

Chapter 5 Development of Adiabatic Force Field for Polyvinyl Chloride (PVC) and Chlorinated PVC (CPVC)

5.1 Introduction

Chlorinated polyvinyl chloride has become an important specialty polymer due to its high glass transition temperature, high heat distortion temperature, outstanding mechanical, dielectric, and flame and smoke properties, chemical inertness, and low sensitivity to hydrocarbon costs. However, the mechanism through which the various desired and undesired properties are resulted from is not fully understood. Hopefully, simulation at the atomistic level could lead us to a better understanding of those mechanisms. Currently, direct *ab initio* calculations for polymer systems are not practical. Thus calculations with classical force fields, which are parameterized based on either experimental results or *ab initio* calculations on smaller model systems, are the method of choice. As a first step towards the understanding of CPVC, we developed the adiabatic quantum force field that accurately described the rotational energy surface of the polymer backbone chains.

For amorphous polymers, the distribution of backbone conformations and the rates of conformational transitions have a strong effect on their properties, such as moduli, glass temperature, dielectric constant, and diffusivity of small molecules. It is critical that the FF leads to the correct relative energies of the minima, e.g., *trans* versus *gauche*, and of the barrier heights between them. Thus torsional FF parameters are particularly important for describing amorphous polymers. In many cases, the existence of the molecule in other local minima can be detected, but energies for

these states cannot be reliably obtained from experiments. In addition, the barriers between the local minima can also not be obtained reliably from the experimental data alone.

To circumvent these problems, we use *ab initio* calculations to provide the torsional potential energy surface. With the 6-31G** basis set, the torsional potentials calculated from Hartree-Fock (HF) wavefunctions are adequate. The HF calculations lead to a total torsional potential function $E^{HF}(\phi)$. The classical force field can be fitted to reproduce the quantum energy surface.

$$E^{HF}(\phi) \simeq E^{FF}(\phi) \quad (5.1)$$

In determining $E^{FF}(\phi)$, the usual and simplest approach would be to determine the non-adiabatic surface by fixing all bonds and angles so that only the torsional angle ϕ changes. However, such rigid rotations about backbones sometimes lead to unfavorable contacts with very short distances between nonbonded atoms. The *ab initio* wavefunction readjusts the molecular orbitals to minimize repulsion, but the functional forms of nonbond interactions in force field representation may not accurately describe the inner repulsive wall and often leads to much higher rotational barriers. In order to accurately describe the rotational energy surface, we calculated adiabatic rotational energy surface of molecules with five backbone carbons. These molecules are used to mimic the corresponding polymer chains. The HF wavefunction was calculated by fixing the dihedrals of interest (in increments of 30°) and optimizing all other degrees of freedom. These calculations lead to the 2D energy surfaces. Torsional parameters were fitted iteratively so that the force field adiabatic energy surface matches to *ab initio* adiabatic energy surface.

5.2 The Molecular Simulation Force Field (MSFF)

The force field is taken to be of the form

$$E_{total} = E_{val} + E_{nb}. \quad (5.2)$$

The valence part includes bond interactions, angle interactions, and torsion interactions, as

$$E_{val} = E_{bond} + E_{angle} + E_{torsion}. \quad (5.3)$$

The nonbond part has van der Waals interaction and Coulomb interaction.

$$E_{nb} = E_{vdw} + E_Q \quad (5.4)$$

The torsion terms involve sums of cosine torsional angles such as

$$E_{torsion}(\phi) = \sum_{m=0}^{12} C_m \cos m\phi. \quad (5.5)$$

The nonbond terms have the form of

$$E_Q = \frac{1}{2} \sum_{i \neq j} \frac{q_i q_j}{R_{ij}} \quad (5.6)$$

for electrostatic, and

$$E_{vdw} = \frac{1}{2} \sum_{i \neq j} D_e (\rho_{ij}^{-12} - 2\rho_{ij}^{-6}) \quad (5.7)$$

for van der Waals, where $\rho_{ij} = R_{ij}/R_e$.

