Action spectroscopy of gas-phase carboxylate anions by multiple photon IR electron detachment/attachment

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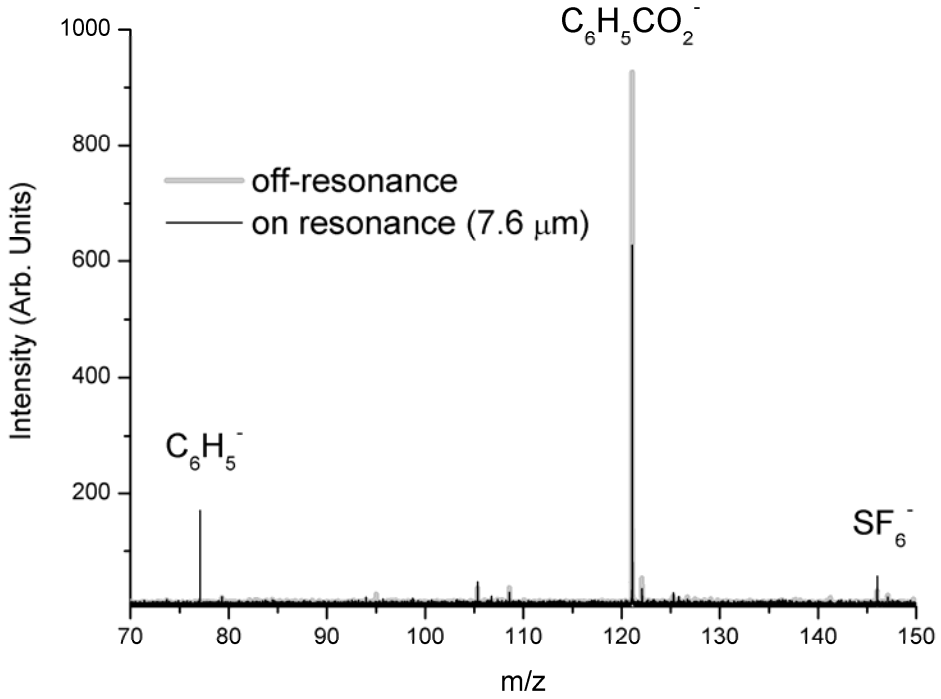
Supplementary Information

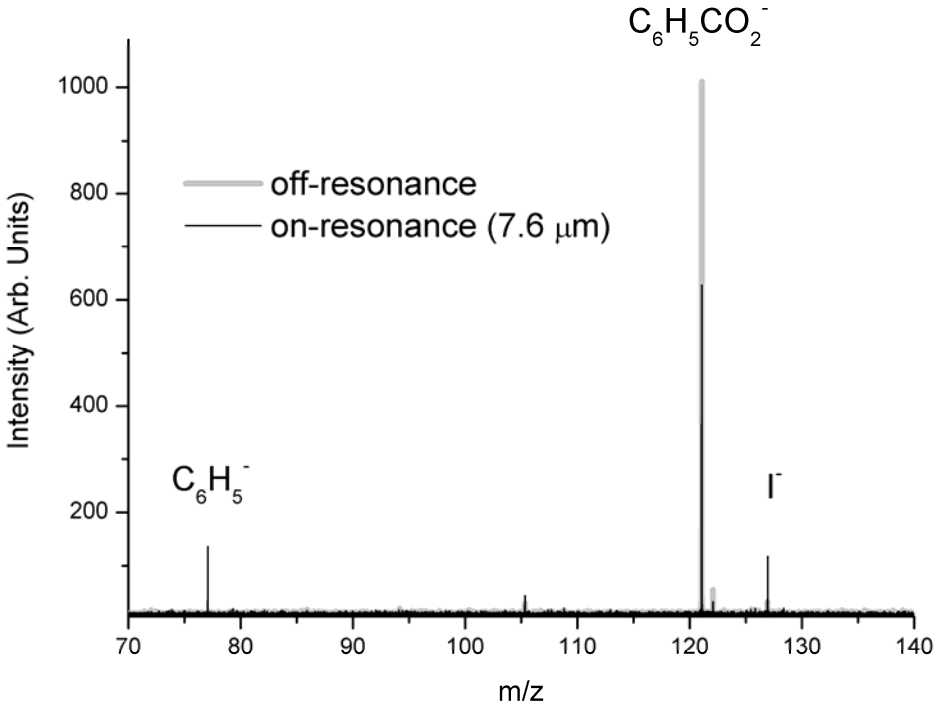
I. Mass Spectra

Benzoate mass spectra for the different scavengers while irradiated at the frequency of the symmetric stretch of the carboxylate group.

