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

Coupled-Cluster Sum-Frequency Generation Nonlinear Susceptibilities of the Methyl (CH_3) and Methylene (CH_2) Groups

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Supplementary information

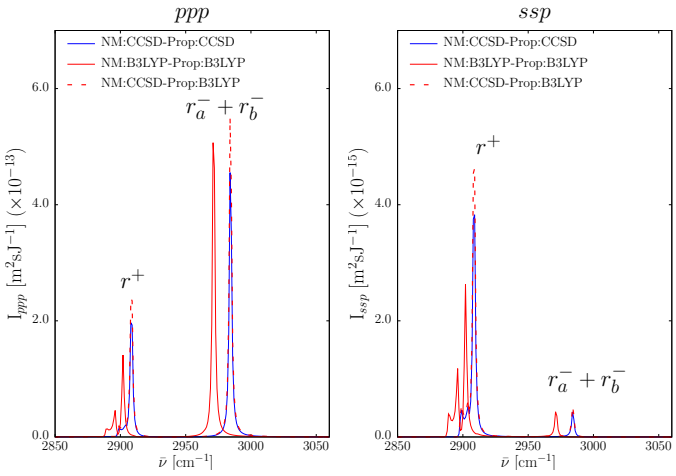

Figure SI-1 Comparison of the SFG spectra calculated at the CCSD and B3LYP (with the `SuperFine` integration grids) levels. NM ≡ Normal Modes (aug-cc-pVDZ), Prop ≡ Cartesian derivatives of the properties : $\partial\mu_\alpha/\partial r_{i\gamma}$ and $\partial\alpha_{\alpha\beta}/\partial r_{i\gamma}$ (aug-cc-pVDZ). In the hybrid results (dashed-red curves), the Cartesian derivatives of the properties calculated using the B3LYP/aug-cc-pVDZ method were projected onto the CCSD/aug-cc-pVDZ normal modes. The spectra are reported for the Free Chain model, at $\theta = 60°$ and $\xi = 150°$, and for ppp and ssp sets of polarizations. $\Gamma = 1$ cm^{-1}.

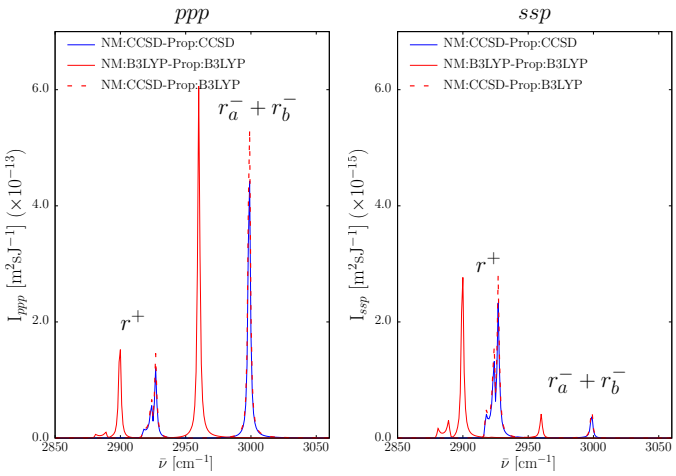

Figure SI-2 Comparison of the SFG spectra calculated at the CCSD and B3LYP (with the `SuperFine` integration grids) levels. NM ≡ Normal Modes (cc-pVTZ), Prop ≡ Cartesian derivatives of the properties : $\partial\mu_\alpha/\partial r_{i\gamma}$ and $\partial\alpha_{\alpha\beta}/\partial r_{i\gamma}$ (aug-cc-pVDZ). The six spectra combine Cartesian derivatives of the properties calculated using the aug-cc-pVDZ basis set with cc-pVTZ normal modes. These spectra are reported for the Free Chain model, at $\theta = 60°$ and $\xi = 150°$, and for ppp and ssp sets of polarizations. $\Gamma = 1$ cm^{-1}.

Table SI-1 Romberg's triangles for the dipole moment and the polarizability derivatives with respect to the x-atomic Cartesian coordinate of H_2 (in a.u.). Calculations were performed at the B3LYP/aug-cc-pVDZ level, for seven amplitudes of geometrical distortion ($\Delta r = 0.005$, 0.01, 0.02, 0.04, 0.08, 0.16, and 0.32 Å). The selected "best" values are highlighted in boxes, and the analytic derivatives (at the same level of calculation) are also reported. n is the Romberg's iteration number. The $\partial\mu_y/\partial x_{H_2}$ values were not reported because they are zero by symmetry.