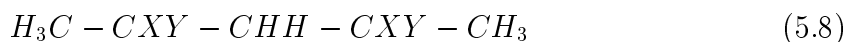
Chain conformation and inter-chain interactions are the dominating factors for amorphous polymers. We'll focus on accurate description of charges and torsional potentials. The forms and parameters of E_{bond} , E_{angle} , and E_{vdw} are taken directly

from DREIDING.

The charges and torsional parameters are based on *ab initio* calculations of clusters with five-backbone carbon atoms.

5.2.1 Charges

In order to determine the proper charges, we did *ab initio* calculation for various conformations of clusters with five-backbone carbon atoms:



where X and Y are Cl or H , depending on the form of the actual chloro-polymers. For PVC, $X = Cl$ and $Y = H$, and for PVDC, $X = Cl$ and $Y = Cl$. Hartree-Fock (HF) wavefunction with the 6-31G** basis set is used. We considered the following three methods of assigning atomic charges in the chain molecules.

- Potential derived charge (PDQ). The charge density from the HF wave function is used to calculate the potential energy over a numerical grid surrounding the molecule and a set of point charges on the atoms is optimized to fit the potential. We carried out these calculation with PSGVB using a grid of 1000 points outside the van der Waals radii (taken as $R_C = 1.949$ (Å), $R_H = 1.597$ (Å), $R_{Cl} = 1.958$ (Å), and $R_F = 1.739$ (Å)).
- Mulliken charges (Mull). The molecular orbital (MO) coefficients are used to estimate a set of atomic charges where overlap terms are assigned equally to each of the two atoms.
- Charge Equilibration (QEq). The charges of molecules are predicted based on electron affinity (EA) and ionization energy (IE).

Since the atomic charges vary with the change of molecular conformation, the best description of Coulomb interactions in dynamics simulations should be such, that the

atomic charges vary with conformation change. However, for amorphous polymer simulations, which require longer chains, assigning charges at every dynamics integration is simply unrealistic. We have to find a way to best balance various conformations, while compensating the errors made in charge assignment in the torsional force field. We based the charges on PDQ while considering symmetry property of the clusters.

5.2.2 Torsional Potential

We can write

$$E^{hf}(\phi_1, \phi_2) = E^{ff}(\phi_1, \phi_2) + E^{cor}(\phi_1, \phi_2) \quad (5.9)$$

where (ϕ_1, ϕ_2) are the two C–C–C–C backbone torsion angles as in Fig (5.1). $E^{hf}(\phi_1, \phi_2)$ is *ab initio* energy, $E^{ff}(\phi_1, \phi_2)$ is force field energy, and $E^{cor}(\phi_1, \phi_2)$ is the correction with which the old force field should be improved. $E^{ff}(\phi_1, \phi_2)$ is calculated by minimizing the structures while (ϕ_1, ϕ_2) are constraint, so that the adiabatic 2D (ϕ_1, ϕ_2) rotational energy surface of optimized force field can match that of *ab initio* computation well.

In order to get accurate adiabatic potentials, we generated 12×12 2D energy surfaces through quantum computation, i.e., constraint the two torsional angles while full Hartree-Fock optimizations were performed. We also used fully optimized structures of all the local minimums. The 2-D torsional potential surfaces were represented by regular grids which are interpolated from the 12×12 points and all of the local minimum points. The C_m in Eq. 5.5 are least-square-fitted to minimize $E^{cor}(\phi_1, \phi_2)$. Many iterations are performed until the changes of C_m are insignificant.

