

Supplementary Material

On how atomic structure and dielectrics relationships in Zr-SiO₂ glasses

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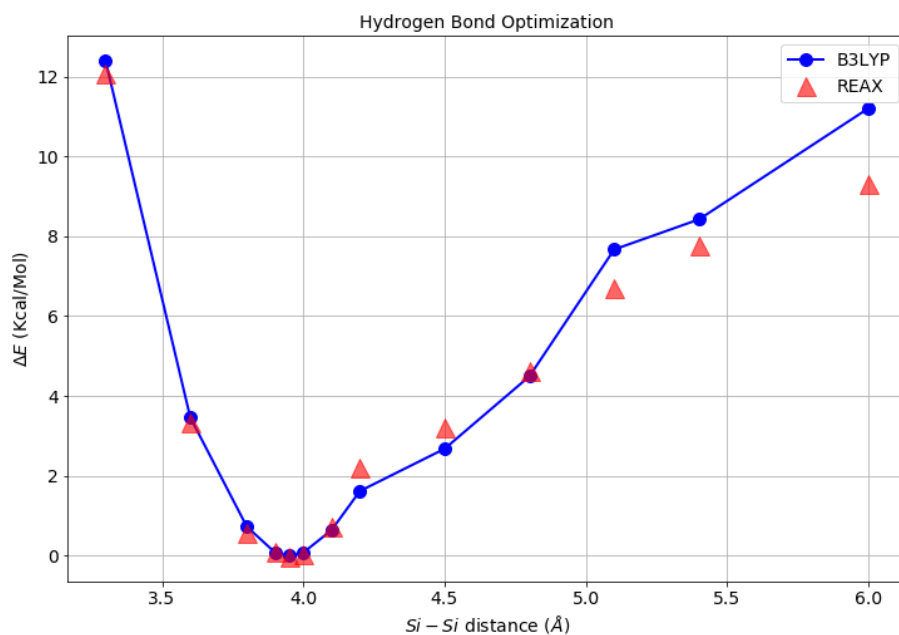
1. Forcefield optimization procedure

We optimized our reax forcefield parameters by merging two existing forcefields and improving the hydrogen parameters as well as training angle parameters. We used density functional theory (B3LYP with dispersion) as implemented in the gaussian software for our target energies and optimized the reax forcefield parameters using simulated annealing and a genetic algorithm as implemented in our own forcefield optimization software (Pyfield). The user manual and complete description of Pyfield is available on our github repository [<https://github.com/sarashs/Python-forcefield-optimizer>].

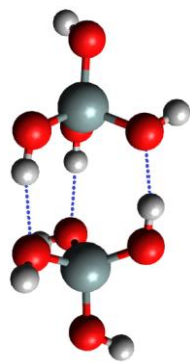
1.1. Hydrogen bonds (Si(OH)₄ molecule)

Hydrogen bonds parameters were optimized using a relevant data set where two Si(OH)₄ molecules are placed near one another and the energy is calculated as a function of the Si-Si distance (**Figure S1.a**). There are two kinks in the DFT energy diagram both of which, are picked up and qualitatively approximated by our optimized forcefield. These kinks are due to the reorientation/rotation of Si(OH)₄ molecules as depicted in **Figure S1.b-d**.

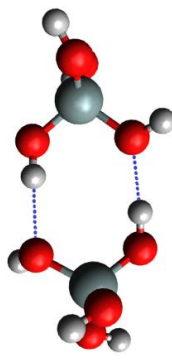
a)



b)



c)



d)