	SuperFine grid							UltraFine grid						
$\Delta r/n$	0	1	2	3	4	5	6	0	1	2	3	4	5	6
							$\partial\mu_x/\partial x_{H_2}$							
0.005	0.00857	0.00857	0.00857	0.00857	0.00857	0.00857	0.00857	0.00857	0.00857	0.00857	0.00857	0.00857	0.00857	0.00857
0.010	0.00857	0.00857	0.00857	0.00857	0.00857	0.00857		0.00857	0.00857	0.00857	0.00857	0.00857	0.00857	
0.020	0.00857	0.00857	0.00857	0.00857	0.00857			0.00857	0.00857	0.00857	0.00857	0.00857		
0.040	0.00857	0.00857	0.00857	0.00857				0.00857	0.00857	0.00857	0.00857			
0.080	0.00857	0.00857	0.00857					0.00857	0.00857	0.00857				
0.160	0.00859	0.00850						0.00859	0.00850					
0.320	0.00885							0.00885						
Analytic				**0.00857**							**0.00855**			
							$\partial\mu_y/\partial x_{H_2}$							
0.005	0.09219	0.09219	0.09219	0.09219	0.09219	0.09219	0.09219	0.09219	0.09219	0.09219	0.09219	0.09219	0.09219	0.09219
0.010	0.09219	0.09219	0.09219	0.09219	0.09219	0.09219		0.09219	0.09219	0.09219	0.09219	0.09219	0.09219	
0.020	0.09218	0.09219	0.09219	0.09219	0.09219			0.09218	0.09219	0.09219	0.09219	0.09219		
0.040	0.09218	0.09219	0.09219	0.09219				0.09218	0.09219	0.09219	0.09219			
0.080	0.09215	0.09219	0.09218					0.09215	0.09219	0.09218				
0.160	0.09203	0.09222						0.09203	0.09222					
0.320	0.09147							0.09147						
Analytic				**0.09218**							**0.09218**			
							$\partial\mu_z/\partial x_{H_2}$							
0.005	0.06294	0.06294	0.06294	0.06294	0.06294	0.06294	0.06294	0.06294	0.06294	0.06294	0.06294	0.06294	0.06294	0.06294
0.010	0.06295	0.06295	0.06295	0.06295	0.06295	0.06295		0.06295	0.06294	0.06294	0.06294	0.06294	0.06294	
0.020	0.06296	0.06295	0.06295	0.06295	0.06295			0.06296	0.06294	0.06294	0.06294	0.06294		
0.040	0.06301	0.06295	0.06295	0.06295				0.06300	0.06294	0.06294	0.06294			
0.080	0.06319	0.06295	0.06295					0.06318	0.06295	0.06294				
0.160	0.06389	0.06299						0.06389	0.06299					
0.320	0.06658							0.06658						
Analytic				**0.06295**							**0.06292**			
							$\partial\alpha_{xx}/\partial x_{H_2}$							
0.005	−1.19380	−1.19377	−1.19377	−1.19377	−1.19377	−1.19377	−1.19377	−1.19490	−1.19487	−1.19487	−1.19487	−1.19487	−1.19487	−1.19487
0.010	−1.19390	−1.19377	−1.19377	−1.19377	−1.19377	−1.19377		−1.19500	−1.19487	−1.19487	−1.19487	−1.19487	−1.19487	
0.020	−1.19428	−1.19377	−1.19377	−1.19377	−1.19377			−1.19538	−1.19487	−1.19487	−1.19487	−1.19487		
0.040	−1.19582	−1.19377	−1.19377	−1.19377				−1.19690	−1.19487	−1.19487	−1.19487			
0.080	−1.20199	−1.19376	−1.19377					−1.20299	−1.19483	−1.19486				
0.160	−1.22670	−1.19359						−1.22745	−1.19445					
0.320	−1.32605							−1.32647						
Analytic				**−1.19384**							**−1.19411**			
							$\partial\alpha_{yy}/\partial x_{H_2}$							
0.005	−2.30948	−2.30952	−2.30952	−2.30952	−2.30952	−2.30952	−2.30952	−2.30956	−2.30959	−2.30959	−2.30959	−2.30959	−2.30959	−2.30959
0.010	−2.30938	−2.30952	−2.30952	−2.30952	−2.30952	−2.30952		−2.30945	−2.30959	−2.30959	−2.30959	−2.30959	−2.30959	
0.020	−2.30897	−2.30952	−2.30952	−2.30952	−2.30952			−2.30904	−2.30959	−2.30959	−2.30959	−2.30959		
0.040	−2.30734	−2.30951	−2.30952	−2.30952				−2.30741	−2.30958	−2.30959	−2.30959			
0.080	−2.30081	−2.30949	−2.30950					−2.30087	−2.30955	−2.30957				
0.160	−2.27479	−2.30926						−2.27484	−2.30928					
0.320	−2.17140							−2.17150						
Analytic				**−2.30943**							**−2.30957**			
							$\partial\alpha_{zz}/\partial x_{H_2}$							
0.005	−1.81362	−1.81363	−1.81363	−1.81363	−1.81363	−1.81363	−1.81363	−1.81537	−1.81538	−1.81538	−1.81538	−1.81538	−1.81538	−1.81538
0.010	−1.81361	−1.81363	−1.81363	−1.81363	−1.81363	−1.81363		−1.81535	−1.81537	−1.81537	−1.81537	−1.81537	−1.81537	
0.020	−1.81354	−1.81363	−1.81363	−1.81363	−1.81363			−1.81528	−1.81537	−1.81537	−1.81537	−1.81537		
0.040	−1.81328	−1.81363	−1.81363	−1.81363				−1.81499	−1.81538	−1.81538	−1.81538			
0.080	−1.81220	−1.81366	−1.81365					−1.81383	−1.81539	−1.81539				
0.160	−1.80784	−1.81386						−1.80916	−1.81539					
0.320	−1.78978							−1.79045						
Analytic				**−1.81383**							**−1.81381**			