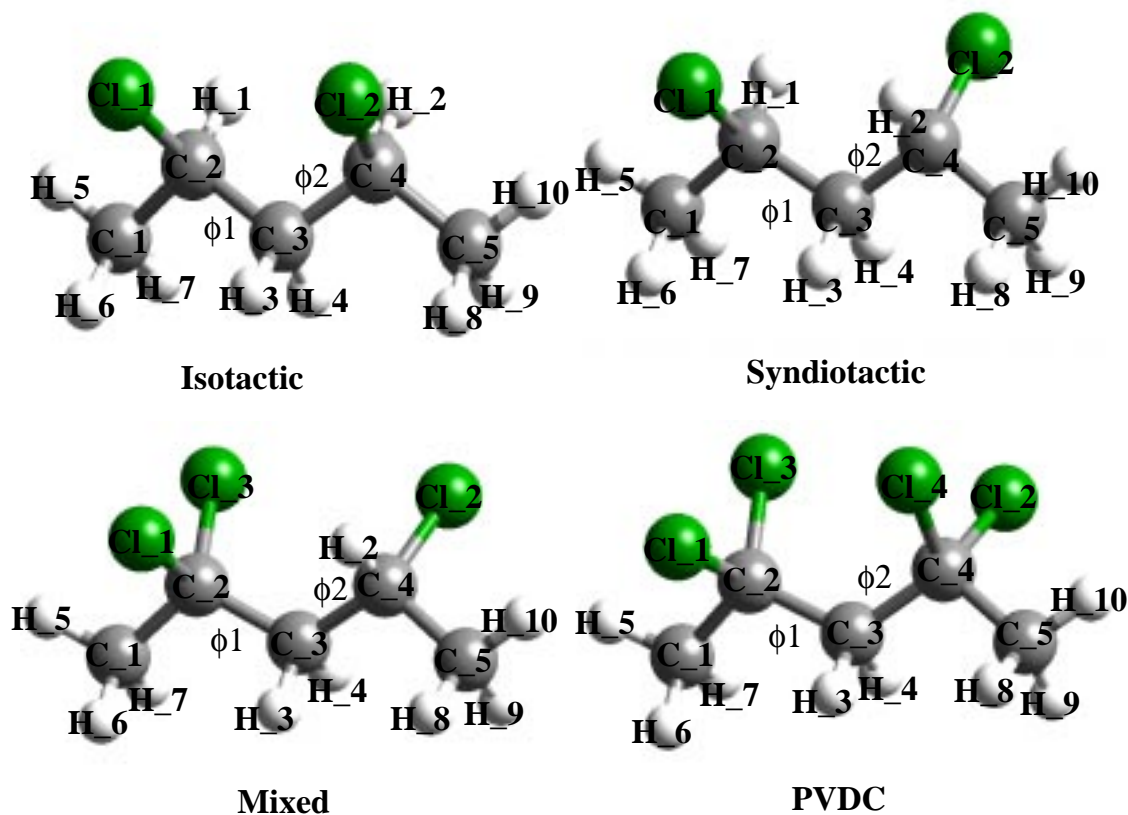


Figure 5.1: Chlorinated clusters used in the calculations

5.3 Quantum Mechanical Adiabatic 2D Rotational Energy Surface and Force Field Parameters

For PVC, both syndiotactic and isotactic, we use $\text{CH}_3\text{CHClCH}_2\text{CHClCH}_3$ to represent longer chain polymer, as shown in Fig. 5.1a and Fig. 5.1b. For CPVC of $-(\text{CCl}_2\text{CH}_2\text{CHClCH}_2)_n-$, we use $\text{CH}_3\text{CCl}_2\text{CH}_2\text{CHClCH}_3$, as in Fig. 5.1c. For PVDC, $-(\text{CCl}_2\text{CH}_2)-$, molecule of $\text{CH}_3\text{CCl}_2\text{CH}_2\text{CCl}_2\text{CH}_3$ is used as in Fig. 5.1d. Figure 5.2 shows the atomic charges assigned to these clusters.

Denote dihedral angle $\text{Cl}-\text{C}_{3x}-\text{C}_3-\text{C}_{3x}$ as ϕ . For C_{3x} , if $\phi > 0$, we use atomic type (label) C_{3R} , while if $\phi < 0$, we use atomic type (label) C_{3L} . C_{32} is used for backbone carbon atoms bonded to two Cl atoms, and C_3 is used for backbone

