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Electronic Supplementary Information for

Hyperconjugation in diethylether cation versus diethylsulfide cation

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Material Summary:

Details concerning the energetics and multidimensional vibrational calculation; a table for the CH stretching vibration using the local mode model for neutral ag diethyl sulfide (DES); four tables comparing the LM versus LM(NM)-4D model for aa diethyl ether (DEE) and gg, gg', and sg DEE^+; a table comparing the relative energies for DEE^+-Ar; a figure on the two dimensional potential energy surface of DEE^+; a figure of the schematic geometry of DEE^+-Ar; a figure for the vibrational modes of DEE^+; a figure comparing the methyl torsion angle dependence of the C3H9 stretching vibrational frequency; a figure comparing the COCH torsion angle dependence of the C3H9 stretching vibrational peak intensity; and Cartesian geometries optimized by the MP2/6-311++G(3df,3pd) method are all available in the ESI.

Relative energies calculated by different quantum chemistry methods

In the following Tables we have summarized the relative energetics calculated by using a variety of quantum chemistry methods. As given in Table S1, for the adiabatic and vertical ionization energies for DEE^+, B3LYP or PBE0 does not show basis set dependence, and both constantly underestimates the CCSD(T) values, given in the manuscript by about 0.3 eV. On the other hand, for DES^+, given in Table S2, the values obtained by B3LYP/6-31++G(d,p) are very close to those obtained by the CCSD(T)//MP2 method given in the manuscript. .

Table S1: Ionization energies, in eV, of diethylether calculated using several different quantum chemistry methods. See Figure 2 in manuscript for naming of the structures.

Method	gg cation[a]	gg' cation[a]	sg cation[a]	gg'' cation[a]	Vertical[b]
B3LYP/6-311++G(3df,3pd)	9.24 (9.30)	9.24 (9.32)	9.29 (9.37)		9.56
PBE0/6-31++G(d,p)	9.20 (9.25)	9.18 (9.26)	9.22 (9.29)	9.15 (9.26)	9.51
PBE0/6-311++G(3df,3pd)	9.21 (9.27)	9.19 (9.27)	9.16 (9.27)	9.16 (9.27)	9.50
MP2/6-311++G(3df,3pd)	9.88 (9.92)	9.89 (9.95)	9.94 (10.00)	9.91 (10.0)	10.18

a: zero point corrected values at the respective level of calculation method, electronic energy differences are given in parentheses; b: electronic energy difference between the neutral and cationic species at the equilibrium geometry of the neutral species at the respective level;

Table S2: Ionization energies, in eV, of diethylsulfide calculated using several different quantum chemistry methods. See Figure 2 in manuscript for the naming of the structures.

Method	aa cation[a]	ag cation[a]	gg cation[a]	Vertical[a]
B3LYP/6-311++G(3df,3pd)	8.28	8.29	8.31	8.36
MP2/6-311++G(3df,3pd)	8.44	8.44	8.44	8.52

a: electronic energy differences at the respective level of calculation method; b: single point CCSD(T)/6-311++G(3df,3pd) energy calculation using MP2/6-311++G(3df,3pd) geometries

Table S3: Relative electronic energies, in eV, of diethylether cation alcohol isomers calculated using several different quantum chemistry methods. See Figure 8 in manuscript for naming of the structures. Zero of energy is neutral diethylether calculated at the respective levels of quantum chemistry.

Method	H^+ transfer1	H^+ transfer2	H bonded1	Transition State1	Transition State2
B3LYP/6-311++G(3df,3pd)	9.47	9.51	9.18	10.66	10.83
PBE0/6-31++G(d,p)	9.41	9.44	9.28	10.56	10.74
PBE0/6-311++G(3df,3pd)	9.41	9.42	9.21	10.56	10.71
MP2/6-311++G(3df,3pd)	9.55	9.62	9.53	10.97	11.03

a: single point CCSD(T)/6-311++G(3df,3pd) energy calculation using MP2/6-311++G(3df,3pd) geometries

Table S4: Relative electronic energies, in eV, of diethylsulfide cation thiol isomers calculated using B3LYP.

See ESI Figure S6 for naming of the structures. Zero of energy is neutral diethylsulfide calculated at the respective levels of quantum chemistry.

Method	H^+ transfer1	H^+ transfer2	H bonded1	Transition State1	Transition State2
B3LYP/6-311++G(3df,3pd)	9.07	9.01	9.17	9.84	10.05
MP2/6-311++G(3df,3pd)	9.23	9.22	9.77	10.02	10.25

a: single point CCSD(T)/6-311++G(3df,3pd) energy calculation using MP2/6-311++G(3df,3pd) geometries

Contributions coming from ag conformer of diethyl sulfide

As shown below in Table S5, the ag isomer for diethyl sulfide (DES) does not show much difference with aa DES in terms of peak positions.

Table S5: Theoretical peak position, in cm^{-1}, and intensity, in km mol^{-1}, of CH stretching vibration of neutral ag DES calculated using the local mode model with B3LYP/6-31++G(d,p). See Figure 2 in text for numbering.