Table SI-2 Vibrational frequencies* (cm^{-1}) and derivatives of the dipole moment ($\partial\mu_\alpha/\partial Q$) and of the polarizability ($\partial\alpha_{\alpha\beta}/\partial Q$),‡ computed at the B3LYP/aug-cc-pVDZ (with the `SuperFine` grid) level.†.The " ′ " indicates the derivative with respect to the corresponding normal coordinate.

	r^+	r_a^-	r_b^-	$d^+(d_1^+/d_2^+)$§	$d^-(d_1^-/d_2^-)$§
	2902	2965	2971	2889/2896	2911/2934
Freq	2902	2965	2972	2893	2922
	2901	2961	2971		
	0.075	0.000	0.205	0.006/0.208	0.000/0.000
μ_x'	0.006	0.000	0.202	0.150	0.000
	0.008	0.000	0.188		
	0.000	0.263	0.000	0.000/0.000	0.013/0.203
μ_y'	0.000	0.233	0.000	0.000	0.135
	0.000	0.186	0.000		
	0.225	0.000	0.019	0.029/0.104	0.000/0.000
μ_z'	0.183	0.000	0.021	0.122	0.000
	0.185	0.000	0.031		
	8.203	0.000	6.486	7.402/2.022	0.000/0.000
α_{xx}'	7.379	0.000	6.618	5.581	0.000
	7.303	0.000	6.091		
	8.799	0.000	2.926	10.248/2.943	0.000/0.000
α_{yy}'	7.865	0.000	2.770	8.153	0.000
	7.753	0.000	3.486		
	7.562	0.000	1.489	4.172/2.243	0.000/0.000
α_{zz}'	7.273	0.000	1.568	3.523	0.000
	7.233	0.000	1.246		
	0.000	2.505	0.000	0.000/0.000	8.771/0.346
α_{xy}'	0.000	1.961	0.000	0.000	6.708
	0.000	3.775	0.000		
	0.198	0.000	5.475	3.374/0.346	0.000/0.000
α_{xz}'	0.515	0.000	5.439	2.653	0.000
	0.556	0.000	5.655		
	0.000	4.053	0.000	0.000/0.000	5.607/1.040
α_{yz}'	0.000	3.791	0.000	0.000	4.738
	0.000	4.978	0.000		

*The harmonic vibrational frequencies have been scaled by a factor of 0.96.
†For each property the first, second, and third rows correspond to the Free Chain, Free Ethyl, and Free Methyl models, respectively.
‡ $\alpha_{xy}' = \alpha_{yx}'$; $\alpha_{xz}' = \alpha_{zx}'$; $\alpha_{yz}' = \alpha_{zy}'$.
§ d_1^+, d_2^+, d_1^-, d_2^- ≡ Free Chain; d^+, d^- ≡ Free Ethyl.

