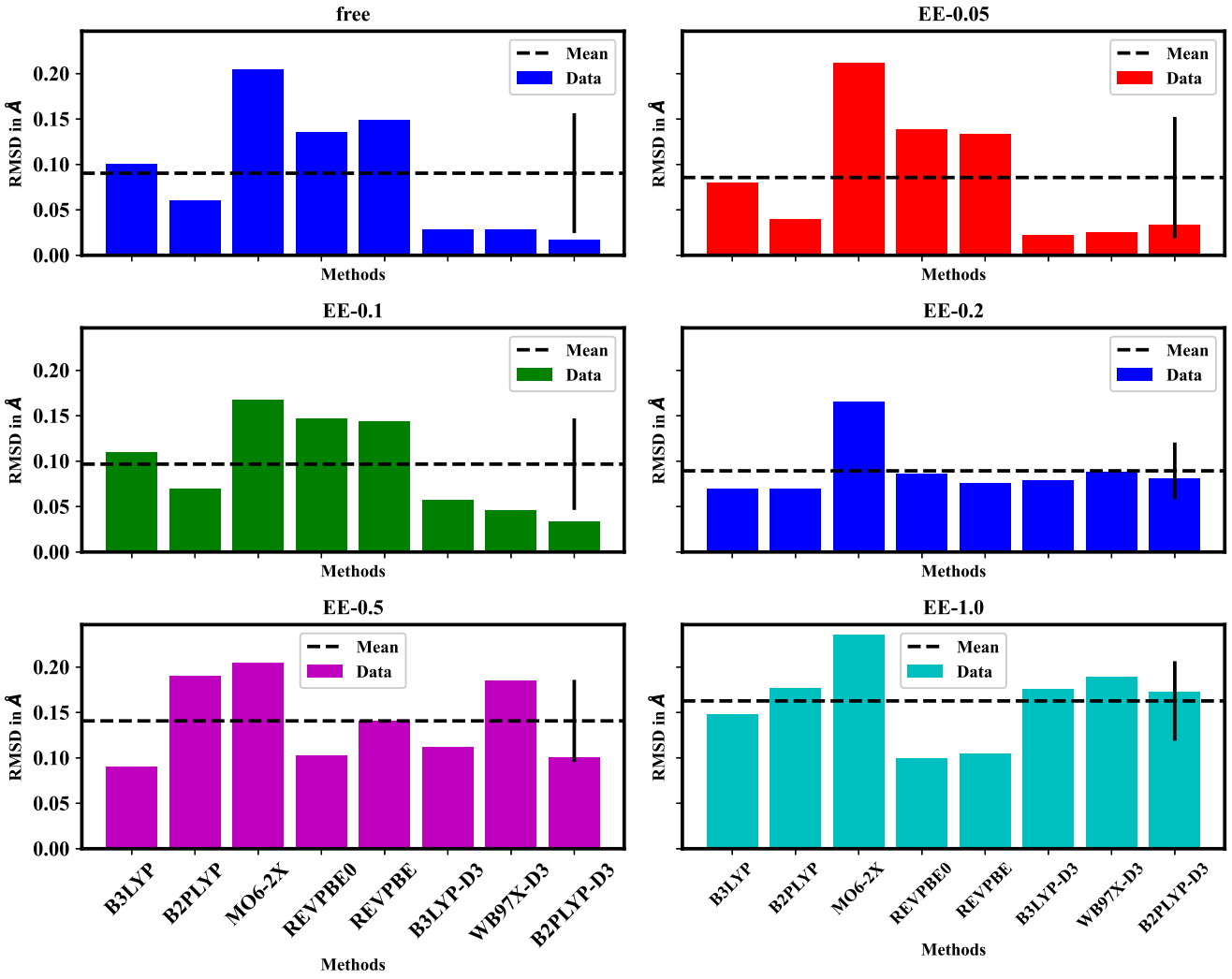

FIG. S1: The root mean square deviation (RMSD) calculation of optimized geometries of M_2 in different electric field strengths (EEF = 0.0, 0.05, 0.1, 0.2, 0.5, 1.0 V/Å) for various functionals. The reference geometry is the optimized geometry at CCSD/cc-PVTZ level of theory. The horizontal and vertical line show the mean and standard deviation of the calculated RMSD values.