DES ag	C2H6	C2H7	C3H8	C3H9	C4H10	C4H11	C4H12	C5H13	C5H14	C5H15
Peak position	2976	2946	2960	2944	2959	2989	2995	2977	2990	2988
Intensity	20.8	38.0	31.4	37.4	59.1	27.2	21.1	43.0	23.5	23.6

Details of the Multidimensional vibrational calculation

Since there are several symmetrically equivalent CH bonds in DEE and DES, the intermode coupling can cause peaks to shift and split from the simple LM treatment results. Therefore, we also performed 65,536 (16^4) single point calculations for the 4 CH bonds next to the ether oxygen for DEE and DEE^+, to obtain a 4-dimensional potential energy surface (PES) and the dipole moment function (DMF). Using these functions, we performed a 4-dimensional vibrational calculation, LM-4D, to determine the extent of the coupling between the CH bonds. Using the direct product of the DVR basis we solved the following Schrödinger equation:

$$H = -\frac{\hbar^2}{2\mu_{CH}}\frac{\partial^2}{\partial R_{C2H6}^2}-\frac{\hbar^2}{2\mu_{CH}}\frac{\partial^2}{\partial R_{C2H7}^2}-\frac{\hbar^2}{2\mu_{CH}}\frac{\partial^2}{\partial R_{C3H8}^2}-\frac{\hbar^2}{2\mu_{CH}}\frac{\partial^2}{\partial R_{C3H9}^2}$$
$$-\frac{\cos(\angle H6C2H7)}{M_C}\frac{\partial}{\partial R_{C2H6}}\frac{\partial}{\partial R_{C2H7}}-\frac{\cos(\angle H8C3H9)}{M_C}\frac{\partial}{\partial R_{C3H8}}\frac{\partial}{\partial R_{C3H9}}$$
$$+V(R_{C2H6},R_{C2H7},R_{C3H8},R_{C3H9})$$

where, μ is the reduced mass and $\angle HCH$ is the angle between the two CH bonds bound to the same carbon (see Figure 2 for labeling of the atoms). As shown below in Tables S6 and S8-S10, the shifting in the peak positions induced by the intermode coupling is only ~20 cm^{-1} for DEE and DEE$^+$ studied using B3LYP.

For the DEE$^+$, in order to quantify the effect of bending motion toward the bands in the 2500 to 3100 cm^{-1} region, we also performed a 4D vibrational calculation using the normal mode (NM) coordinates give in Figure S3. Since the NM's have no coupling in the kinetic energy term, we solved the following Schrödinger equation:

$$\sum_{i=1}^{4} -\frac{\hbar^2}{2m_i}\frac{\partial^2}{\partial Q_i^2} + V(Q_1, Q_2, \ldots Q_n),$$

where Q_i , and m_i are the NM coordinate and the mass for mode *i*. The NM Cartesian displacements are extracted from the Gaussian output by using the "freq=hpmodes" keyword. Similar to the case above we used DVR method to solve the vibrational Hamiltonian and the single point values required for the PES and DMF are obtained from B3LYP. As given in Figure S3, the bending modes have harmonic frequencies at the 1300 to 1500 cm^{-1} range which is about half of the CH stretching modes at 2800 to 3000 cm^{-1}. Therefore, one may speculate that Fermi resonance like coupling may cause large variations in the CH stretching peaks. However as given in Tables S8-S10, the peak position for the two CH stretching modes considered is only slightly red shifted from the inclusion of the bending motion. Furthermore, we also found that the HCH bending overtones are fairly weak in intensity signifying that the interaction with the strong CH stretching mode is not strong for the DEE$^+$. These studies show that the peak positions originates from the local nature of the CH bond and only slightly modified ~50 cm^{-1} shifts, by the coupling to the bending modes. As a conclusion, these studies confirm that using the local mode model will give the correct physics to explain the spectral features seen in the experiments.

Table S6: Theoretical peak position, in cm^{-1}, and intensity, in km mol^{-1}, of CH stretching vibration of neutral aa DEE calculated using the 4 dimensional local mode (LM-4D) and the local mode (LM) model with B3LYP/6-31++G(d,p).

LM-4D		LM	
Peak position	Intensity	Peak position	Intensity
2852	14.3	2864	75
2866	126.2	2863	75
2875	1.1	2863	75
2878	141.6	2864	75

Table S7: Peak positions (in cm^{-1})and intensity (in km mol^{-1}) for the 10 CH stretching normal mode for aaDES. They were calculated using the vibrational perturbation theory method with normal modes by the B3LYP/6-31++G(d,p) method.

Assignment	Peak Position	Intensity
CH_2 A_1	2933	81
CH_2 A_2	2928	0
CH_2 B_1	2923	30
CH_2 B_2	2850	333
CH_3 A_1	2962	53
CH_3 A_1	2951	122
CH_3 A_2	2973	0
CH_3 B_1	2973	44
CH_3 B_2	2962	10
CH_3 B_2	2872	68

Table S8: Theoretical peak position, in cm^{-1}, and intensity, in km mol^{-1}, of CH stretching vibration of gg' DEE^+ calculated using the 4 dimensional normal mode (NM-4D), 4 dimensional local mode (LM-4D) and the local mode (LM) model with B3LYP/6-31++G(d,p).

NM-4D		LM-4D		LM	
Peak position	Intensity	Peak position	Intensity	Peak position	Intensity
2718	202.0	2765	172.9	2766	168.5
		2939	20.1	2958	31.0
2965	1.1	2986	1.2	2982	3.4
		3033	8.2	3013	0.5

Table S9: Theoretical peak position, in cm^{-1}, and intensity, in km mol^{-1}, of CH stretching vibration of gg DEE^+ calculated using the 4 dimensional normal mode (NM-4D), 4 dimensional local mode (LM-4D) and the local mode (LM) model with B3LYP/6-31++G(d,p).

