

Appendix C

Anharmonic Force Fields and the B3LYP Exchange Correlation Functional

Small molecules are convenient for testing the quality of a certain method, both from the experimental and the theoretical point of view. The smaller the system, the smaller is the number of anharmonic terms, so their empirical determination is less demanding and more precise. The empirical force fields were calculated by fitting the experimental vibration-rotation data [48]. Concerning the theoretical approach, smaller molecules require less computational effort and can, therefore, be investigated by means of more sophisticated methods. Breidung et al. [48] used higher level quantum chemistry method and larger basis set, CCSD(T)/cc-pVQZ, for obtaining the anharmonic terms of F₂O. We performed the same calculations with B3LYP/6-31+G(d,p), in order to check how well this DFT method treats the problem at hand. The results for the quadratic, cubic and quartic derivatives of the potential are compiled in Tables C.1, C.2 and C.3, respectively.

force constant	experimental	CCSD(T) cc-pVQZ	B3LYP 6-31+G(d,p)
$K_{1,1}$	461	465 ^{anh} /474	473
$K_{2,2}$	829	845 ^{anh} /868	912
$K_{3,3}$	928	936 ^{anh} /955	1025

Table C.1: Frequencies of the bending (1), symmetric stretching (2) and the asymmetric stretching (3) vibration of F₂O. "anh" stands for the anharmonic value. The other values in the last two columns correspond to the harmonic approximation.

For the computation of the cubic and the quartic anharmonic terms we used the displacements $\tilde{Q} = 0.030$ and $\tilde{Q} = 0.040$, respectively, as in the case of the PMME

force field	empirical	CCSD(T) cc-pVQZ	B3LYP 6-31+G(d,p)
$k_{1,1,1}$	-97.6	-97.3	-80.6
$k_{1,2,2}$	-63.4	-52.0	-41.7
$k_{1,1,3}$	-19.4	-17.4	-8.8
$k_{2,2,3}$	-288.4	-295.9	-257.0
$k_{1,3,3}$	-48.4	-41.7	-41.4
$k_{3,3,3}$	-247.4	-247.2	-203.6

Table C.2: Cubic anharmonic terms for F₂O in cm⁻¹.

force field	empirical	CCSD(T) cc-pVQZ	B3LYP 6-31+G(d,p)
$k_{1,1,1,1}$	10.2	21.8	20.4
$k_{1,1,2,2}$	-6.7	-19.2	-19.2
$k_{2,2,2,2}$	111.5	81.4	62.0
$k_{1,1,3,3}$	3.9	-5.5	-12.1
$k_{2,2,3,3}$	92.5	73.3	52.4
$k_{3,3,3,3}$	50.6	35.2	27.6

Table C.3: Quartic anharmonic terms for F₂O in cm⁻¹.

molecule, Chapter 3. The cubic terms are in relatively good agreement with the empirical results. The values computed with CCSD(T) are more precise, but the relative ratio of the terms calculated with the DFT method are in good accord as well. The quartic terms are, however, less precise, but apart from the term $k_{3,3,3}$ which has the wrong sign, the results are satisfactory. We did not aim in an exact reproduction of the empirical values: our calculations correspond to molecules in the gas phase, whereas the PMME molecule was in the experiment dissolved in CCl₄. The solvent influences the force fields, and therefore it is not necessary to compute the anharmonic fields with extremely high precision. What is important are the relative ratios of different terms, and they are relatively well reproduced.

Note that the couplings between all modes are not equal. Specifically, modes ν_2 and ν_3 are strongly coupled, according to the values of k_{223} and k_{2233} . This would suggest to treat this two - mode interaction explicitly, i.e., on a grid in order to capture the anharmonicity that otherwise would probably not be well described by truncating the potential as proposed with the AFF approach. On the other hand, mode ν_1 does not seem to interact strongly with the other two modes, and could most likely be well described with the AFF method.