The average performance of different DFT functionals with respect to CCSD optimized structures of M_2 is tested with root mean square deviation (RMSD) calculation. For the low field strengths ($|E| > 0.2$ V/Å), the M06-2X functional shows the large rmsd deviation of 0.20 Å. In high field strengths ($|E| > 0.2$ V/Å), all functionals show a large deviation, varying from 0.10 to 0.20 Å.

S2 Nature of H-Bonding in Methanol Dimer in the Presence of EEFs: AIM Picture

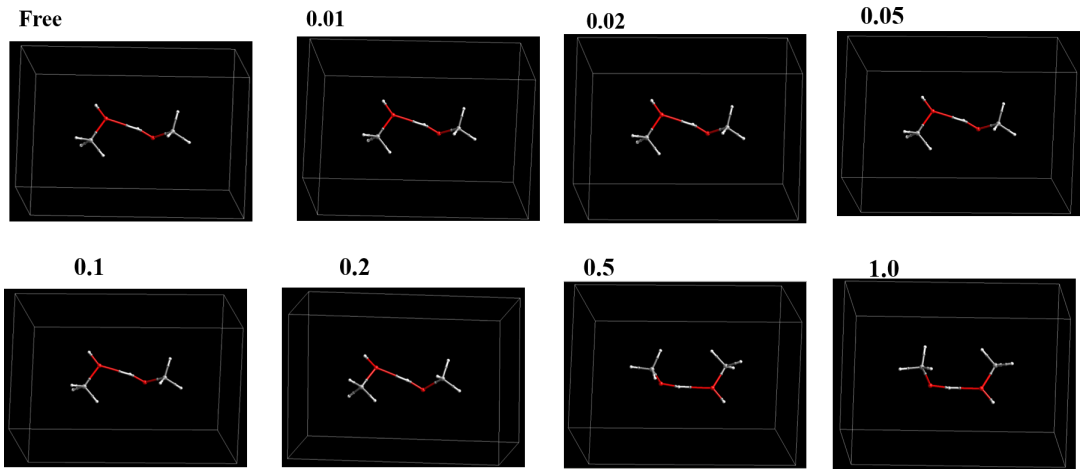

FIG. S2: QTAIM picture of methanol dimer (M_2) in the presence of EEFs strength of 0.0 to 1.0 V/Å. This figure represents one BCP corresponding for H-bond.

S3 The optimized geometry of mixed trifluoro methanol dimer (FM) under the presence of EEFs at the B3LYP/cc-pVTZ level of theory.

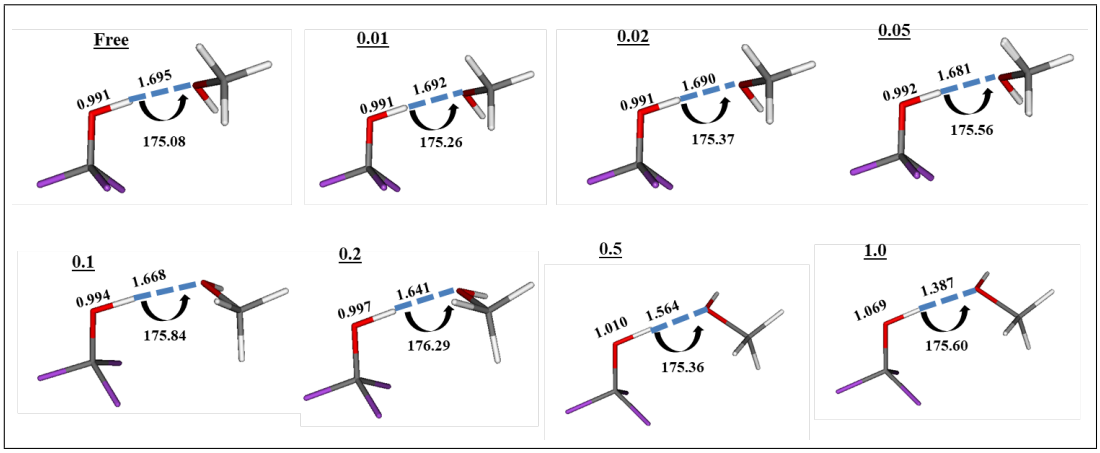

FIG. S3: Key geometrical parameters of the optimized geometry of FM under the presence of EEFs strengths of 0.0 to 1.0 V/Å