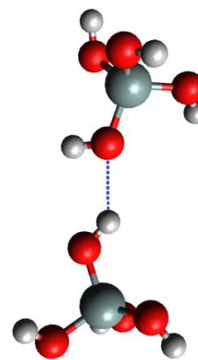


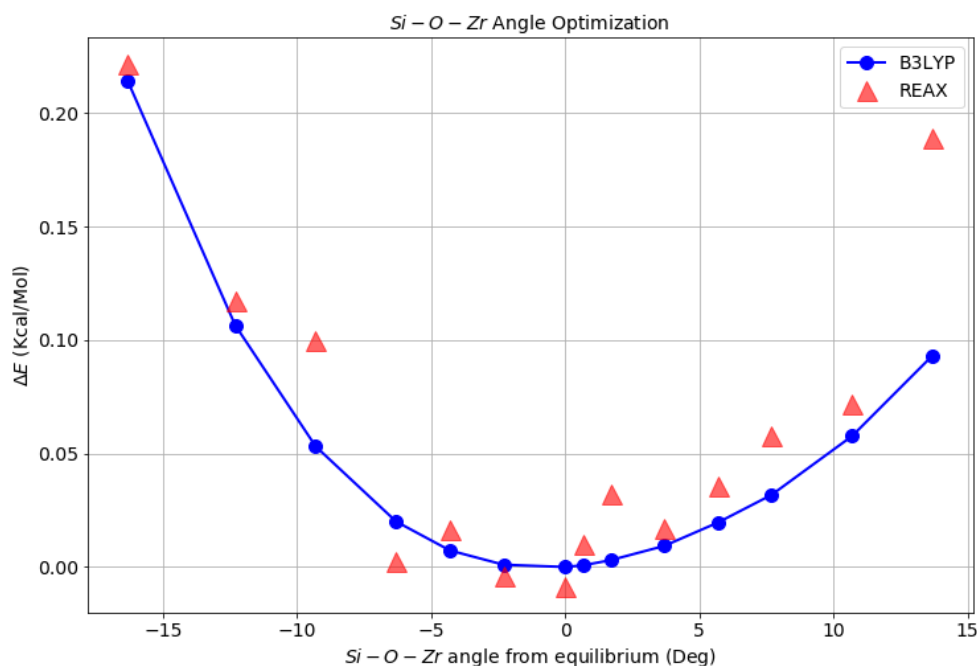
Figure S1. a) Hydrogen bond energy as a function of Si-Si distance. b-d) Various formations of hydrogen bonds as the Si-Si distance increases. These changes of formation are responsible for the kinks in the part a) plot. The hydrogen bonds are depicted as dotted lines.

1.2.Si-O-Zr angle ($\text{Si}_4\text{ZrO}_{16}\text{H}_{12}$ Cluster)

Considering our desire to simulate silicon dioxide glasses with a lower percentage of zirconium dioxide content, we believe the most common scenario for Zr atoms will be to be

surrounded by silica tetrahedra. Therefore, the only parameter we needed to introduce such that the two forcefield are connected is the Zr-O-Si angle parameters as well as possibly the O-Zr-O-Si torsion parameters. This is fully achieved by our choice of cluster. We first set up our cluster in a way that hydrogen bonds have the least effect on our equilibrium Zr-O-Si angle (**Figure S2.b**). We then relaxed our system, found the equilibrium angle, and calculated the relative system energy at different nonequilibrium angles. As shown in **Figure S2.a**, the angle energy is very small within a wide range (+/- 15 degrees).

a)



b)

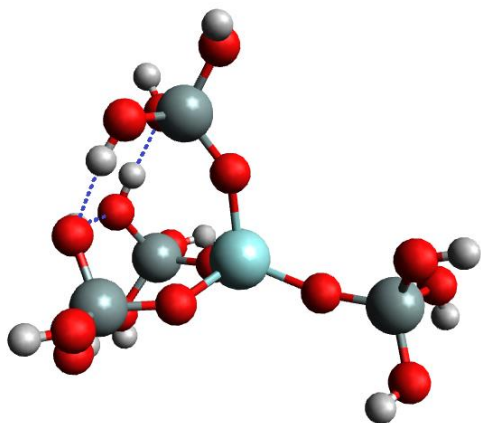


Figure S2. a) Energy as a function of angle from the equilibrium. b) Zr-O-Si angle at equilibrium. Note that the hydrogen bonds do not affect the desired angle at equilibrium (~163 degrees). The hydrogen bonds are depicted as dotted lines.

2. Forcefield Optimization Tool (Pyfield)

Our forcefield optimization tool is written in Python. It is designed to be available to the community both as a stand-alone software and a Python package that can be imported and used within other codes. Python was our language of choice due to its ease of use and prevalence of usage among the numerical chemist and material scientists. A brief explanation of the software is given here. More documentation along with the full complimentary downloadable and usable code is provided via the repository [<https://github.com/sarashs/Python-forcefield-optimizer>].