A.) SF_6 associative electron attachment:



B.) CH_3I dissociative electron attachment:



II. Full table of calculated dissociation versus detachment energies (in eV)

	Benzoate			**Acetate**			**Propionate**		
	Diss.	**AEA**	**VDE**	**Diss.**	**AEA**	**VDE**	**Diss.**	**AEA**	**VDE**
B3LYP/									
6-31+G*	2.49	3.43	3.97	2.71	3.14	3.64	2.93	3.16	3.60
6-31+G**	2.49	3.44	3.97	2.67	3.14	3.64	2.90	3.17	3.60
6-311++G**	2.31	3.48	4.02	2.50	3.17	3.66	2.70	3.20	3.61
aug-cc-pVDZ	2.39	3.42	3.95	2.54	3.13	3.64	2.75	3.16	3.59
aug-cc-pVTZ	2.41	3.43	3.96	2.41	3.14	3.63	2.61	3.17	3.58
CCSD(T)/									
6-31+G*	2.55	3.28	3.80	2.86	2.94	3.37	3.11	2.98	3.49
6-31+G**	2.52	3.30	3.81	2.79	2.97	3.40	3.04	3.01	3.52
6-311+G*	2.31	3.30	3.78	2.63	2.93	3.35	2.87	2.98	3.47
6-311++G**	2.27	3.33	3.80	2.51	2.98	3.39	2.74	3.03	-
aug-cc-pVDZ	-	-	-	2.55	3.12	3.54	2.84	3.16	-

III. Full table of calculated electron affinities (in eV) for the radicals corresponding to the anionic dissociation products resulting from CO_2 loss from benzoate, acetate and propionate.

	Adiabatic Electron Affinities		
	C_6H_5	**CH_3**	**C_2H_5**
B3LYP/			
6-31+G*	1.06	0.000	-0.32
6-31+G**	1.06	0.001	-0.30
6-311++G**	1.09	0.002	-0.24
aug-cc-pVDZ	1.09	-0.004	-0.19
aug-cc-pVTZ	0.94	-0.004	-0.20
CCSD(T)/			
6-31+G*	0.84	0.018	-0.73
6-31+G**	0.90	0.015	-0.64
6-311+G*	-	0.015	-0.64
6-311++G**	1.03	0.010	-0.48
aug-cc-pVDZ	-	0.002	-0.30

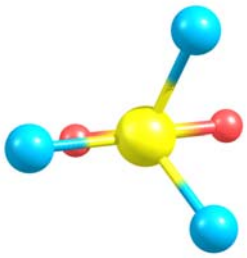
IV. Calculated Structures of Acetate and Propionate Ions: Rotamers.

A. Acetate

Acetate Cs #1 (staggered) B3LYP/aug-cc-pVDZ

6	-0.000664000	-1.353269000	0.000000000
1	1.047099000	-1.697879000	0.000000000
1	-0.486897000	-1.749594000	0.903872000
1	-0.486897000	-1.749594000	-0.903872000
6	-0.009781000	0.207239000	0.000000000
8	-0.000664000	0.754578000	-1.136678000
8	-0.000664000	0.754578000	1.136678000

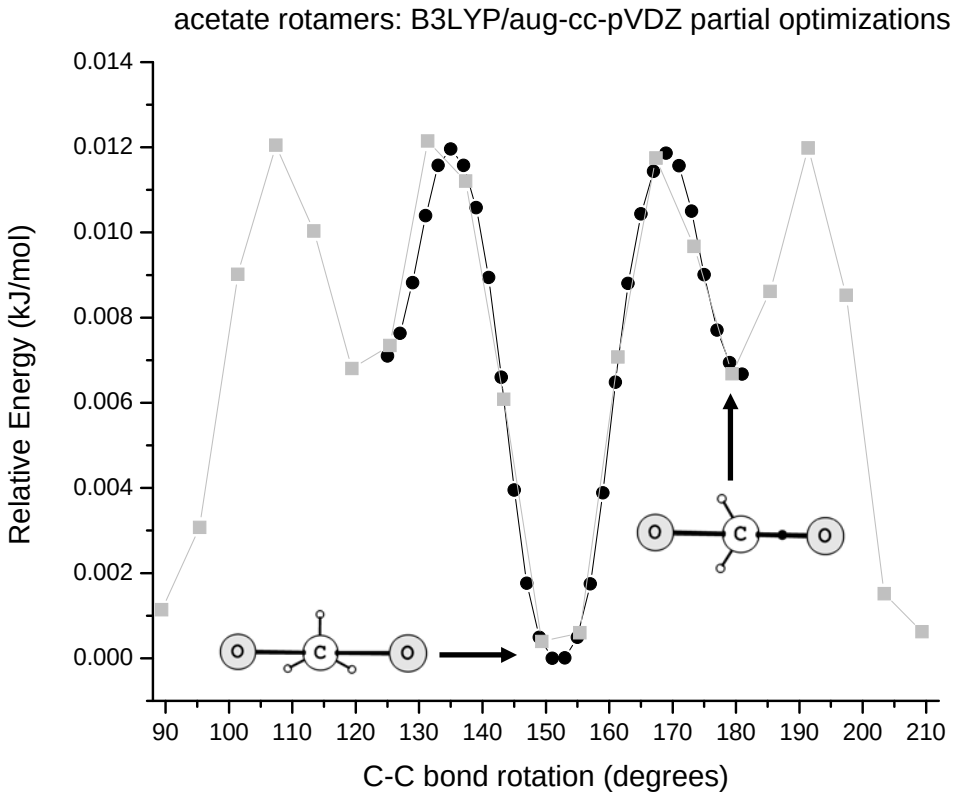
Acetate Cs #2 (eclipsed) B3LYP/aug-cc-pVDZ