S4 The optimized geometry of trifluoro methanol dimer (F_2) under the presence of EEFs at the B3LYP/cc-pVTZ level of theory.

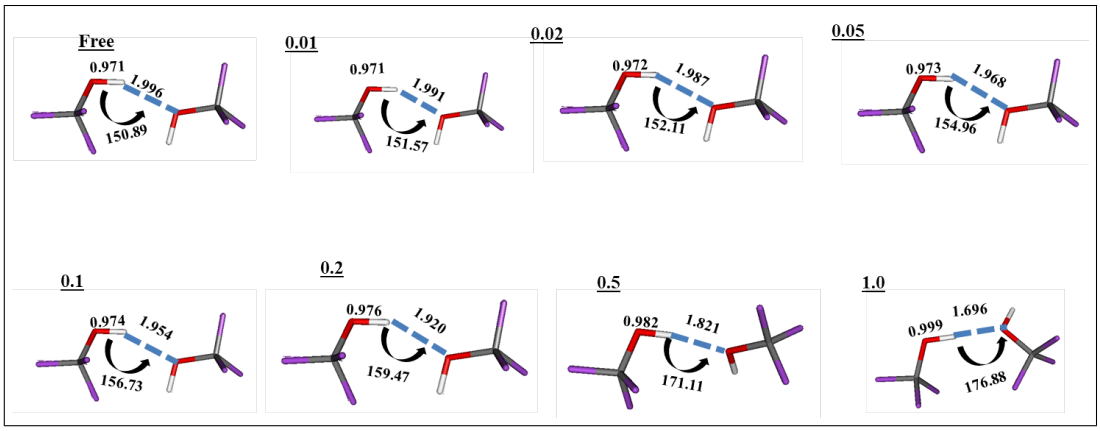

FIG. S4: Key geometrical parameters of the optimized geometry of F_2 under the presence of EEFs strengths of 0.0 to 1.0 V/Å

S4.1 Cartesian coordinates (in Å) of the B3LYP/cc-pVTZ optimized structure of free FM

Atomic Type	X	Y	Z
C	1.96878628336693	-0.04062951457845	-0.05625439022393
H	2.04083087665108	-0.91564735947185	-0.69708554745421
H	2.95644210190296	0.18273773502670	0.34990974450689
H	1.60969172517894	0.80426118708491	-0.64625513456427
O	1.05072506077543	-0.37684324793245	0.99493114895331
H	0.96901291048491	0.36902234610837	1.59755522906248
C	-2.05784859672062	-0.01626333777253	-0.08593623312226
F	-1.49264381527190	0.67273338939966	-1.11441761564972
F	-2.10115738922850	0.86044179642136	0.95434386293482
F	-3.31305775539608	-0.30064520643027	-0.43249484290085
O	-1.40329771162449	-1.13112274187531	0.21073123848355
H	-0.48652869011866	-0.90402904598015	0.51121053997421

S4.2 Cartesian coordinates (in Å) of the B3LYP/cc-pVTZ optimized structure of FM in the presence of electric field at the strength of 0.01 V/Å

Atomic Type	X	Y	Z
C	1.96213948864290	-0.03845467245279	-0.05863646069714
H	2.01992244285104	-0.90729740377510	-0.70870889551822
H	2.95525937575479	0.17316265329161	0.33879257431869
H	1.60253887404826	0.81475745835306	-0.63565496954131
O	1.05321823423080	-0.37844846642839	0.99967770061692
H	0.98413657352669	0.36163044466771	1.61052386024733
C	-2.05396437264107	-0.01739212923992	-0.08894257438989
F	-1.48083821327152	0.66522405293453	-1.11729985235522
F	-2.10783565411381	0.86627330012347	0.94461184961673
F	-3.30642402752204	-0.30576740899683	-0.44474450074976
O	-1.40106773802359	-1.12959131250131	0.22071251787237
H	-0.48612998348244	-0.90008051597606	0.52590675057952