Architecture: The optimization software consists of two parent classes: the *forcefield* class and the *optimization* class. The forcefield class can have daughter classes for every different type of forcefields. These classes are responsible for reading, preparing, writing and updating the forcefield. The optimization class can have various daughter classes to implement different optimization algorithms. Currently, simulated annealing and genetic algorithm are implemented.

The program uses LAMMPS to perform structural minimizations. Therefore, a LAMMPS utility package is required to prepare the LAMMPS input and atom files. The optimization and forcefield classes use this package in order to employ LAMMPS.

Usage Preparation: our forcefield optimizer is ready for use and does not require any preparations except for the compilation of LAMMPS as a library. There are two ways that our package can be used.

- 1) As it currently stands, Pyfield can use an input file containing the desired optimization instructions. Pyfield then performs a corresponding forcefield optimization. More information on the formatting and preparation of the input file is available through the repository.
- 2) The other mode of usage is to import the package or any of its classes within a Python code and then use them as desired within a Python code. This enables users to write their own optimization schemes and algorithms.

3. Dielectric constant calculations

The dielectric constant is calculated based on Equation 1. The way we perform the computation is by computing the values of $\langle M \rangle$ and $\langle M^2 \rangle$ over a set of atoms that are within a sphere with diameter of 12 Angstrom around the origin. As the timesteps proceed we perform our computations on the same set (original set) and we do not update the set with atoms that enter or leave the sphere. Note that this is critical to reproduce our work and the correct way to perform these calculations.

All of the our analysis codes (including the above code) along with LAMMPS scripts and bash scripts for compute Canada cloud are given in the following Github repository: https://github.com/sarashs/Dielectric_prediction

4. Forcefield File

The following is the reax forcefield file we trained and used for our simulations.

This force field was generated by Pyfield optimization tool developed at Ivanov-SOC, UBC

39 ! Number of general parameters
50.0 !Overcoordination parameter
9.5469 !Overcoordination parameter
26.5405 !Valency angle conjugation parameter
1.7224 !Triple bond stabilisation parameter
6.8702 !Triple bond stabilisation parameter
60.485 !C2-correction
1.0588 !Undercoordination parameter
4.6 !Triple bond stabilisation parameter
12.1176 !Undercoordination parameter
13.3056 !Undercoordination parameter
-70.5044 !Triple bond stabilization energy
0.0 !Lower Taper-radius
10.0 !Upper Taper-radius
2.8793 !Not used
33.8667 !Valency undercoordination
6.0891 !Valency angle/lone pair parameter
1.0563 !Valency angle
2.0384 !Valency angle parameter
6.1431 !Not used
6.929 !Double bond/angle parameter
0.3989 !Double bond/angle parameter: overcoord
3.9954 !Double bond/angle parameter: overcoord
-2.4837 !Not used
5.7796 !Torsion/BO parameter
10.0 !Torsion overcoordination
1.9487 !Torsion overcoordination
-1.2327 !Conjugation 0 (not used)
2.1645 !Conjugation
1.5591 !vdWaals shielding
0.1 !Cutoff for bond order (*100)
2.1365 !Valency angle conjugation parameter
0.6991 !Overcoordination parameter
50.0 !Overcoordination parameter