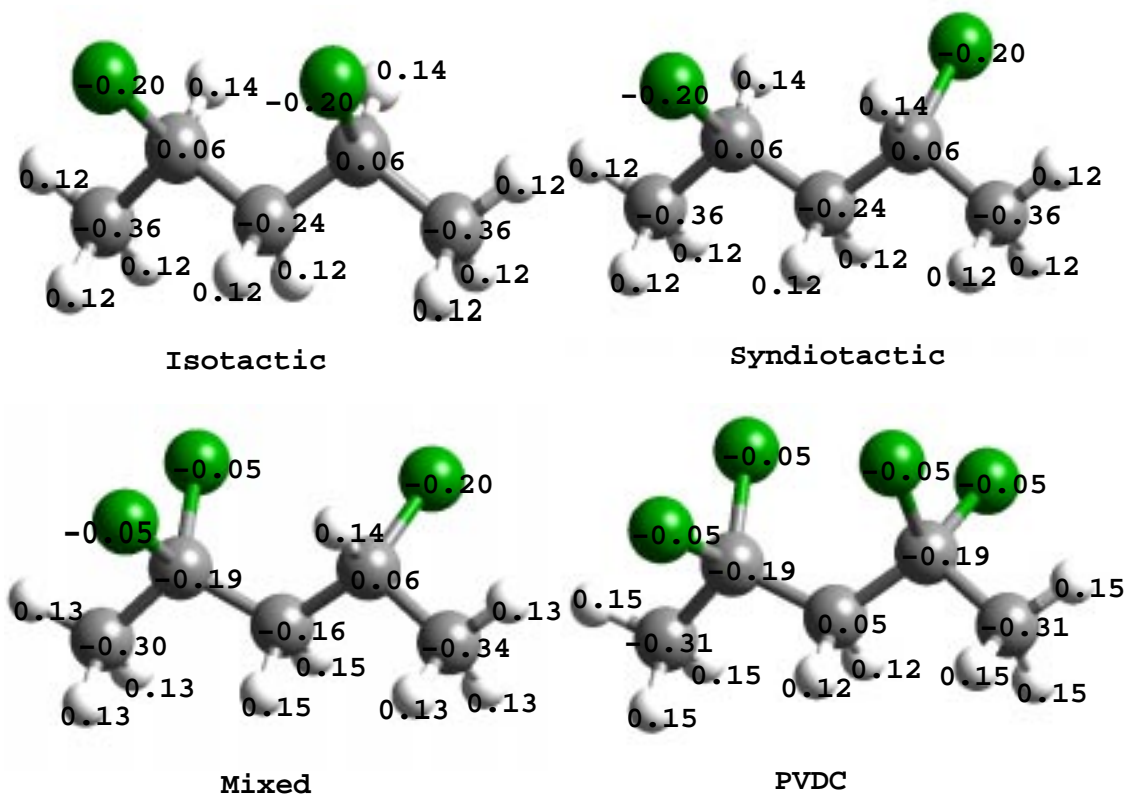


Figure 5.2: Atomic charges of the chlorinated clusters

carbon atoms that are not bonded to any Cl atoms. By doing so, we can use iPVC torsion parameters for C₃-C_{3L}-C₃-C_{3L}, or C₃-C_{3R}-C₃-C_{3R}, and sPVC torsion parameters for C₃-C_{3R}-C₃-C_{3L}. PVDC segments and mixed segments are obvious. All other torsion parameters are default DREIDII parameters ($C_0 = 1.0000$, $C_3 = 1.0000$, and the rest are $C_m = 0$). They are listed in Table 5.1. The optimized torsion parameters are listed in Table 5.2.

Table 5.1: DREIDING Parameters

LJ 12-6 van der Waals			Simple Harmonic Bond		
Atom	R_0^a	D_0^b	Bond	K_{bond}^c	R_0^a
H	3.1950	0.0152	C-C	699.5920	1.514
C	3.8983	0.0951	C-H	659.7507	1.111
Cl	3.9503	0.2833	C-Cl	510.4743	1.801

Simple Harmonic Cosine Angle					
Angle	K_{angle}^d	θ_0^e	Angle	K_{angle}^d	θ_0^e
H-C-H	75.2779	109.4710	C-C-C	214.2065	109.4710
H-C-C	117.2321	109.4710	Cl-C-C	197.7159	109.4710
H-C-Cl	99.2533	109.4710	Cl-C-Cl	191.9793	109.4710

^a Å; ^b Kcal/Mol; ^c Kcal/Mol/Å²; ^d Kcal/Mol/Degree², ^e degree.