Table SI-3 Vibrational frequencies* (cm^{-1}), and derivatives of the dipole moment ($\partial\mu_\alpha/\partial Q$) and of the polarizability ($\partial\alpha_{\alpha\beta}/\partial Q$),‡. Cartesian dipole moment and polarizability derivatives have been calculated at B3LYP/aug-cc-pVDZ (with the `SuperFine` grid) level and projected onto the CCSD/aug-cc-pVDZ normal modes.†.The " ′ " indicates the derivative with respect to the corresponding normal coordinate.

	r^+	r_a^-	r_b^-	$d^+(d_1^+/d_2^+)$§	$d^-(d_1^-/d_2^-)$§
	2909	2978	2984	2898/2904	2926/2948
Freq	2908	2977	2984	2901	2936
	2908	2974	2984		
	0.032	0.000	0.205	0.003/0.219	0.000/0.000
μ_x'	0.021	0.000	0.202	0.149	0.000
	0.005	0.000	0.190		
	0.000	0.260	0.000	0.000/0.000	0.013/0.207
μ_y'	0.000	0.232	0.000	0.000	0.137
	0.000	0.186	0.000		
	0.197	0.000	0.021	0.045/0.147	0.000/0.000
μ_z'	0.161	0.000	0.023	0.151	0.000
	0.185	0.000	0.032		
	9.089	0.000	6.466	6.712/0.449	0.000/0.000
α_{xx}'	8.296	0.000	6.583	4.346	0.000
	7.420	0.000	6.102		
	10.013	0.000	3.060	9.576/1.165	0.000/0.000
α_{yy}'	9.104	0.000	2.919	6.825	0.000
	7.779	0.000	3.577		
	8.151	0.000	1.490	3.569/0.740	0.000/0.000
α_{zz}'	7.741	0.000	1.559	2.324	0.000
	7.240	0.000	1.264		
	0.000	2.594	0.000	0.000/0.000	8.776/0.364
α_{xy}'	0.000	2.070	0.000	0.000	6.705
	0.000	3.806	0.000		
	0.070	0.000	5.556	3.419/0.331	0.000/0.000
α_{xz}'	0.162	0.000	5.522	2.709	0.000
	0.643	0.000	5.718		
	0.000	4.096	0.000	0.000/0.000	5.639/1.002
α_{yz}'	0.000	3.834	0.000	0.000	4.736
	0.000	4.976	0.000		

*The harmonic vibrational frequencies have been scaled by a factor of 0.96.
†For each property the first, second, and third rows correspond to the Free Chain, Free Ethyl, and Free Methyl models, respectively.
‡ $\alpha_{xy}' = \alpha_{yx}'$; $\alpha_{xz}' = \alpha_{zx}'$; $\alpha_{yz}' = \alpha_{zy}'$.
§ d_1^+, d_2^+, d_1^-, d_2^- ≡ Free Chain; d^+, d^- ≡ Free Ethyl.

Table SI-4 Vibrational frequencies* (cm^{-1}), and derivatives of the dipole moment ($\partial\mu_\alpha/\partial Q$) and of the polarizability ($\partial\alpha_{\alpha\beta}/\partial Q$),‡. Cartesian dipole moment and polarizability derivatives have been calculated at the CCSD/aug-cc-pVDZ level and projected onto CCSD/cc-pVTZ normal modes.†.The " $'$ " indicates the derivative with respect to the corresponding normal coordinate.