NM-4D		LM-4D		LM	
Peak position	Intensity	Peak position	Intensity	Peak position	Intensity
		2936	44.8	2955	30.3
2927	9.6	2939	2.5	2958	29.4
2989	20.5	3033	14.0	3015	0.7
		3037	0.2	3015	0.7

Table S10: Theoretical peak position, in cm^{-1}, and intensity, in km mol^{-1}, of CH stretching vibration of sg DEE^+ calculated using the 4 dimensional normal mode (NM-4D), 4 dimensional local mode (LM-4D) and the local mode (LM) model with B3LYP/6-31++G(d,p).

NM-4d		LM-4D		LM	
Peak positions	Intensity	Peak position	Intensity	Peak position	Intensity

2790	72.0	2798	99.4	2817	104.2
2816	159.0	2852	117.1	2836	110.9
		2921	25.9	2930	38.5
		3088	4.7	3062	0.6

Table S11: Relative energies, in eV, of the argon tagged complex of diethylether cation. See Figure S2 for the naming.

Conformer	DE(eV)
gg1	0.0000
gg2	0.0086
gg3	0.0127
gg4	0.0157
gg'1	0.0263
gg'2	0.0332
gg"1	0.0487
gg"2	0.0571
sg1	0.0502
sg2	0.0602
sg3	0.0610

FIGURES

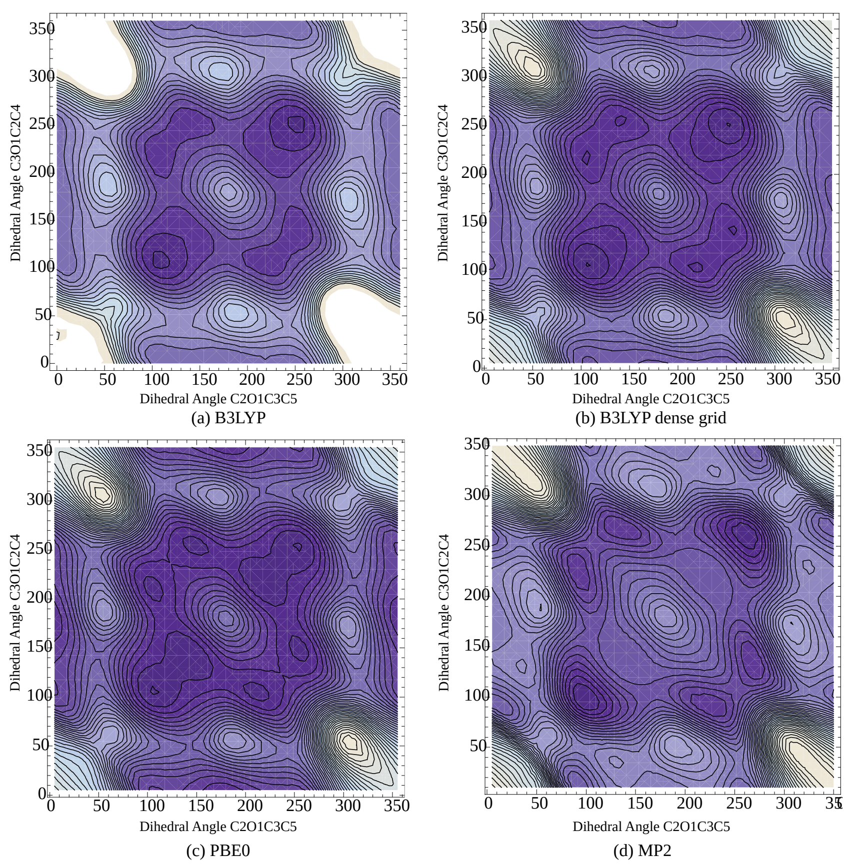
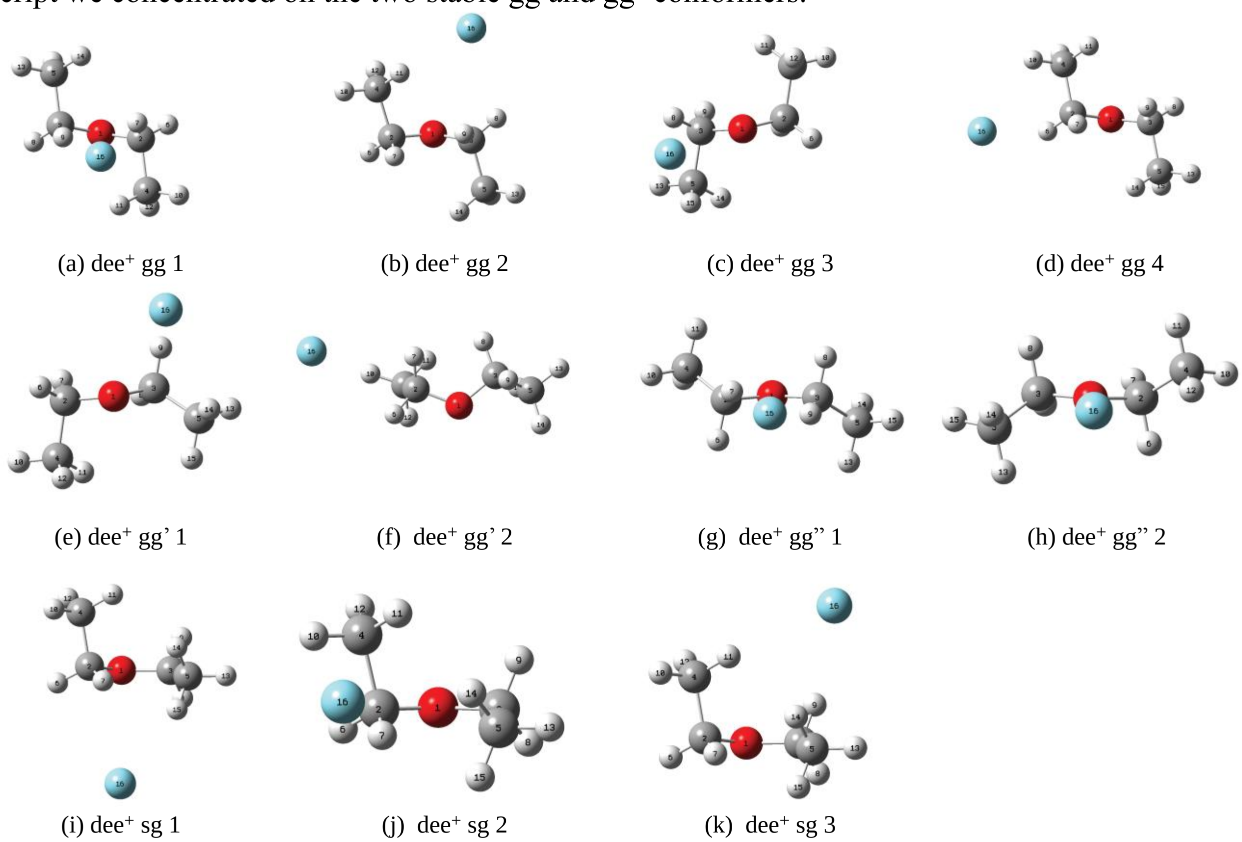