S4.3 Cartesian coordinates (in Å) of the B3LYP/cc-pVTZ optimized structure of FM in the presence of electric field at the strength of 0.02 V/Å

Atomic Type	X	Y	Z
C	1.96004478975691	-0.03674843146215	-0.05958175204583
H	2.00922475488230	-0.90091920440124	-0.71603260416741
H	2.95543451389434	0.16528164298192	0.33545852469719
H	1.60333846949198	0.82279886635601	-0.62836686375447
O	1.05310405008268	-0.37883252877219	1.00013430074966
H	0.99099935204202	0.35702644964004	1.61638416933120
C	-2.05280497579473	-0.01842504466812	-0.09004041581815
F	-1.47706147573341	0.65850889766654	-1.12068886885799
F	-2.11029221011899	0.87118346254874	0.93816687283068
F	-3.30476474448517	-0.30911306681689	-0.44796589463159
O	-1.40090879741270	-1.12875568483626	0.22767501399944
H	-0.48535872660524	-0.89798935823641	0.53109551766730

S4.4 Cartesian coordinates (in Å) of the B3LYP/cc-pVTZ optimized structure of FM in the presence of electric field at the strength of 0.05 V/Å

Atomic Type	X	Y	Z
C	1.95228217797008	-0.03203523312199	-0.06268369959676
H	1.98194516790204	-0.88466012176947	-0.73375733617851
H	2.95260598378729	0.14967384774826	0.32471832903794
H	1.59965346432443	0.84120110742793	-0.61112214031263
O	1.05248512622170	-0.38122613104906	1.00184256327340
H	1.00961424603241	0.34228046829019	1.63295838027093
C	-2.04760800941464	-0.02045987685309	-0.09292349259486
F	-1.46243589310622	0.64100271555207	-1.12814755445174
F	-2.11545379122692	0.88430143697577	0.92112225257602
F	-3.29828931980273	-0.31565184715626	-0.45878593705046
O	-1.40055713294665	-1.12667154910982	0.24665085764062
H	-0.48328701974079	-0.89373881693454	0.54636577738606

S4.5 Cartesian coordinates (in Å) of the B3LYP/cc-pVTZ optimized structure of FM in the presence of electric field at the strength of 0.1 V/Å

Atomic Type	X	Y	Z
C	1.94013080492516	-0.02538634661979	-0.06737049064559
H	1.93925094868338	-0.86029120761426	-0.75875143127591
H	2.94730926271207	0.12552578405988	0.30685305350166
H	1.59448991884748	0.86737416339419	-0.58503465013716
O	1.05159013104240	-0.38425153582370	1.00517006114151
H	1.04036460694427	0.31899409780066	1.65817309831563
C	-2.03971477854349	-0.02331505035764	-0.09763079688462
F	-1.44108053849016	0.61677639167959	-1.13828857565603
F	-2.12533128747813	0.90274876851851	0.89540115053933
F	-3.28785973819401	-0.32737309592837	-0.47644982105943
O	-1.39865326724134	-1.12190973354835	0.27389384965053
H	-0.47954106320762	-0.88487623556074	0.57027255251010

S4.6 Cartesian coordinates (in Å) of the B3LYP/cc-pVTZ optimized structure of FM in the presence of electric field at the strength of 0.2 V/Å