Table 5.2: Optimized DREIDING Torsion Parameters for PVC

LLL-CCC-CCC-RRR	v_1	v_2	v_3	v_4	v_5	v_6
Isotactic Polyvinyl Chloride (iPVC)						
C_3-C_31-C_3-C_31	-19.021	-8.5939	21.2379	1.9153	-1.3116	3.8905
Cl-C_31-C_3-C_31	-9.3167	-6.6164	-27.937	3.6748	-1.5746	-4.5182
Syndiotactic Polyvinyl Chloride (sPVC)						
C_3-C_31-C_3-C_31	-15.263	-7.8935	-0.8143	1.7958	-5.1511	-0.1850
Cl-C_31-C_3-C_31	-8.9259	-4.5495	-4.4370	5.0627	-5.2440	-1.1746
Polyvinylidene Chloride (PVDC)						
C_3-C_32-C_3-C_32	-166.83	-107.80	-34.733	20.7666	7.9938	-0.7472
Cl-C_32-C_3-C_32	-156.64	-112.12	6.8933	16.2328	19.6499	1.9258
PVC-PVDC						
C_3-C_31-C_3-C_32	-19.193	-12.804	16.4478	-1.9437	-1.0113	-17.410
C_31-C_3-C_32-C_3	0.3342	-162.19	-5.0429	8.4211	25.9489	-9.0685
Cl-C_31-C_3-C_32	-8.0484	-9.8507	-26.899	1.1705	3.9923	19.0126
Cl-C_32-C_3-C_31	7.8963	-167.00	-7.6044	2.5645	37.3312	0.2991

- C_32 is C atom bonded to two Cl atoms, C_31 is C atom bonded to one Cl atom, while C_3 is C atom without Cl atom bonded to. The unit is (kcal/mol).

5.3.1 Isotactic Polyvinyl Chloride

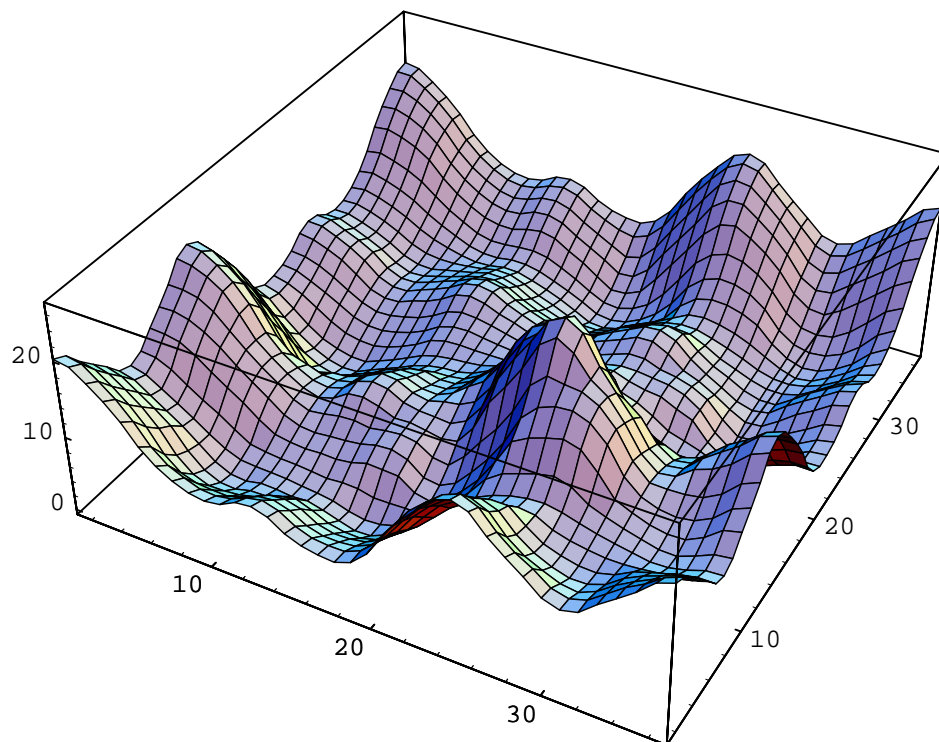


Figure 5.3: 3D plot of the adiabatic 2D-rotation energy surface. The unit of the two torsion angles is in 10° , while the unit of energy(z-axis) is in kcal/mol