Figure S1: Two dimensional potential energy surface for the torsion motion of the ethyl group for DEE+ calculated using B3YP/6-31++G(d,p), (c) PBE0/6-31++G(d,p), and (d) MP2/6-311++G(3df,3pd). The quantum chemistry calculation was done for each 10 degree grids. For (b) we obtained the results using a 5 degree grid. Each contour line corresponds to 0.01 eV and the darker the plot, the lower the energy.

As can be seen from the above Fig S1, using more points in the grid for the quantum chemistry calculation clarifies the minima locations, but the general trend is given by the calculation from 10 degree grids. Furthermore, the contour of the potential is similar for all methods. This gives us confidence in using B3LYP for the analysis in the manuscript.

To search for possible Ar-tagged DEE^{+} conformers, we performed successive constraint optimization. First, fixing the DEE^{+} geometry we placed the Ar atom on a 30 point sphere grid points around the central oxygen for 5 polar angles (θ: 30, 60, 90, 120, 150) and 6 azimuthal angles (ϕ: 0, 60, 120, 180, 240, 300) and optimized the OAr distance. Then using the obtained OAr bond distance as initial geometry we simultaneously optimized the OAr distance and the polar/azimuthal angles while keeping the DEE^{+} geometry fixed. Lastly, using these previous Ar geometries as initial geometries we performed full optimization of the 1:1 complex. In Figure S2 we present the structure of the low energy argon bound complexes calculated by MP2 method. Though there are many positions which argon is bound, in most cases here the argon binds to the tip of the XH bond, as similar to the protonated water clusters. As can be seen from the relative energies given in Table S6, generally speaking the relative energy orderings is similar to the bare MP2 results gg<gg'<gg"<sg, thus in the vibrational calculation section of the manuscript we concentrated on the two stable gg and gg' conformers.



(a) dee^{+} gg 1 (b) dee^{+} gg 2 (c) dee^{+} gg 3 (d) dee^{+} gg 4

(e) dee^{+} gg' 1 (f) dee^{+} gg' 2 (g) dee^{+} gg" 1 (h) dee^{+} gg" 2

(i) dee^{+} sg 1 (j) dee^{+} sg 2 (k) dee^{+} sg 3

Figure S2: Schematic diagram of the argon bound diethylether cation cluster: (a-d) gg conformer, (e,f) gg' conformer, (g,h) gg" conformer, and (i-k) sg conformer.

