Supplementary Information

Vibrational Spectroscopy of the Hexahydrated Sulfate Dianion Revisited: Role of Isomers and Anharmonicities

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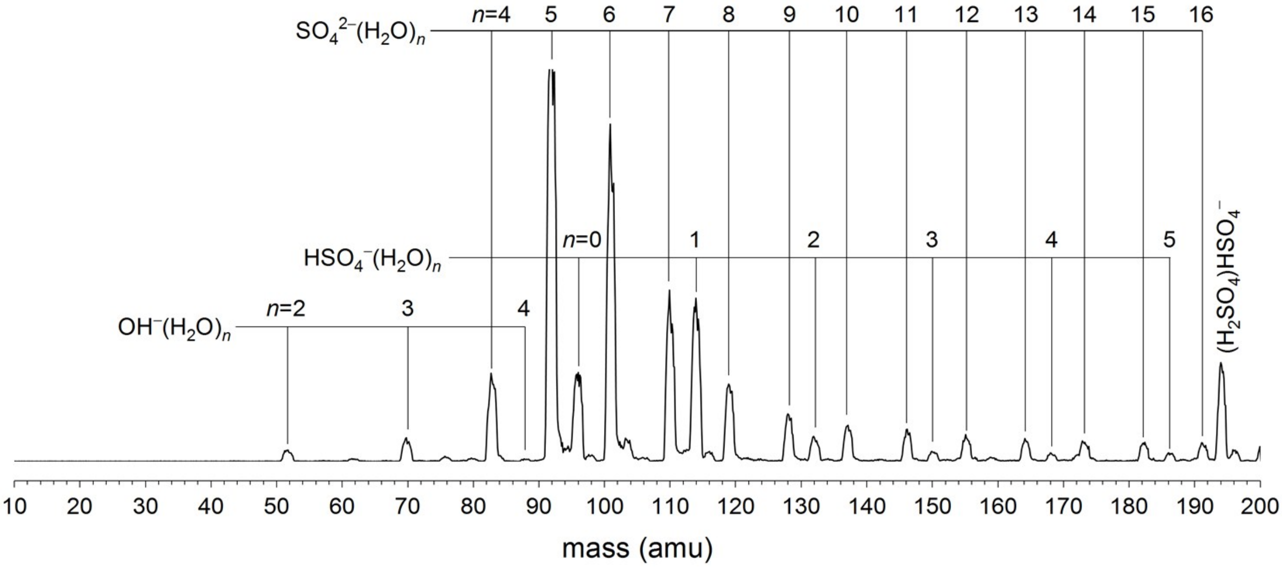


Figure S1: Mass spectrum of a 10 mmol H_2SO_4 in Water/Acetonitrile (ratio 2:1) solution. The ion optics are optimized for the mass of $SO_4^{2-}(H_2O)_6$.

Table S1: Relative electronic energies (all in kJ/mol) with zero-point-correction of $SO_4^{2-}(H_2O)_6$ and $SO_4^{2-}(D_2O)_6$ for different isomers taken form Lambrecht *et al.*[1] The values are calculated at CCSD(T)/CBS* and ZPE is estimated at B3LYP/6-311++G** level of theory.

Isomer[a]	E_{el}	$E_{el} + E_{ZPE}$(H)	$E_{el} + E_{ZPE}$(D)
6.6.6-1	0.0	6.7	4.3
6.6.6-2	0.8	7.8	5.4
6.7.5-1	2.1	8.3	6.3
6.7.5-2	2.1	8.3	6.3
6.7.5-3	4.1	9.7	7.8
6.7.5-4	4.1	9.7	7.8
6.7.5-5	4.4	8.6	6.9
6.7.5-6	4.3	8.7	6.9
6.8.4-1	3.5	5.9	4.6
6.8.4-2	3.4	5.9	4.6
6.8.4-3	4.8	6.8	5.6
6.8.4-4	4.8	6.8	5.6
6.8.4-5	2.7	4.1	3.0
6.8.4-6	3.3	5.1	3.9
6.8.4-7	2.8	4.2	3.1
6.8.4-8	3.3	5.1	3.9
6.9.3-1	3.2	**0.0**	**0.0**
6.12.0-1	17.5	5.8	7.8