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1.8512 !Valency/lone pair parameter
0.5 !Not used
20.0 !Not used
5.0 !Molecular energy (not used)
0.0 !Molecular energy (not used)
2.6962 !Valency angle conjugation parameter
7 ! Nr of atoms; cov.r; valency;a.m;Rvdw;Evdw;gammaEEM;cov.r2;#
  alfa;gammavdW;valency;Eunder;Eover;chiEEM;etaEEM;n.u.
  cov r3;Elp;Heat inc.;n.u.;n.u.;n.u.;n.u.
  Rov/un;val1;n.u.;val3,vval4
C 1.3817 4.0 12.0 1.8903 0.1838 0.9 1.1341 4.0
  9.7559 2.1346 4.0 34.935 79.5548 5.9666 7.0 0.0
  1.2114 0.0 202.5551 8.9539 34.9289 13.5366 0.8563 0.0
  -2.8983 2.5 1.0564 4.0 2.9663 0.0 0.0 0.0
H 0.893 1.0 1.008 1.355 0.093 0.8203 -0.1 1.0
  8.223 33.2894 1.0 0.0 121.125 3.7248 9.6093 1.0
  -0.1 0.0 61.6606 3.0408 2.4197 0.0003 1.0698 0.0
  -19.4571 4.2733 1.0338 1.0 2.8793 0.0 0.0 0.0
O 1.245 2.0 15.999 2.389 0.1 1.0898 1.0548 6.0
  9.73 13.8449 4.0 37.5 116.0768 8.5 8.3122 2.0
  0.9049 0.4056 59.0626 3.5027 0.764 0.0021 0.9745 0.0
  -3.55 2.9 1.0493 4.0 2.9225 0.0 0.0 0.0
Ca 1.9927 2.0 40.087 2.7005 0.1848 0.7939 1.0 2.0
  10.6123 27.5993 3.0 38.0 0.0 -1.9372 6.5275 0.0
  -1.3 0.0 220.0 49.9248 0.337 0.0 0.0 0.0
  -2.0 4.0 1.0564 6.2998 2.9663 0.0 0.0 0.0
Si 2.1932 4.0 28.06 1.8951 0.1737 0.5947 1.2962 4.0
  11.3429 5.2054 4.0 21.7115 139.9309 4.2033 5.5558 0.0
  -1.0 0.0 128.2031 9.0751 23.8188 0.8381 0.8563 0.0
  -4.1684 2.0754 1.0338 4.0 2.5791 1.4 0.2 13.0
X -0.1 2.0 1.008 2.0 0.0 1.0 -0.1 6.0
  10.0 2.5 4.0 0.0 0.0 8.5 1.5 0.0
  -0.1 0.0 -2.37 8.741 13.364 0.669 0.9745 0.0
  -11.0 2.7466 1.0338 2.0 2.8793 0.0 0.0 0.0

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Zr 2.6606 4.0 91.224 2.2821 0.2556 0.7127 -1.0 4.0
11.5975 48.3221 4.0 -5.0 0.0 -2.7483 6.0 0.0
-1.0 0.0 144.608 48.1308 0.0807 0.0 0.8563 0.0
-7.4872 3.3675 1.0338 8.0 2.2632 0.0 0.0 0.0
16 ! Nr of bonds; Edis1;LPpen;n.u.;pbe1;pbo5;13corr;pbo6
pbe2;pbo3;pbo4;n.u.;pbo1;pbo2;ovcorr
1 1 158.2004 99.1897 78.0 -0.7738 -0.455 1.0 37.6117 0.4147
0.459 -0.1 9.1628 1.0 -0.0777 6.7268 1.0 0.0
1 2 169.476 0.0 0.0 -0.6083 0.0 1.0 6.0 0.7652
5.229 1.0 0.0 1.0 -0.05 6.9136 0.0 0.0
2 2 153.3934 0.0 0.0 -0.46 0.0 1.0 6.0 0.73
6.25 1.0 0.0 1.0 -0.079 6.0552 0.0 0.0
1 3 158.6946 107.4583 23.3136 -0.424 -0.1743 1.0 10.8209 1.0
0.5322 -0.3113 7.0 1.0 -0.1447 5.245 0.0 0.0
3 3 142.2858 145.0 50.8293 0.2506 -0.1 1.0 29.7503 0.6051
0.3451 -0.1055 9.0 1.0 -0.1225 5.5 1.0 0.0
2 3 160.0 0.0 0.0 -0.5725 0.0 1.0 6.0 0.5626
1.115 1.0 0.0 1.0 -0.092 4.279 0.0 0.0
2 4 0.0 0.0 0.0 -0.0203 -0.1418 1.0 13.126 0.023
8.2136 -0.131 0.0 1.0 -0.2692 6.4254 0.0 24.4461
3 4 50.8757 0.0 43.3991 1.0 -0.3 1.0 36.0 0.0025
0.7609 -0.25 12.0 1.0 -0.0515 8.9041 1.0 24.4461
4 4 36.9494 0.0 0.0 -0.0412 -0.2 0.0 16.0 0.3233
0.3708 -0.2 10.0 1.0 -0.0822 4.2104 0.0 0.0
2 5 250.0 0.0 0.0 -0.7128 0.0 1.0 6.0 0.1186
18.579 1.0 0.0 1.0 -0.0731 7.4983 0.0 0.0
3 5 274.8339 5.0 0.0 -0.5884 -0.3 1.0 36.0 0.2131
9.9772 -0.2572 28.8153 1.0 -0.113 8.479 6.0658 0.0
4 5 0.0 0.0 0.0 0.5 -0.3 1.0 16.0 0.5
0.5 -0.25 15.0 1.0 -0.1 9.0 0.0 0.0
5 5 70.912 54.0531 30.0 0.4931 -0.3 1.0 16.0 0.0392
0.2476 -0.8055 7.1248 1.0 -0.1009 8.7229 0.0 0.0
2 7 38.8626 0.0 0.0 -0.1577 0.0 1.0 6.0 0.5
17.8821 1.0 0.0 1.0 -0.2095 6.3931 0.0 0.0