6	0.035689000	-1.352495000	0.000000000
1	-0.496856000	-1.733837000	0.886248000
6	0.000000000	0.207171000	0.000000000
1	-0.496856000	-1.733837000	-0.886248000
1	1.068129000	-1.731456000	0.000000000
8	1.118018000	0.791713000	0.000000000
8	-1.154087000	0.717171000	0.000000000

acetate rotamers	acet- E	acet- zpe	acet-	diff Cs1(kJ/mol)
B3LYP/				
aug-cc-pVDZ (Cs-1:staggered)	-228.5625069	0.047462	-228.51504	
aug-cc-pVDZ (Cs-2:eclipsed)	-228.5625044	0.047449	-228.51506	-0.0275677
CCSD(T)/				
(@B3LYP/aug-cc-pVDZ opt)				
6-31+G* (Cs-1:staggered)	-227.9198154			
6-31+G* (Cs-2:eclipsed)	-227.9198071			0.0217916
6-31+G** (Cs-1:staggered)	-227.9449106			
6-31+G** (Cs-2:eclipsed)	-227.9448899			0.0543478
6-311+G* (Cs-1:staggered)	-228.01879			
6-311+G* (Cs-2:eclipsed)	-228.0187648			0.0661626
6-311++G** (Cs-1:staggered)	-228.0433741			
6-311++G** (Cs-2:eclipsed)	-228.0433161			0.1522790
aug-cc-pVDZ(Cs-1:staggered)	-228.0082621			
aug-cc-pVDZ (Cs-2:eclipsed)	-228.0082907			-0.0750893

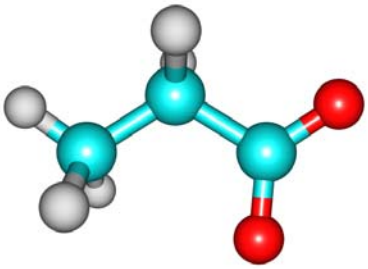
Calculated barrier to internal rotation for acetate



B. Propionate

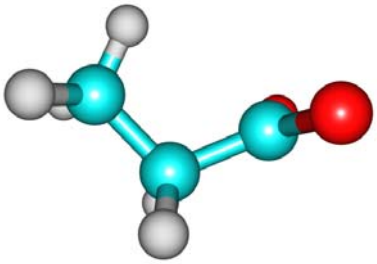
B3LYP/aug-cc-pVDZ

Cs1 E= -267.8805055 (0 imag. Freqs.)

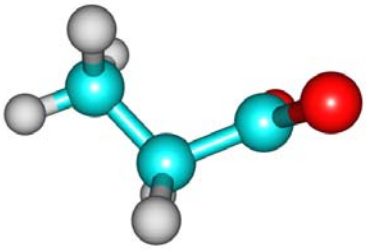


6	-0.262899000	-1.894691000	0.000000000
6	0.687453000	-0.694654000	0.000000000
1	0.290392000	-2.851320000	0.000000000
1	-0.919549000	-1.870920000	0.881149000
1	1.353040000	-0.730895000	0.878548000
1	-0.919549000	-1.870920000	-0.881149000
1	1.353040000	-0.730895000	-0.878548000
6	0.000000000	0.711177000	0.000000000
8	0.797932000	1.688350000	0.000000000
8	-1.261019000	0.727145000	0.000000000

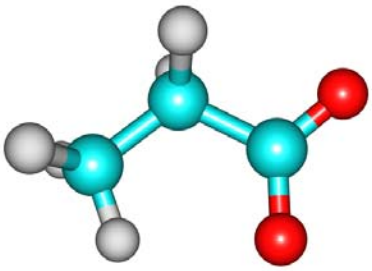
Cs2 E=-267.8742571 (2 imag. Freqs.)