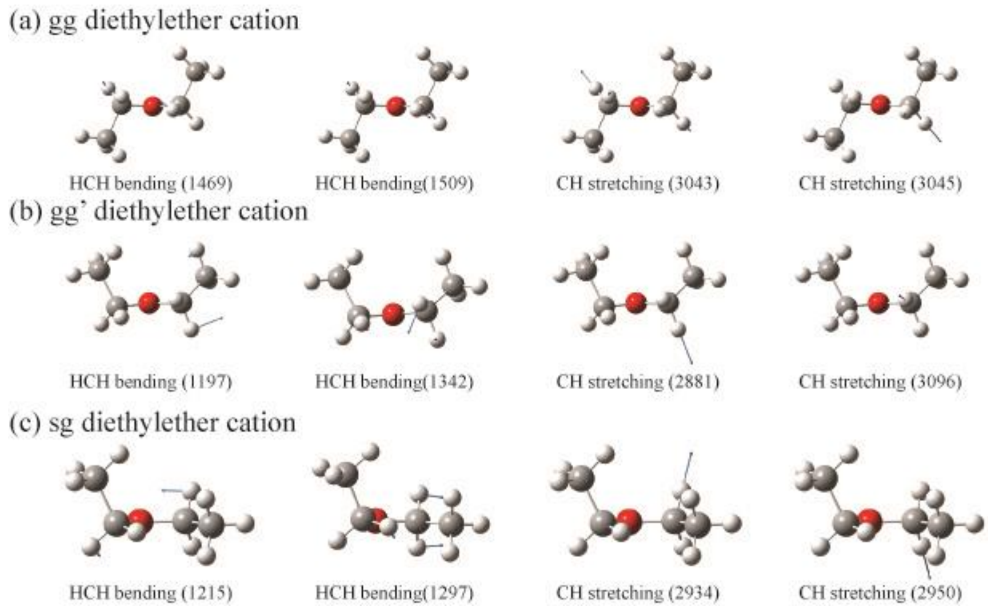


Figure S3: Schematic diagram of the HCH bending and CH stretching vibration that are considered in the present study for (a) gg (b) gg' and (c) sg diethyl ether cation. The harmonic frequencies, in cm^{-1}, are given in parenthesis.

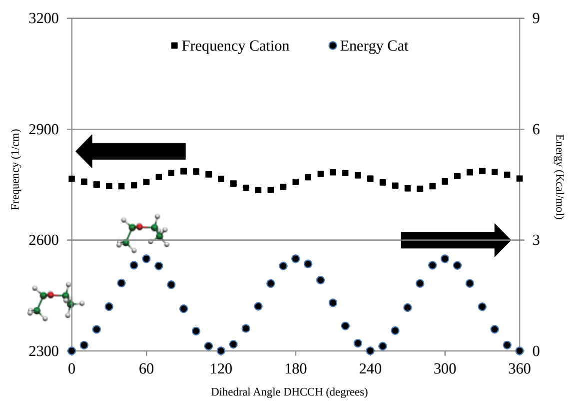


Figure S4: Methyl rotation dihedral angle dependence of the energy (circles), in kcal/mol, and C3H9 vibrational frequency (squares), in cm^{-1}, for diethylether cation. Calculated using B3LYP/6-31++G(d,p).

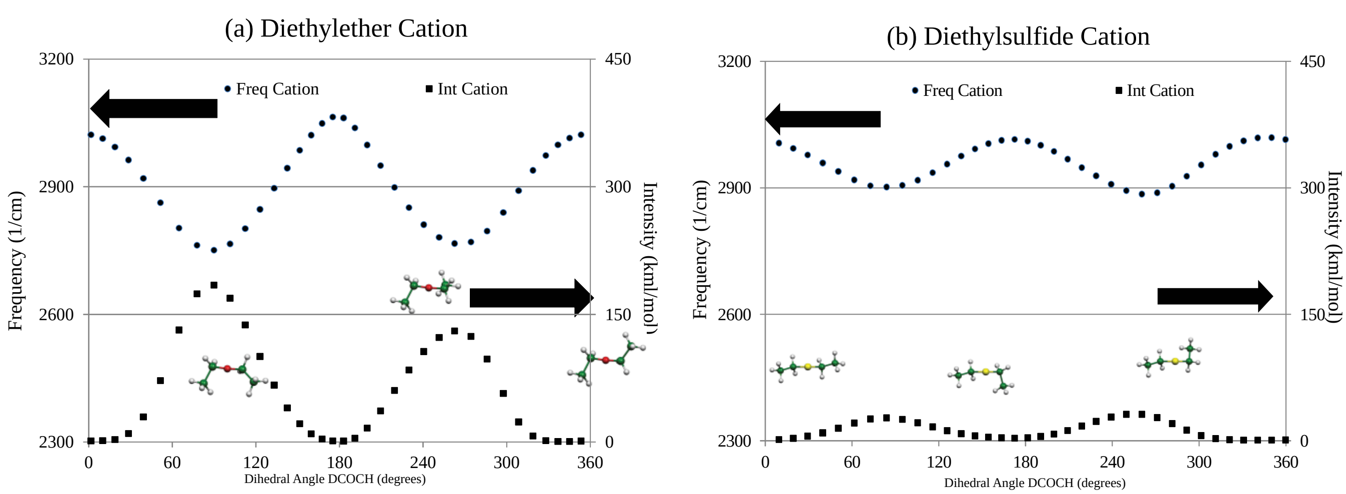
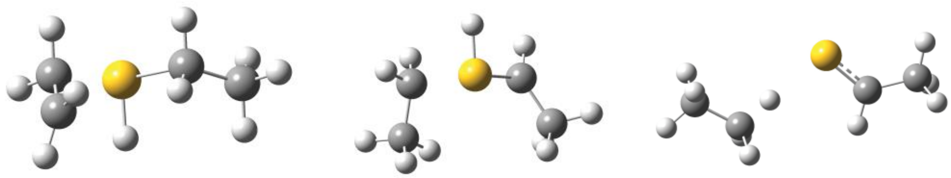
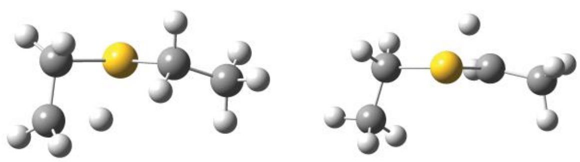


Figure S5: COCH dihedral angle dependence of the C3H9 vibrational frequency (circles), in cm^{-1}, and intensity (squares), in km/mol, for (a) diethylether cation and (b) diethylsulfide cation. Calculated using B3LYP/6-31++G(d,p).