Atomic Type	X	Y	Z
C	1.92647181249883	-0.02192188922158	-0.07863045769366
H	1.83635188554269	-0.82091320386690	-0.80193445886877
H	2.94860589346385	0.03715463646231	0.26255238161897
H	1.62707530987463	0.91393447201013	-0.53925752072297
O	1.05190557563324	-0.36555285164162	1.01350249117968
H	1.12264661061935	0.29761873330277	1.69974229053125
C	-2.03752626506335	-0.03058519107659	-0.10393720502057
F	-1.40670923563492	0.60809568666797	-1.12554171490626
F	-2.21279999043984	0.91147542817024	0.86171569637986
F	-3.25945974736303	-0.38333821404921	-0.54451199091993
O	-1.38620004704189	-1.10075704101904	0.32310442832168
H	-0.46940680208955	-0.84119456573850	0.61943406010076

S4.7 Cartesian coordinates (in Å) of the B3LYP/cc-pVTZ optimized structure of FM in the presence of electric field at the strength of 0.5 V/Å

Atomic Type	X	Y	Z
C	1.85164039594050	0.04902871698724	-0.06573208935782
H	1.53527774183795	-0.52702283899367	-0.91771387444912
H	2.87513180282962	-0.14945821810832	0.14368761993497
H	1.69590926478162	1.09495692770226	-0.25538102535037
O	1.02566942328158	-0.39455377326035	1.03750136976658
H	1.30772899505472	0.02281968059317	1.84125790710350
C	-1.98586367099294	-0.04965833683247	-0.16266188440490
F	-1.32256806201839	0.36759310615093	-1.27270892124897
F	-2.15454843501493	1.05993372928206	0.60648956226869
F	-3.23190051129992	-0.43403337341097	-0.57189612190674
O	-1.39669272388794	-1.04779365821194	0.46556162220828
H	-0.45882922051185	-0.78779596189795	0.73783383543592

S4.8 Cartesian coordinates (in Å) of the B3LYP/cc-pVTZ optimized structure of FM in the presence of electric field at the strength of 1.0 V/Å

Atomic Type	X	Y	Z
C	1.67473641539826	0.17473902328771	-0.04080265420684
H	1.44532609842840	-0.32254780641542	-0.95595888353467
H	2.69985983989987	0.17280650540611	0.12230677015081
H	1.28438732377550	1.16398315240095	-0.02637705257007
O	1.02158211906533	-0.61749763642275	1.00104774531751
H	1.41374917406750	-0.46442996865471	1.83829830592037
C	-1.84097611318956	-0.05179259347810	-0.19697732462251
F	-1.33921164160190	-0.16624939012453	-1.46564419029097
F	-1.65024969211007	1.24158990792411	0.16134005053696
F	-3.23363627606400	-0.20144934195768	-0.34913983678794
O	-1.38796028839337	-0.93218370680769	0.64981589858578
H	-0.34665195927595	-0.79295214515801	0.84832917150159

S4.9 Cartesian coordinates (in Å) of the B3LYP/cc-pVTZ optimized structure of free F_2

Atomic Type	X	Y	Z
C	2.20267019909876	-0.00656434367660	0.03270171911677
F	3.13980319031189	0.31187325404169	0.93816294416988
F	2.54270757661709	-1.14647016559913	-0.55579315190693
F	2.18894435076656	0.97233751343554	-0.88559724404271
O	0.98386291663470	-0.17874141643361	0.60798199319852
H	0.66982042431454	0.65207204021692	0.99196513532893
H	-0.68461140477119	-1.18102320336558	0.16178318414134
O	-1.65211418163721	-1.26920757531449	0.17845002315277
C	-2.20369482703831	-0.06177153473251	0.02402491684491
F	-1.96487458036817	0.47780318389408	-1.18820463996839
F	-1.72241698889707	0.84218525378738	0.93116308215227
F	-3.51649667503159	-0.14959300625371	0.19346203781265

S4.10 Cartesian coordinates (in Å) of the B3LYP/cc-pVTZ optimized structure of F_2 in the presence of electric field at the strength of 0.01 V/Å