	r^+	r_a^-	r_b^-	$d^+(d_1^+/d_2^+)$§	$d^-(d_1^-/d_2^-)$§
	2927	2993	2999	2917/2924	2941/2963
Freq	2926	2992	2999	2921	2951
	2926	2989	2998		
	0.074	0.003	0.202	0.004/0.198	0.000/0.003
μ_x'	0.007	0.003	0.200	0.142	0.002
	0.006	0.002	0.186		
	0.001	0.258	0.003	0.000/0.003	0.012/0.197
μ_y'	0.000	0.229	0.003	0.002	0.131
	0.000	0.182	0.003		
	0.216	0.000	0.020	0.035/0.100	0.000/0.000
μ_z'	0.165	0.000	0.022	0.133	0.000
	0.176	0.000	0.032		
	7.978	0.069	5.828	6.440/2.044	0.208/0.015
α_{xx}'	7.459	0.056	5.926	4.509	0.168
	7.015	0.100	5.439		
	8.551	0.066	2.646	9.364/2.843	0.227/0.003
α_{yy}'	7.994	0.052	2.526	7.039	0.165
	7.315	0.097	3.208		
	6.983	0.001	1.352	3.707/2.123	0.005/0.004
α_{zz}'	6.853	0.002	1.410	2.758	0.001
	6.585	0.001	1.105		
	0.013	2.331	0.119	0.048/0.001	7.806/0.348
α_{xy}'	0.006	1.831	0.119	0.035	5.997
	0.004	3.467	0.122		
	0.100	0.046	4.872	3.145/0.280	0.068/0.014
α_{xz}'	0.306	0.043	4.844	2.481	0.059
	0.538	0.059	5.046		
	0.004	3.574	0.065	$0.039-0.010$	5.069/0.928
α_{yz}'	0.003	3.325	0.065	0.035	4.278
	0.007	4.413	0.068		

*The harmonic vibrational frequencies have been scaled by a factor of 0.96.
†For each property the first, second, and third rows correspond to the Free Chain, Free Ethyl, and Free Methyl models, respectively.
‡ $\alpha_{xy}' = \alpha_{yx}'$; $\alpha_{xz}' = \alpha_{zx}'$; $\alpha_{yz}' = \alpha_{zy}'$.
§ d_1^+, d_2^+, d_1^-, d_2^- ≡ Free Chain; d^+, d^- ≡ Free Ethyl.

Table SI-5 Vibrational frequencies* (cm^{-1}), and derivatives of the dipole moment ($\partial\mu_\alpha/\partial Q$) and of the polarizability ($\partial\alpha_{\alpha\beta}/\partial Q$),‡. Cartesian dipole moment and polarizability derivatives have been calculated at the B3LYP/aug-cc-pVDZ (with the `SuperFine` grid) level and projected onto B3LYP/cc-pVTZ (with the `SuperFine` grid) normal modes.†.The " ′ " indicates the derivative with respect to the corresponding normal coordinate.

	r^+	r_a^-	r_b^-	$d^+(d_1^+/d_2^+)$§	$d^-(d_1^-/d_2^-)$§
	2900	2955	2960	2881/2889	2897/2921
Freq	2899	2954	2960	2885	2907
	2899	2951	2959		
	0.052	0.002	0.204	0.004/0.212	0.000/0.001
μ_x'	0.016	0.001	0.201	0.146	0.001
	0.008	0.001	0.185		
	0.000	0.257	0.001	0.000/0.001	0.012/0.205
μ_y'	0.000	0.229	0.001	0.001	0.135
	0.000	0.184	0.001		
	0.212	0.000	0.017	0.016/0.126	0.000/0.000
μ_z'	0.189	0.000	0.020	0.110	0.000
	0.183	0.000	0.032		
	7.601	0.020	6.463	7.975/0.778	0.096/0.002
α_{xx}'	6.902	0.015	6.584	5.891	0.069
	7.178	0.035	6.006		
	8.051	0.026	2.744	10.910/1.594	0.088/0.004
α_{yy}'	7.236	0.020	2.598	8.541	0.071
	7.659	0.039	3.393		
	7.301	0.002	1.548	4.811/1.231	0.003/0.001
α_{zz}'	6.961	0.002	1.620	3.923	0.002
	7.151	0.002	1.268		
	0.000	2.499	0.047	0.014/0.005	8.627/0.324
α_{xy}'	0.004	1.981	0.047	0.013	6.591
	0.003	3.714	0.048		
	0.435	0.026	5.360	3.355/0.283	0.030/0.006
α_{xz}'	0.666	0.024	5.325	2.639	0.025
	0.559	0.029	5.572		
	0.001	4.020	0.032	0.019/0.001	5.504/0.981
α_{yz}'	0.005	3.766	0.031	0.014	4.633
	0.004	4.899	0.032		

*The harmonic vibrational frequencies have been scaled by a factor of 0.96.
†For each property the first, second, and third rows correspond to the Free Chain, Free Ethyl, and Free Methyl models, respectively.
‡ $\alpha_{xy}' = \alpha_{yx}'$; $\alpha_{xz}' = \alpha_{zx}'$; $\alpha_{yz}' = \alpha_{zy}'$.
§ d_1^+, d_2^+, d_1^-, d_2^- ≡ Free Chain; d^+, d^- ≡ Free Ethyl.