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3 7 112.7221 0.0    0.0    0.4102 -0.3    1.0    36.0    0.3592
    0.1355 -0.2    15.0    1.0    -0.1016 10.621    1.0    0.0
7 7 76.6674 0.0    0.0    -0.1508 -0.2    0.0    16.0    0.363
    0.8019 -0.2    15.0    1.0    -0.1682 6.4675    0.0    0.0
10  ! Nr of off-diagonal terms; Ediss;Ro;gamma;rsigma;rpi;rpi2
1 2 0.1239 1.4004 9.8467 1.121  -1.0  -1.0
2 3 0.0283 1.2885 10.919 0.9215 -1.0  -1.0
1 3 0.1156 1.852 9.8317 1.2854 1.1352 1.0706
2 4 0.01 1.6 13.2979 -1.0 -1.0 -1.0
3 4 0.0955 1.7587 11.9417 1.9052 -1.0 -1.0
2 5 0.2 1.5207 12.9535 1.2125 -1.0 -1.0
3 5 0.1836 1.9157 10.907 1.7073 1.2375 -1.0
4 5 0.1 1.9 11.0 -1.0 -1.0 -1.0
2 7 0.1 1.761 10.4809 0.1 -1.0 -1.0
3 7 0.157 1.7138 12.0409 1.9449 -1.0 -1.0
38  ! Nr of angles;at1;at2;at3;Thetao,o;ka;kb;pv1;pv2
1 1 1 59.0573 30.7029 0.7606 0.0 0.718 6.2933 1.1244
1 1 2 65.7758 14.5234 6.2481 0.0 0.5665 0.0 1.6255
2 1 2 70.2607 25.2202 3.7312 0.0 0.005 0.0 2.75
1 2 2 0.0 0.0 6.0 0.0 0.0 0.0 1.04
1 2 1 0.0 3.411 7.735 0.0 0.0 0.0 1.04
2 2 2 0.0 27.9213 5.8635 0.0 0.0 0.0 1.04
1 1 3 49.6811 7.1713 4.3889 0.0 0.7171 10.2661 1.0463
3 1 3 77.7473 40.1718 2.9802 -25.3063 1.617 -46.1315 2.2503
2 1 3 65.0 13.8815 5.0583 0.0 0.4985 0.0 1.49
1 3 1 73.5312 44.7275 0.7354 0.0 3.0 0.0 1.0684
1 3 3 79.4761 36.3701 1.8943 0.0 0.7351 67.6777 3.0
3 3 3 80.7324 30.4554 0.9953 0.0 1.631 50.0 1.0783
1 3 2 70.188 20.9562 0.3864 0.0 0.005 0.0 1.6924
2 3 3 75.6935 50.0 2.0 0.0 1.0 0.0 1.168
2 3 2 85.8 9.8453 2.272 0.0 2.8635 0.0 1.58
1 2 3 0.0 25.0 3.0 0.0 1.0 0.0 1.04
3 2 3 0.0 15.0 2.89 0.0 0.0 0.0 2.8774
2 2 3 0.0 8.5744 3.0 0.0 0.0 0.0 1.0421

```


3	4	3	1.0	4.9611	2.4541	0.0	0.5754	0.0	1.0
4	3	4	9.5066	4.264	3.1438	0.0	1.9819	0.0	1.6463
2	3	4	51.3829	2.5	0.25	0.0	0.05	0.0	1.0
3	3	4	70.0	25.0	1.0	0.0	1.0	0.0	1.25
5	5	5	78.5339	36.4328	1.0067	0.0	0.1694	0.0	1.6608
2	5	5	77.2616	5.019	7.8944	0.0	4.0	0.0	1.04
2	5	2	75.7983	14.4132	2.864	0.0	4.0	0.0	1.04
3	5	5	86.3294	18.3879	5.8529	0.0	1.7361	0.0	1.231