Atomic Type	X	Y	Z
C	2.20146920673301	-0.00857221810231	0.03148661261269
F	3.14713522304423	0.30117734761184	0.93002059142400
F	2.52600451563351	-1.15204129349095	-0.55875632401251
F	2.19028756589998	0.96967213721661	-0.88718911171567
O	0.98458822270169	-0.16893153450354	0.61515686387749
H	0.68226679375065	0.66482018753309	1.00158739235534
H	-0.67757769974276	-1.17027514659065	0.16938626886500
O	-1.64457177878489	-1.26740938553905	0.17586266099457
C	-2.20524549461690	-0.06392754569680	0.02232982905041
F	-1.96211779694373	0.48246793367886	-1.18655137235215
F	-1.73945763369425	0.84007745962853	0.93618374328110
F	-3.51918112398054	-0.16415794174567	0.18058284561975

S4.11 Cartesian coordinates (in Å) of the B3LYP/cc-pVTZ optimized structure of F_2 in the presence of electric field at the strength of 0.02 V/Å

Atomic Type	X	Y	Z
C	2.19762612482013	-0.00861612287024	0.02895315900737
F	3.15561275804812	0.28838257258198	0.91760428915558
F	2.50676384168498	-1.15034338950626	-0.57273508633322
F	2.18160320289345	0.97565281508901	-0.88286356579777
O	0.98635296161162	-0.16462921126059	0.62617532046837
H	0.69263377558645	0.66992258099782	1.01693419690928
H	-0.67361810841535	-1.16582035671644	0.18704634314514
O	-1.64046100341717	-1.26673046963702	0.18275272687900
C	-2.20331330665467	-0.06536837629160	0.01900267070691
F	-1.94795306215940	0.47787321820075	-1.18922649081688
F	-1.75229809944776	0.84263658130413	0.93513863537466
F	-3.51934908455039	-0.17005984189157	0.16131780130156

S4.12 Cartesian coordinates (in Å) of the B3LYP/cc-pVTZ optimized structure of F_2 in the presence of electric field at the strength of 0.05 V/Å

Atomic Type	X	Y	Z
C	2.19493177487944	-0.01569701490795	0.02231162187654
F	3.18486138417770	0.24581644960181	0.88351539536339
F	2.44588997720606	-1.16609707178054	-0.58953847111808
F	2.18568921301275	0.96978684467619	-0.88701983004843
O	0.99499809348663	-0.13200450273016	0.65343748388815
H	0.75049251437915	0.70685864386961	1.06628821614257
H	-0.65101391165595	-1.12003241851558	0.21977067796802
O	-1.61359188888333	-1.25594070246808	0.18262441034091
C	-2.21287759027058	-0.07288271021670	0.01103581048989
F	-1.93949848176356	0.48891409221978	-1.18639487374720
F	-1.82583885064341	0.84089434595664	0.94625130735766
F	-3.53044223392489	-0.22671595570504	0.10781825148659

S4.13 Cartesian coordinates (in Å) of the B3LYP/cc-pVTZ optimized structure of F_2 in the presence of electric field at the strength of 0.1 V/Å

Atomic Type	X	Y	Z
C	2.20456426531079	-0.03591483515016	0.02570243515007
F	3.16972838633524	0.29503508199271	0.88633816911500
F	2.46403797038872	-1.23362261358358	-0.48287636487006
F	2.22090364099096	0.86755330078583	-0.96398351344795
O	0.98764065722196	-0.09786997912797	0.63343168360504
H	0.76939075464525	0.75317367531068	1.03370503652053
H	-0.63550681522246	-1.08221168457816	0.16789400658960
O	-1.59290338818845	-1.24389857676494	0.09118727566053
C	-2.22582439312766	-0.06746219436844	0.02390179592630
F	-1.97325822074105	0.60398533946940	-1.12243172249333
F	-1.86376552453964	0.77142917052951	1.03311150161912
F	-3.54140733307367	-0.26729668451490	0.10411969662515

S4.14 Cartesian coordinates (in Å) of the B3LYP/cc-pVTZ optimized structure of F_2 in the presence of electric field at the strength of 0.2 V/Å