[a] The following structures given by Lambrecht *et al.*[1] are enantiomers: 6.7.5-1 and 6.7.5-2, 6.7.5-3 and 6.7.5-4, 6.7.5-5 and 6.7.5-6, 6.8.4-1 and 6.8.4-2, 6.8.4-3 and 6.8.4-4

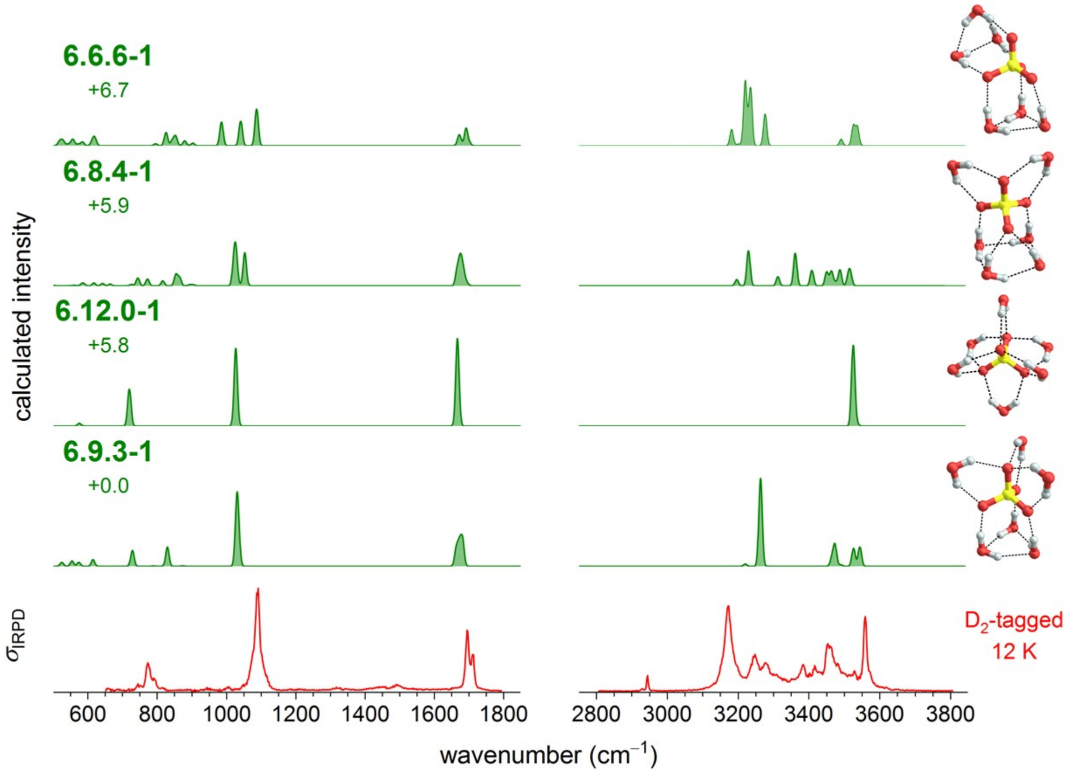


Figure S2: Comparison between the experimental IRPD spectrum and Gaussian convolution (FWHM = 12 cm^{-1}) of the harmonic B3LYP/aug-cc-pVTZ stick spectra for different isomers. Structures and their relative energies[1] (in kJ/mol) are also reported.