2	5	3	73.6998	40.0	1.8782	0.0	4.0	0.0	1.129
3	5	3	79.5581	34.914	1.0801	0.0	0.1632	0.0	2.2206
5	3	5	82.3364	4.735	1.3544	0.0	1.4627	0.0	1.04
2	3	5	90.0	6.6857	1.6689	0.0	2.5771	0.0	1.04
3	3	5	92.1207	24.3937	0.5	0.0	1.7208	0.0	3.0
2	2	5	0.0	47.13	6.0	0.0	1.6371	0.0	1.04
5	2	5	0.0	27.4206	6.0	0.0	1.6371	0.0	1.04
3	2	5	0.0	5.0	1.0	0.0	1.0	0.0	1.25
2	3	7	42.5058	10.0776	5.0	0.0	0.9289	0.0	1.1912
3	3	7	80.0	10.0	1.25	0.0	0.5554	0.0	1.2
7	3	7	8.3158	7.8049	0.2315	0.0	2.2934	0.0	3.0
7	3	5	16.5919	1.5953	1.4382	0.0	-2.3201	-0.8267	0.9931
27 ! Nr of torsions;at1;at2;at3;at4;;V1;V2;V3;V2(BO);vconj;n.u;n									
1	1	1	1	-0.25	34.7453	0.0288	-6.3507	-1.6	0.0
1	1	1	2	-0.25	29.2131	0.2945	-4.9581	-2.1802	0.0
2	1	1	2	-0.25	31.2081	0.4539	-4.8923	-2.2677	0.0
1	1	1	3	-0.3495	22.2142	-0.2959	-2.5	-1.9066	0.0
2	1	1	3	0.0646	24.3195	0.6259	-3.9603	-1.0	0.0
3	1	1	3	-0.5456	5.5756	0.8433	-5.1924	-1.018	0.0
1	1	3	1	1.7555	27.9267	0.0072	-2.6533	-1.0	0.0
1	1	3	2	-1.4358	36.783	-1.0	-8.1821	-1.0	0.0
2	1	3	1	-1.3959	34.5053	0.72	-2.5714	-2.1641	0.0
2	1	3	2	-2.5	70.0597	1.0	-3.5539	-2.9929	0.0
1	1	3	3	0.6852	11.2819	-0.4784	-2.5	-2.1085	0.0
2	1	3	3	0.1933	80.0	1.0	-4.059	-3.0	0.0
3	1	3	1	-1.9889	76.482	-0.1796	-3.8301	-3.0	0.0

3	1	3	2	0.216	72.7707	-0.7087	-4.21	-3.0	0.0	0.0	
3	1	3	3	-2.5	71.0772	0.2542	-3.1631	-3.0	0.0	0.0	
1	3	3	1	2.5	-0.6002	1.0	-3.4297	-2.8858	0.0	0.0	
1	3	3	2	-2.5	-3.3822	0.7004	-5.4467	-2.9586	0.0	0.0	
2	3	3	2	2.5	-4.0	0.9	-2.5	-1.0	0.0	0.0	
1	3	3	3	1.2329	-4.0	1.0	-2.5	-1.7479	0.0	0.0	
2	3	3	3	0.8302	-4.0	-0.7763	-2.5	-1.0	0.0	0.0	
3	3	3	3	-2.5	-4.0	1.0	-2.5	-1.0	0.0	0.0	
0	1	2	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
0	2	2	0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	
0	2	3	0	0.0	0.1	0.02	-2.5415	0.0	0.0	0.0	
0	1	1	0	0.0	50.0	0.3	-4.0	-2.0	0.0	0.0	
0	3	3	0	0.5511	25.415	1.133	-5.1903	-1.0	0.0	0.0	
5	3	7	3	-0.2111	-1.9016	-0.3657	-0.6283	-0.4168	0.0	0.0	
1	! Nr of hydrogen bonds;at1;at2;at3;Rhb;Dehb;vhb1										
3	2	3	1	1.4548	-39.4025	-0.8403	58.6489				