Cs3 E=-267.8793643 (1 imag. Freq.)



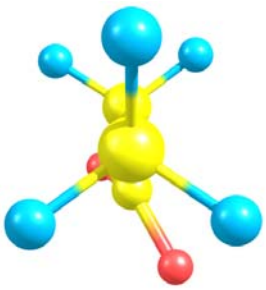
Cs4 E=-267.8779313 (1 imag. Freq.)



Cs#1 vs other Cs symmetry rotamers

B3LYP/aug-cc-pVDZ	prop- E	zpe	prop-	diff(kJ/mol)
Cs1	-267.88049	0.076	-267.8046	
Cs2	-267.87426	*imag*		16.36
Cs3	-267.87936	*imag*		2.95
Cs4	-267.87793	*imag*		6.72

C1: no symmetry

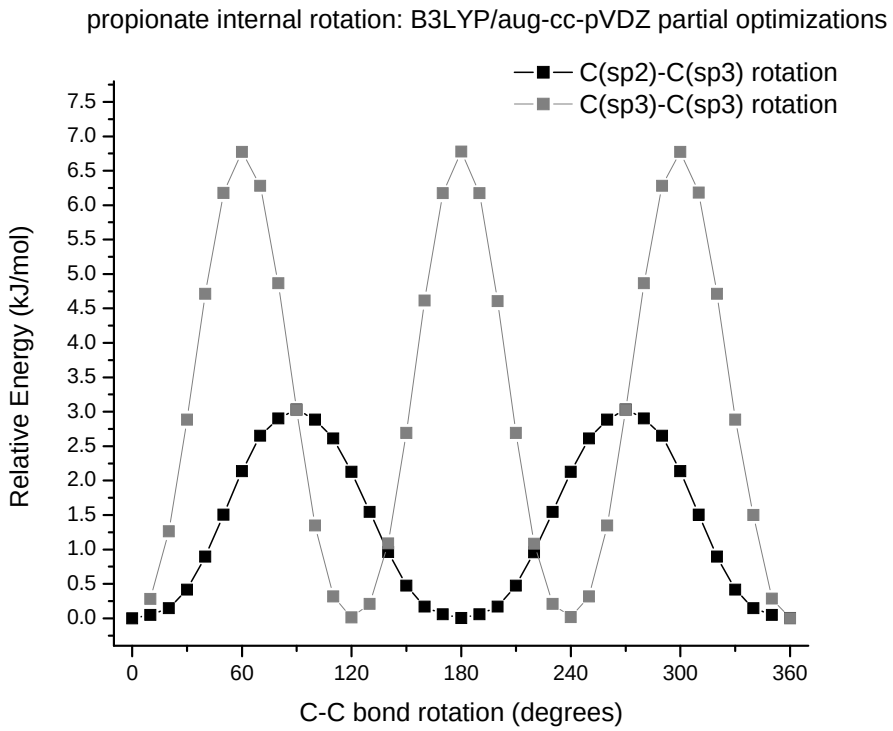


propionate C1 symmetry vs. Cs#1 symmetry

	prop- E	Zpe	prop-	diff(kJ/mol)
B3LYP/				
6-311++G** (Cs #1)	-267.9277	0.076	-267.8516	
6-311++G** (C1:no symmetry)	-267.92773	0.076	-267.8515	-0.06
aug-cc-pVDZ (Cs #1)	-267.88051	0.076	-267.8046	
aug-cc-pVDZ (C1:no symmetry)	-267.88049	0.076	-267.8046	0.04
CCSD(T)/(@B3LYP/aug-cc-pVDZ opt)				
6-31+G* (Cs1)	-267.10429			
6-31+G* (C1:no symmetry)	-267.10359			1.83
6-31+G** (Cs1)	-267.14617			
6-31+G** (C1:no symmetry)	-267.14569			1.27
6-311++G** (Cs1)	-267.25822			
6-311++G** (C1:no symmetry)	-267.25821			0.01
aug-cc-pVDZ (Cs1)	-267.2155			
aug-cc-pVDZ (C1:no symmetry)	-267.21437			2.96

The above calculations compare the energy of the optimized "staggered" propionate structure with no symmetry (C1) to the lowest energy optimized structure of Cs symmetry, for each of the given levels of theory. For most calculations, the symmetric structure is slightly lower in energy, as is also shown by the torsional barrier calculations below.

Calculated barriers to internal rotation for propionate



C. Comparison to Internal Rotation for Benzoate