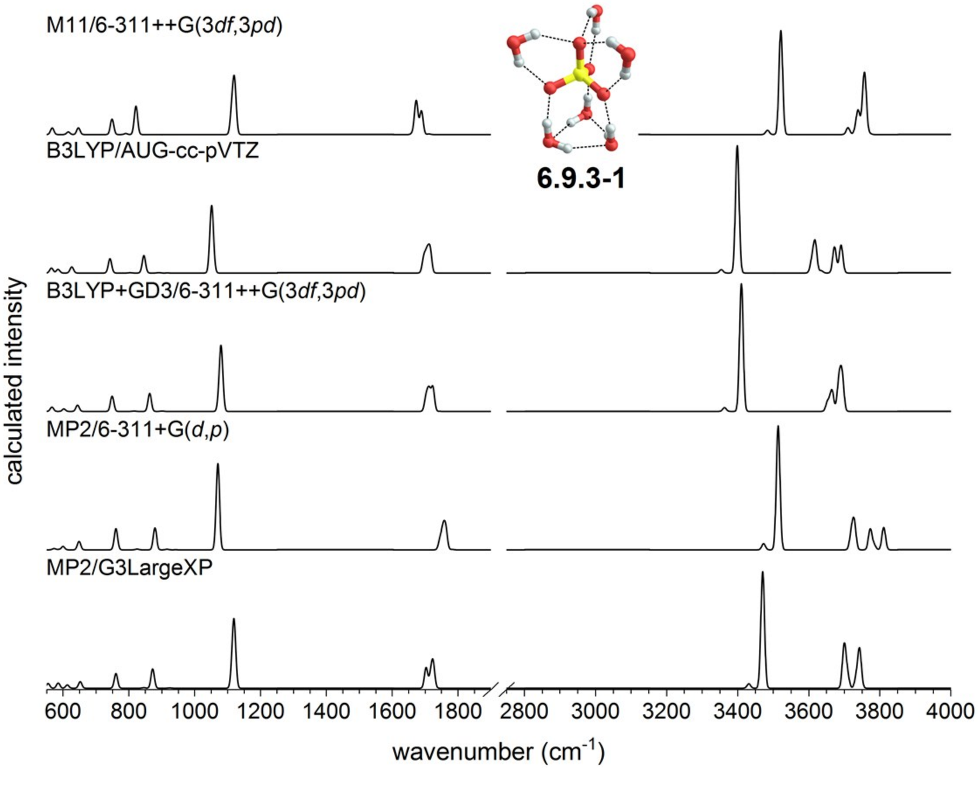


Figure S3: Comparison of Gaussian line function convoluted (FWHM = 12 cm^{-1}) harmonic stick spectra for different combinations of theory and basis set of the isomer **6.9.3-1**. For better comparison, the spectra are not scaled.