Based on the reflection symmetry of the molecule, we can obtain the whole energy surface by reflecting half of the ϕ_1 - ϕ_2 space, as shown in Fig. 5.3. The grid points are generated at interval of 30° , total of 12×12 grid points. Considering the reflection symmetry and rotational symmetry of two torsion angles, we have 76 independent grid points. For each of the 76 points, as first step approximation, we optimize the structure by using DREIDII force field with the two torsion angles fixed. This gives us a better starting point for quantum optimization that is quite expensive computationally. Then we perform quantum mechanical structural minimization,

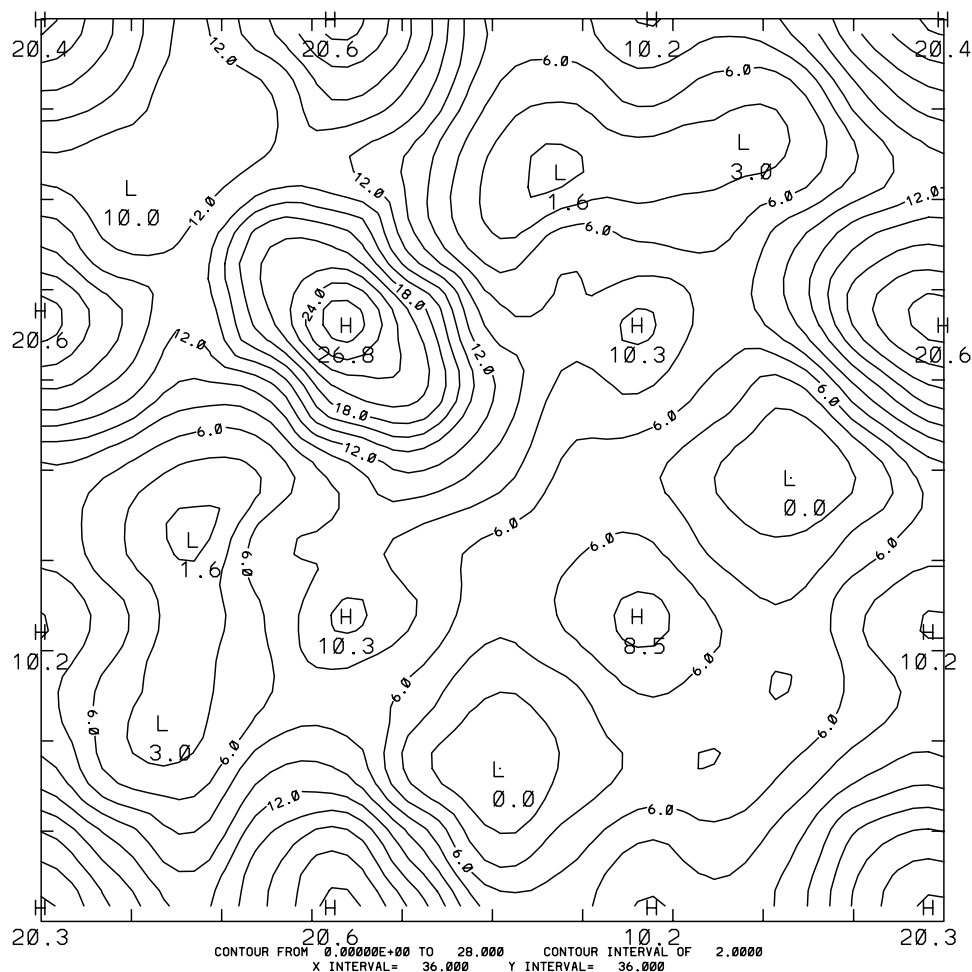


Figure 5.4: Quantum adiabatic 2D rotational surface for iPVC

keeping the two backbone torsions fixed. By plotting the whole energy surface, we can extract 6 local minimum grid points. Starting from those points, we optimized the whole structures, including the backbone torsion angles. Quantum adiabatic energy surface is interpolated based on 76 grid points and the 6 local minimum points. By doing so, we can capture both the rotational barriers and minimum energies of local minima. Figure 5.3 is the 3D plot of the energy surface, while Fig. 5.4 is 2D contour plot.