Table SI-6 Vibrational frequencies* (cm^{-1}), and derivatives of the dipole moment ($\partial\mu_\alpha/\partial Q$) and of the polarizability ($\partial\alpha_{\alpha\beta}/\partial Q$),‡. Cartesian dipole moment and polarizability derivatives have been calculated at the B3LYP/aug-cc-pVDZ (with the `SuperFine` grid) level and projected onto CCSD/cc-pVTZ normal modes.†.The " ′ " indicates the derivative with respect to the corresponding normal coordinate.

	r^+	r_a^-	r_b^-	$d^+(d_1^+/d_2^+)$§	$d^-(d_1^-/d_2^-)$§
	2927	2993	2999	2917/2924	2941/2963
Freq	2926	2992	2999	2921	2951
	2926	2989	2998		
	0.076	0.003	0.202	0.004/0.204	0.000/0.003
μ_x'	0.008	0.003	0.200	0.147	0.002
	0.006	0.002	0.186		
	0.001	0.260	0.003	0.000/0.003	0.012/0.199
μ_y'	0.000	0.230	0.003	0.002	0.132
	0.000	0.183	0.002		
	0.223	0.000	0.019	0.036/0.103	0.000/0.000
μ_z'	0.171	0.000	0.021	0.137	0.000
	0.183	0.000	0.032		
	8.314	0.073	6.323	6.975/2.105	0.229/0.016
α_{xx}'	7.737	0.058	6.427	4.873	0.184
	7.259	0.107	5.903		
	8.897	0.070	2.885	9.838/2.966	0.249/0.003
α_{yy}'	8.311	0.054	2.760	7.399	0.181
	7.598	0.104	3.476		
	7.522	0.002	1.502	3.927/2.285	0.006/0.004
α_{zz}'	7.387	0.002	1.564	2.923	0.001
	7.102	0.002	1.239		
	0.014	2.466	0.130	0.048/0.001	8.581/0.349
α_{xy}'	0.007	1.913	0.129	0.035	6.574
	0.004	3.711	0.132		
	0.162	0.050	5.384	3.387/0.295	0.074/0.015
α_{xz}'	0.381	0.047	5.354	2.677	0.065
	0.633	0.065	5.571		
	0.005	3.922	0.072	0.042/0.011	5.552/1.020
α_{yz}'	0.004	3.650	0.072	0.037	4.688
	0.008	4.841	0.075		

*The harmonic vibrational frequencies have been scaled by a factor of 0.96.
†For each property the first, second, and third rows correspond to the Free Chain, Free Ethyl, and Free Methyl models, respectively.
‡ $\alpha_{xy}' = \alpha_{yx}'$; $\alpha_{xz}' = \alpha_{zx}'$; $\alpha_{yz}' = \alpha_{zy}'$.
§ d_1^+, d_2^+, d_1^-, d_2^- ≡ Free Chain; d^+, d^- ≡ Free Ethyl.

Table SI-7 Ratio between the intensity (maximum) of the peaks $r_a^- + r_b^-$ and r^+ calculated within the Free Chain model (see figs. SI-1 and SI-2)

	ppp		*ssp*
		NM: aug-cc-pVDZ Properties: aug-cc-pVDZ	
NM:CCSD Properties:CCSD	2.3		0.11
NM:B3LYP Properties:B3LYP	3.6		0.14
NM:CCSD Properties:B3LYP	2.3		0.12
		NM: cc-pVTZ Properties: aug-cc-pVDZ	
NM:CCSD Properties:CCSD	3.6		0.16
NM:B3LYP Properties:B3LYP	4.0		0.15
NM:CCSD Properties:B3LYP	3.6		0.16