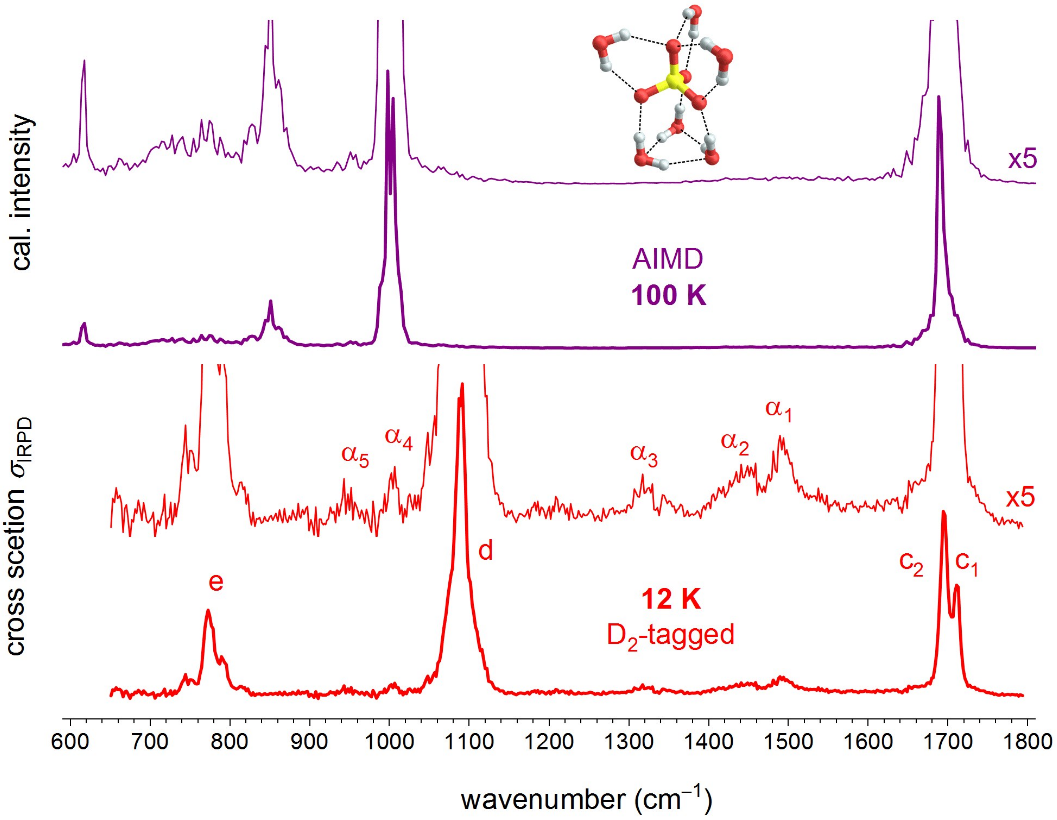


Figure S4: Magnification of the IRPD spectrum and the AIMD simulation in the spectral range from 600 to 1800 cm^{-1}.

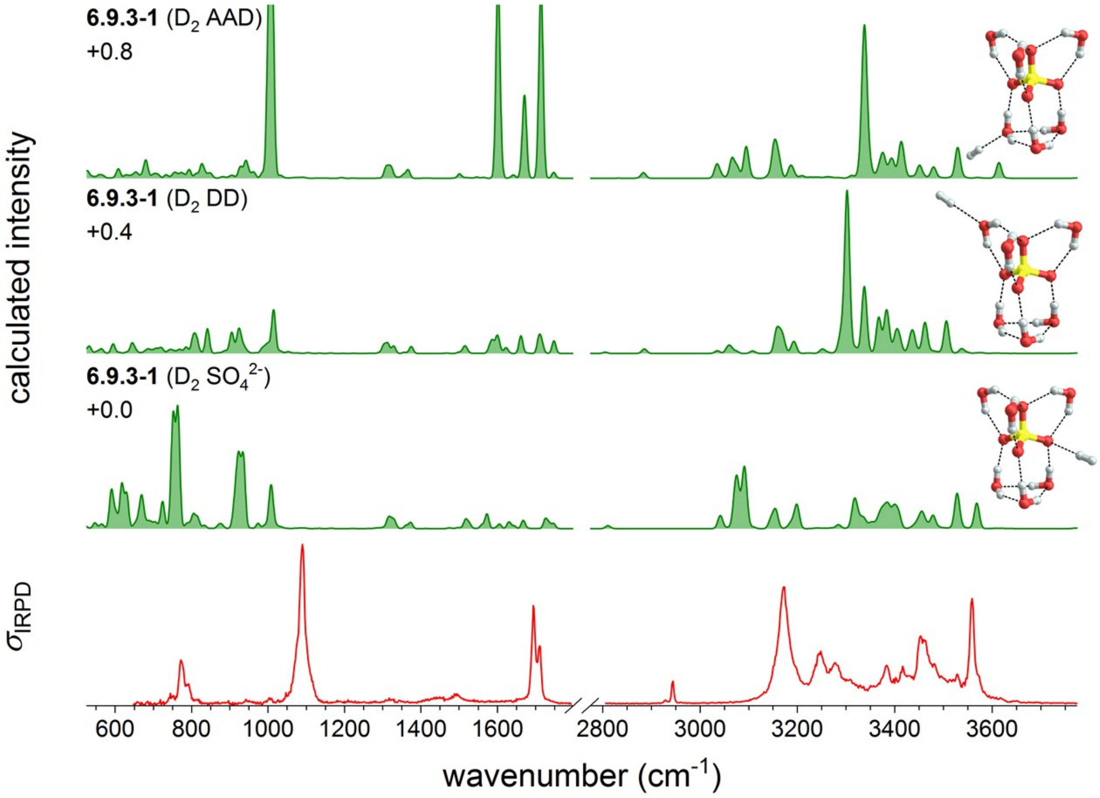
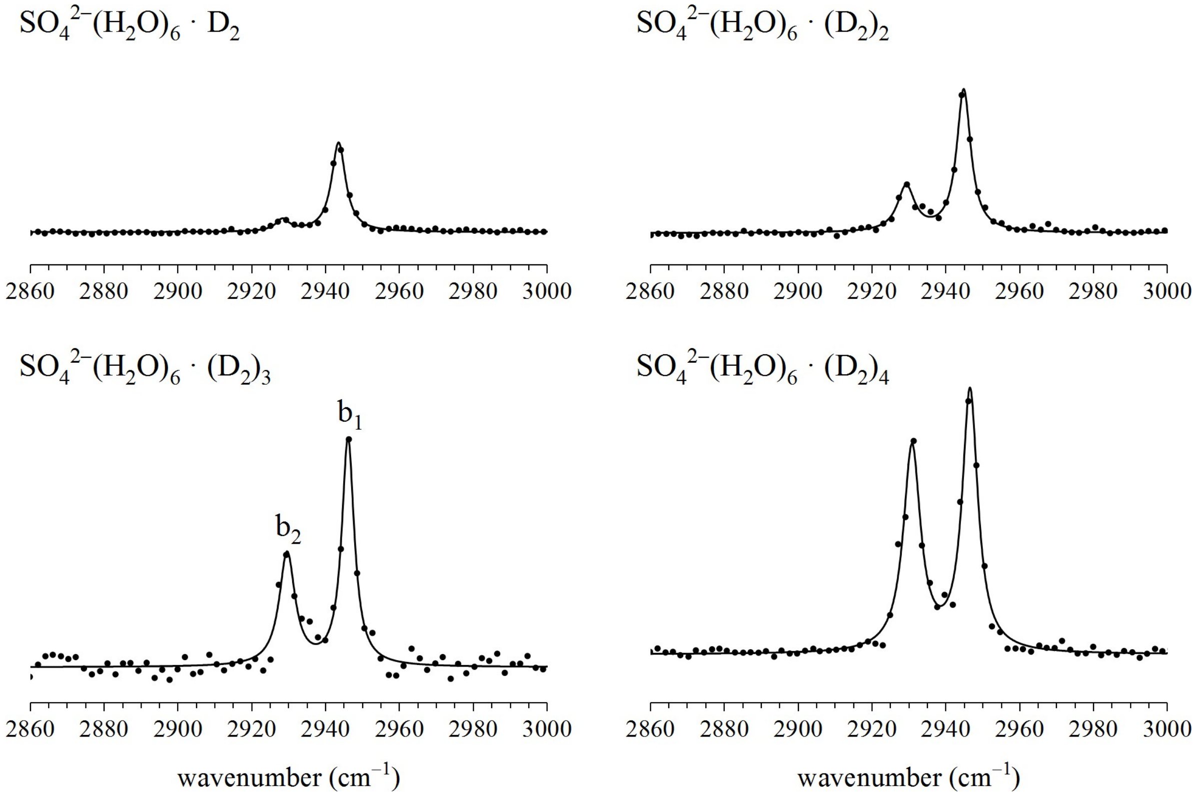