(a) H^+ transfer isomer 1 (b) H^+ transfer isomer 2 (c) H bonded isomer



(e) gg' to H^+ transfer TS (e) gg' to H^+ transfer TS

Figure S6: Schematic diagram of the (a) proton transfer isomer 1 of DES^+, (b) proton transfer isomer 2 of DES^+, (c) the hydrogen bonded complex, (d) the transition state connecting ag DES^+ to the proton transfer isomer 1 and (e) the transition state connecting ag DES^+ isomer to proton transfer isomer 2.

XYZ geometries optimized using MP2/6-311++G(3df,3pd)

DEE aa Neutral

O	0.0000	0.0000	0.2727
C	0.0000	1.1712	-0.5175
C	0.0000	-1.1712	-0.5175
C	0.0000	-2.3666	0.4058
C	0.0000	2.3666	0.4058
H	-0.8849	-1.1809	-1.1653
H	0.8849	-1.1809	-1.1653
H	0.8849	1.1809	-1.1653
H	-0.8849	1.1809	-1.1653
H	0.0000	-3.2898	-0.1712
H	0.8829	-2.3517	1.0406
H	-0.8829	-2.3517	1.0406
H	0.0000	3.2898	-0.1712
H	-0.8829	2.3517	1.0406
H	0.8829	2.3517	1.0406

DEE ag Neutral

O	0.0765	-0.6001	-0.3072
C	-1.2452	-0.6238	0.2000
C	0.9166	0.3215	0.3591
C	2.3227	0.1265	-0.1586
C	-2.0551	0.6088	-0.1641
H	0.5868	1.3490	0.1776

H	0.8726	0.1423	1.4406
H	-1.7040	-1.5109	-0.2329
H	-1.2188	-0.7537	1.2886
H	3.0047	0.8216	0.3283
H	2.6588	-0.8893	0.0361
H	2.3546	0.3016	-1.2316
H	-3.0866	0.4812	0.1629
H	-1.6649	1.5057	0.3117
H	-2.0487	0.7551	-1.2425

DEE gg cation

O	0.0000	0.0000	0.6047
C	0.0000	1.2061	-0.1071
C	0.0000	-1.2061	-0.1071
C	-1.4846	-1.6587	-0.1205
C	1.4846	1.6587	-0.1205
H	0.3748	-1.0492	-1.1163
H	0.5928	-1.9067	0.4756
H	-0.3748	1.0492	-1.1163
H	-0.5928	1.9067	0.4756
H	-1.4846	-2.6213	-0.6283
H	-1.8559	-1.7777	0.8916
H	-2.0951	-0.9530	-0.6752
H	1.4846	2.6213	-0.6283
H	1.8559	1.7777	0.8916
H	2.0951	0.9530	-0.6752

DEE gg' cation

O	-0.0262	-0.5654	-0.4948
C	-1.3162	-0.6185	0.0201
C	1.0768	-0.4651	0.3926
C	2.0281	0.6031	-0.1121
C	-1.7733	0.8744	0.0804
H	0.7134	-0.3216	1.4083
H	1.5356	-1.4616	0.2971
H	-1.9214	-1.1556	-0.7045
H	-1.3161	-1.0577	1.0155
H	2.9025	0.5917	0.5348
H	2.3399	0.3937	-1.1308
H	1.5665	1.5848	-0.0595
H	-2.8039	0.8318	0.4272
H	-1.1682	1.4292	0.7903
H	-1.7311	1.3241	-0.9054

DEE gg" cation

O	0.0000	-0.2715	-0.0012
C	1.1803	0.4400	-0.3264
C	2.3914	-0.3278	0.1511
C	-1.1800	0.4393	0.3268
C	-2.3917	-0.3274	-0.1506

H	1.1272	0.4496	-1.4306
H	1.0933	1.4637	0.0364
H	-1.1254	0.4470	1.4310
H	-1.0933	1.4637	-0.0341
H	3.2752	0.2015	-0.1975
H	2.4158	-0.3669	1.2362
H	2.3999	-1.3339	-0.2570
H	-2.4175	-0.3644	-1.2358
H	-2.3999	-1.3343	0.2555
H	-3.2751	0.2013	0.2000

DEE sg cation

O	-0.0512	-0.1195	0.0164
C	-0.0312	-0.0986	1.3972
C	1.1289	0.0182	-0.7692
C	-0.2493	1.4132	1.7646
C	2.4497	-0.0953	-0.0653
H	-0.9009	-0.6613	1.7269
H	0.9104	-0.4571	1.7988
H	0.9689	-0.7278	-1.5557
H	0.9646	0.9880	-1.2626
H	-0.2963	1.4233	2.8515
H	0.5888	2.0096	1.4199
H	-1.1829	1.7693	1.3442
H	3.2199	0.0242	-0.8253
H	2.5978	0.6849	0.6769
H	2.5855	-1.0743	0.3886