Atomic Type	X	Y	Z
C	2.18490485054797	-0.02884046362912	0.01334255089275
F	3.20116681962004	0.18737843002405	0.84124737474768
F	2.34218620966155	-1.20635179850795	-0.57865390543328
F	2.20863785113235	0.93061509280774	-0.91903628831363
O	0.99291323952253	-0.05721765304647	0.67464599625482
H	0.84431724464357	0.78095859425947	1.12557707187432
H	-0.60424121351920	-1.03912840152044	0.25632805850334
O	-1.55411550752592	-1.23770239112683	0.15126259183140
C	-2.21960808279210	-0.08578947770495	0.00555318650642
F	-1.93713435164209	0.54438717282998	-1.16037047713438
F	-1.93906594813299	0.80499161270411	0.99046535638523
F	-3.53636111151572	-0.33040071708962	0.02973848388532

S4.15 Cartesian coordinates (in Å) of the B3LYP/cc-pVTZ optimized structure of F_2 in the presence of electric field at the strength of 0.5 V/Å

Atomic Type	X	Y	Z
C	2.12217855719912	-0.01176590653334	-0.02704670483347
F	3.24907665269915	-0.16739097293004	0.62879940254966
F	1.93039353268616	-1.05054557089047	-0.83879821928069
F	2.21434954670432	1.09117918202610	-0.76199677295562
O	1.04790273364850	0.03845502431549	0.81736647035831
H	1.17726421730253	0.72996052062665	1.46406002088812
H	-0.53170571349755	-0.81295717650586	0.50527532237411
O	-1.44840145459031	-1.13758620212623	0.36636423094873
C	-2.21514319397064	-0.12803691594172	-0.05487123335231
F	-1.88377897270876	0.30983696565968	-1.30467947166107
F	-2.17190566015183	0.95284228205534	0.75106445000689
F	-3.50663024532069	-0.55109122975560	-0.11543749504267

S4.16 Cartesian coordinates (in Å) of the B3LYP/cc-pVTZ optimized structure of F_2 in the presence of electric field at the strength of 1.0 V/Å

Atomic Type	X	Y	Z
C	1.95399013415170	0.07953513876049	0.05806052477705
F	2.58590987243186	1.00394303439794	0.69145559407265
F	2.81905401113168	-0.75168984636462	-0.48877066049231
F	1.21083637813460	0.60973322394980	-0.91843738307556
O	1.08180374582599	-0.59411594301359	0.88537203012811
H	1.50060244487215	-0.76798329475180	1.71725137891646
H	-0.54527927472815	-0.86557550047169	0.49032610593239
O	-1.51893534205483	-1.01322769942906	0.32113784576514
C	-2.07952193740029	0.09580864631200	-0.17023508593097
F	-1.91884805430131	0.21247452685189	-1.54544318659320
F	-1.65148047759933	1.23318700099234	0.37303727202025
F	-3.45453150046408	0.02081071276628	0.01634556448000

ORCA Input File

A sample input file is included as part of the supplementary information, which optimize the methanol dimer under external electric field. Here, the strength of electric field is given in Cartesian form.

For the electric field strength of 0.01 V/Å, a sample file is given here:

```
! B3LYP cc-pVTZ cc-pVTZ/c defgrid3 OPT NumFreq
! VeryTightSCF VeryTightOpt

%pal nprocs=24 end

%scf
  efield -0.0001785,0.000073268,0.000024029
end

%geom
  maxiter 500
end

*xyz 0 1
  C   -2.10528970766294    -0.46025888219917     0.17425053596523
  H   -1.47732722407165    -1.16949254304354     0.70825526599508
  H   -2.47089913787943    -0.93916089990552    -0.73739746894561
  H   -2.95417751921681    -0.18837438249063     0.80685211572958
  O   -1.28442750835208     0.67417928760223    -0.11300597254007
  H   -1.76569489127637     1.27685650025781    -0.68602992068254
  C    2.22443179136278     0.10432317044409     0.39449800887117
  H    2.49219029963420     1.13908627624973     0.14829106781163
  H    3.13312378259213    -0.49642782081359     0.35174321513685
  H    1.85338599397655     0.08447171700917     1.42616554142678
  O    1.30224909537127    -0.44970874927096    -0.52433448478468
```

H 0.47752602552237 0.05586932616039 −0.47397490398345

*

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