Figure S5: Calculated VPT2 spectra of 6.9.3-1 with D_2 tagging for different binding positions using B3LYP/6-31+G(d,p) with GD3BJ empirical dispersion correction. As a comparison, the IRPD spectrum is shown below.

The VPT2 implementation in Gaussian16 can cause problems.[2] For example, the calculation for isomer **VI-9-3a** failed regardless of the options used. This was solved by breaking the C_3 symmetry by attaching a D_2 molecule to the cluster. But, adding D_2 to **VI-12-0a** reduces the T_d symmetry to C_{2v} is resulting in a failed calculation. As already mentioned there are three positions for the addition of D_2 to **VI-9-3a**. The spectra of these "sub"-isomers differ clearly between themselves (Figure S5), so that the spectrum shown here must be regarded as problematic.



$SO_4^{2-}(H_2O)_6 \cdot D_2$

$SO_4^{2-}(H_2O)_6 \cdot (D_2)_2$

$SO_4^{2-}(H_2O)_6 \cdot (D_2)_3$

$SO_4^{2-}(H_2O)_6 \cdot (D_2)_4$

Figure S6: IRPD spectrum of $SO_4^{2-}(H_2O)_6\ (D_2)_n$ in the D_2 stretching region. Experimental values are represented as dots, while the line show a fit of two Lorentzian functions.

Table S2a-d: Parameters of the Lorentzian fit shown in figure S3. Given errors are estimated for a confidence level of 68%.