DEE cation H^+ transfer1

O	-0.0243	-0.0189	1.5521
C	-0.0037	-0.0745	0.0229
C	1.3054	0.0170	2.2527
C	1.9988	-1.2973	2.0489
C	1.8465	0.8683	1.8460
H	-0.5751	0.7356	1.8242
H	-1.3429	0.2711	-0.4671
H	0.7748	0.6176	-0.2848
H	0.2777	-1.1043	-0.1653
H	2.9027	-1.2841	2.6560
H	1.3773	-2.1239	2.3830
H	2.3021	-1.4503	1.0170
H	1.0331	0.1921	3.2889
H	-1.5252	1.2310	-0.9193
H	-2.1428	-0.4470	-0.3993

DEE cation H^+ transfer2

O	0.0000	0.0000	1.5197
C	0.0000	0.0000	0.0000

C	1.2810	0.0000	2.1917
C	1.1868	0.2892	3.6314
C	1.9126	-0.7519	1.7489
H	-0.5602	0.7117	1.8744
H	0.3120	-1.3839	-0.4803
H	-1.0111	0.3140	-0.2389
H	0.7253	0.7546	-0.2889
H	2.1939	0.3439	4.0364
H	0.6962	1.2439	3.8237
H	0.6481	-0.4992	4.1636
H	0.2262	-1.3696	-1.5663
H	1.3257	-1.6899	-0.2389
H	-0.3998	-2.1062	-0.0910

DEE cation H bonded1

O	0.0000	0.0000	2.7551
C	0.0000	0.0000	0.0000
C	1.1394	0.0000	3.2719
C	1.3046	-0.0001	4.7175
C	2.0062	0.0001	2.6093
H	0.0237	0.0001	1.7162
H	-1.4744	0.0000	-0.1838
H	0.5513	0.9191	-0.1585
H	0.5513	-0.9191	-0.1584
H	1.9103	0.8701	4.9860
H	0.3557	-0.0002	5.2412
H	1.9104	-0.8703	4.9859
H	-1.6841	-0.0001	-1.2602
H	-1.9454	-0.8902	0.2263
H	-1.9454	0.8902	0.2262

DEE cation OH TS1

O	-0.0236	0.0973	1.5067
C	0.0147	0.0407	0.0343
C	1.2827	0.0024	2.1751
C	1.0538	-0.2908	3.6288
C	1.8713	-0.7594	1.6629
H	1.7260	0.9835	1.9951
H	-0.5040	-1.3601	0.1215
H	-0.6715	0.7865	-0.3459
H	1.0265	0.1686	-0.3319
H	2.0177	-0.2903	4.1345
H	0.4257	0.4695	4.0846
H	0.6007	-1.2702	3.7684
H	-1.5459	-1.5402	-0.1228
H	0.2132	-2.1696	0.0438
H	-0.5821	-1.1951	1.3750

DEE cation OH TS2

O	0.0000	0.0000	1.4970
C	0.0000	0.0000	0.0000
C	1.2945	0.0000	2.1243
C	1.3456	-0.5805	3.4753
C	2.1219	0.0079	1.4244
H	0.4760	1.0081	1.9808
H	0.2261	-1.4146	-0.4517
H	-0.9837	0.3854	-0.2438
H	0.7740	0.6940	-0.3235
H	2.2312	-0.2161	3.9903
H	0.4543	-0.3461	4.0510
H	1.4275	-1.6674	3.3804
H	0.1871	-1.4282	-1.5399
H	1.2041	-1.7840	-0.1493
H	-0.5498	-2.0740	-0.0726

DES aa netral

S	0.0000	0.0000	0.5484
C	0.0000	-1.3747	-0.6205
C	0.0000	1.3747	-0.6205
C	0.0000	-2.6910	0.1414
C	0.0000	2.6910	0.1414
H	-0.8842	-1.2981	-1.2542
H	0.8842	-1.2981	-1.2542
H	0.8842	1.2981	-1.2542
H	-0.8842	1.2981	-1.2542
H	0.0000	-3.5298	-0.5527
H	0.8821	-2.7702	0.7743
H	-0.8821	-2.7702	0.7743
H	0.0000	3.5298	-0.5527
H	-0.8821	2.7702	0.7743
H	0.8821	2.7702	0.7743

DES ag netral

S	0.0704	-0.8372	-0.2024
C	-1.5357	-0.3404	0.4541
C	1.0631	0.5926	0.2755
C	-2.1828	0.8177	-0.2897
C	2.5190	0.3277	-0.0784
H	-2.1568	-1.2332	0.3822
H	-1.4190	-0.1109	1.5143
H	0.7062	1.4809	-0.2438
H	0.9509	0.7509	1.3491
H	-3.1628	1.0401	0.1331
H	-1.5780	1.7196	-0.2181
H	-2.3050	0.5734	-1.3429
H	3.1355	1.1822	0.1957

H	2.8910	-0.5490	0.4482
H	2.6306	0.1561	-1.1477

DES aa cation

S	0.0000	0.0000	0.4978
C	0.0000	1.4029	-0.6056
C	0.0000	-1.4029	-0.6056
C	0.0005	2.7075	0.1770
C	-0.0005	-2.7075	0.1770
H	0.8829	1.2853	-1.2402
H	-0.8834	1.2856	-1.2396
H	-0.8829	-1.2853	-1.2402
H	0.8834	-1.2856	-1.2396
H	0.0004	3.5315	-0.5320
H	-0.8854	2.7955	0.8009
H	0.8869	2.7952	0.8003
H	-0.0004	-3.5315	-0.5320
H	0.8854	-2.7955	0.8009
H	-0.8869	-2.7952	0.8003