$SO_4^{2-}(H_2O)_6\ (D_2)_1$

parameter	value
A_1	1957 ± 44
μ_1	2943.41 ± 0.05
σ_1	2.31 ± 0.07
A_2	248 ± 42
μ_2	2928.20 ± 0.30
σ_2	2.23 ± 0.61

$SO_4^{2-}(H_2O)_6\ (D_2)_2$

parameter	value
A_1	3133 ± 68
μ_1	2944.76 ± 0.05
σ_1	2.32 ± 0.07
A_2	1228 ± 76
μ_2	2929.15 ± 0.16
σ_2	2.87 ± 0.23

$SO_4^{2-}(H_2O)_6\ (D_2)_3$

parameter	value
A_1	4420 ± 220
μ_1	2945.96 ± 0.11
σ_1	2.05 ± 0.12
A_2	2760 ± 250
μ_2	2929.47 ± 0.22
σ_2	2.59 ± 0.30

$SO_4^{2-}(H_2O)_6\ (D_2)_4$

parameter	value
A_1	6326 ± 219
μ_1	2946.46 ± 0.08
σ_1	2.57 ± 0.12
A_2	5470 ± 230
μ_2	2930.74 ± 0.11
σ_2	2.83 ± 0.16

Table S3: Relative energies with thermal correction to Gibbs free energy (kJ/mol) for the two relevant isomers. Electronic energy is taken form the reference

Isomer		$E_{\text{electronic}}$	temperature (K)						
			0	50	100	150	200	250	300
all-H	VI-12-0a	14.4	5.5	5.8	5.3	4.5	3.3	1.7	0.0
	VI-9-3a	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
all-D	VI-12-0a	14.4	7.7	7.9	7.3	6.1	4.5	2.7	0.6
	VI-9-3a	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table S4: B3LYP+GD3BJ/aug-cc-pVTZ optimized geometries (charge = -2, multiplicity = 1) for $SO_4^{2-}(H_2O)_6$ isomers

Isomer	**Coordinates**			
6.12.0	S	-0.000000	0.000000	0.000000
	O	0.870971	-0.870971	0.870971
	O	-0.870971	0.870971	0.870971
	O	0.870971	0.870971	-0.870971
	O	-0.870971	-0.870971	-0.870971
	O	0.000000	3.476199	0.000000
	H	0.516679	2.834442	-0.516679
	H	-0.516679	2.834442	0.516679
	H	-2.834442	0.516679	0.516679
	O	-3.476199	0.000000	0.000000
	H	-2.834442	-0.516679	-0.516679
	H	0.516679	-2.834442	0.516679
	O	-0.000000	-3.476199	0.000000
	H	-0.516679	-2.834442	-0.516679
	H	2.834442	0.516679	-0.516679
	O	3.476199	-0.000000	0.000000
	H	2.834442	-0.516679	0.516679
	H	0.516679	-0.516679	2.834442
	O	-0.000000	0.000000	3.476199
	H	-0.516679	0.516679	2.834442
	H	-0.516679	-0.516679	-2.834442
	O	-0.000000	-0.000000	-3.476199
	H	0.516679	0.516679	-2.834442

Isomer	**Coordinates**			
6.9.3	S	0.000000	0.000000	0.341956
	O	0.000000	0.000000	1.837929
	O	0.000000	1.407190	-0.155587
	O	1.218663	-0.703595	-0.155587
	O	-1.218663	-0.703595	-0.155587
	O	0.017264	2.857799	2.312821
	H	0.014091	1.917460	2.556056
	H	0.011524	2.733193	1.348018
	O	2.466294	-1.443851	2.312821
	H	1.653523	-0.970933	2.556056
	H	2.361252	-1.376576	1.348018
	O	-2.483558	-1.413948	2.312821
	H	-1.667615	-0.946526	2.556056
	H	-2.372776	-1.356616	1.348018
	O	-0.402830	1.670433	-2.873014
	H	-0.273404	1.672414	-1.895275
	H	-0.923192	0.862510	-3.007465
	O	1.648053	-0.486355	-2.873014
	H	1.585055	-0.599432	-1.895275
	H	1.208551	0.368253	-3.007465
	O	-1.245223	-1.184078	-2.873014
	H	-1.311651	-1.072982	-1.895275
	H	-0.285359	-1.230763	-3.007465

References

1 D. S. Lambrecht, L. McCaslin, S. S. Xantheas, E. Epifanovsky and M. Head-Gordon, *Mol. Phys.*, 2012, **110**, 2513–2521.

2 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, Wallingford, CT, 2016.