DES ag cation

S	-0.0281	-0.7621	-0.2518
C	-1.1567	0.4045	0.4888
C	1.5398	-0.3256	0.4779
C	-2.5128	0.3666	-0.1984
C	2.1824	0.8181	-0.3214
H	-1.2094	0.1156	1.5438
H	-0.6717	1.3820	0.4363
H	1.3600	-0.0501	1.5165
H	2.1465	-1.2285	0.4317
H	-3.1711	1.0707	0.3044
H	-2.4355	0.6579	-1.2428
H	-2.9615	-0.6218	-0.1355
H	3.1469	1.0291	0.1350
H	2.3469	0.5343	-1.3576
H	1.5815	1.7230	-0.2847

DES gg cation

S	-0.0262	0.0000	-0.0202
C	0.0063	-0.0361	1.7620
C	1.7055	0.0361	-0.4426
C	0.1269	1.3966	2.3032
C	2.2596	-1.3966	-0.4638
H	-0.9308	-0.4979	2.0677
H	0.8456	-0.6602	2.0667
H	1.7625	0.4979	-1.4267
H	2.2140	0.6602	0.2915
H	0.1231	1.3331	3.3891
H	1.0547	1.8697	1.9915

H	-0.7140	2.0100	1.9906
H	3.3087	-1.3331	-0.7440
H	2.1944	-1.8697	0.5128
H	1.7431	-2.0100	-1.1974

DES cation H^+ transfer1

S	0.0134	-0.8387	0.0828
C	1.0512	0.5646	-0.3858
C	-1.7090	-0.2897	-0.3113
C	2.4542	0.3631	0.1667
C	-2.0740	1.0052	0.2797
H	1.0349	0.5580	-1.4754
H	0.5751	1.4700	-0.0175
H	-2.3106	-1.1222	0.0532
H	-1.7213	-0.2984	-1.4004
H	3.0724	1.1943	-0.1644
H	2.4564	0.3561	1.2548
H	2.9002	-0.5591	-0.1979
H	-1.9834	1.9141	-0.2900
H	-2.4301	1.0524	1.2957
H	-0.0207	-0.6194	1.4059

DES cation H^+ transfer2

S	-0.0069	-0.9536	-0.3414
C	-1.5432	-0.2491	0.3545
C	1.2963	-0.1869	0.5115
C	2.0239	0.9346	-0.1223
C	-1.6754	1.1945	-0.0945
H	1.4845	-0.5189	1.5217
H	-0.0308	-2.1349	0.2948
H	-2.3286	-0.8874	-0.0517
H	-1.4935	-0.3609	1.4348
H	3.0977	0.7461	-0.0755
H	1.7401	1.0821	-1.1611
H	1.8447	1.8619	0.4271
H	-2.6156	1.5846	0.2884
H	-0.8721	1.8110	0.3025
H	-1.6903	1.2761	-1.1792

DES cation H bonded

S	1.0448	1.1502	0.0001
C	-2.0233	-0.3073	-0.0003
C	1.3375	-0.4257	-0.0018
C	2.6676	-1.0601	0.0011
C	-3.5439	-0.2101	0.0007
H	0.4476	-1.0609	-0.0054

H	-1.5846	0.6965	-0.0223
H	-1.6710	-0.8519	-0.8781
H	-1.6680	-0.8153	0.8980
H	2.7169	-1.7150	-0.8736
H	3.4906	-0.3549	0.0047
H	2.7117	-1.7179	0.8739
H	-3.9893	-1.2016	0.0221
H	-3.8976	0.3370	0.8707
H	-3.9009	0.3005	-0.8899

DES cation SH TS1

S	0.0833	-0.7191	-0.3467
C	-1.1450	0.1835	0.6327
C	1.6416	-0.3292	0.5590
C	-2.4036	0.3773	-0.1977
C	1.9019	0.9112	-0.2392
H	-1.3180	-0.4403	1.5092
H	-0.6954	1.1255	0.9430
H	2.3413	-1.1432	0.3997
H	1.4263	-0.1924	1.6144
H	-3.1470	0.8772	0.4190
H	-2.2122	0.9976	-1.0705
H	-2.8173	-0.5752	-0.5211
H	1.6183	1.8696	0.1741
H	2.6735	0.8883	-0.9974
H	0.6736	0.4943	-1.0401

DES cation SH TS2

S	0.0191	-0.8029	-0.2780
C	-1.5568	-0.3068	0.4703
C	1.1469	0.3948	0.4296
C	2.5085	0.4902	-0.1457
C	-2.1248	0.8904	-0.2753
H	0.6864	1.1398	1.0642
H	0.8087	-1.0100	0.9006
H	-2.1877	-1.1897	0.3815
H	-1.3719	-0.1093	1.5249
H	3.1996	0.8744	0.6004
H	2.8704	-0.4723	-0.5044
H	2.4986	1.1801	-0.9943
H	-3.0816	1.1491	0.1730
H	-1.4717	1.7574	-0.2018
H	-2.2933	0.6601	-1.3248