Based on the procedure outlined in Section 2, we calculated the torsional parameters. Figure 5.5 is the contour map of force field adiabatic 2D rotational energy surface. They are in good agreement with the *ab initio* results. The torsion param-

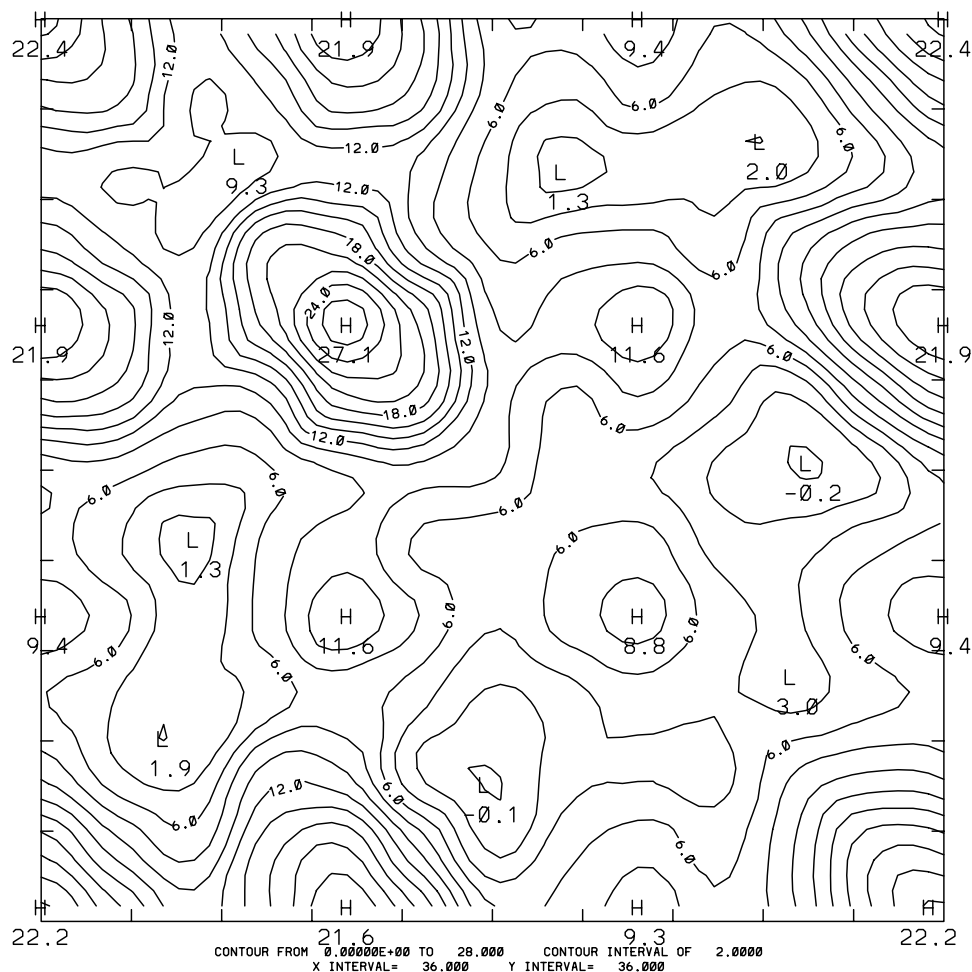


Figure 5.5: Force field adiabatic 2D rotational surface for iPVC

eters are in Table 5.2. The comparisons of quantum and force field energy at each grid point are tabulated in Table 5.3, while comparison of local minimums are in Table 5.4.

Since *ab initio* constraint structure minimization are very expensive, most of researchers calculate quantum energy based on generic force field generated grid points. For 28 grid points (interval of 30°), we used DREIDII force field minimized the structures while keeping the two backbone torsion angles fixed. For each of those structures, we did one energy quantum calculation. Figure 5.6 is the 2D contour map based on those grid points. The energies are tabulated in Table 5.5 By focusing on the relative energy differences of local minimums and the energy barriers between

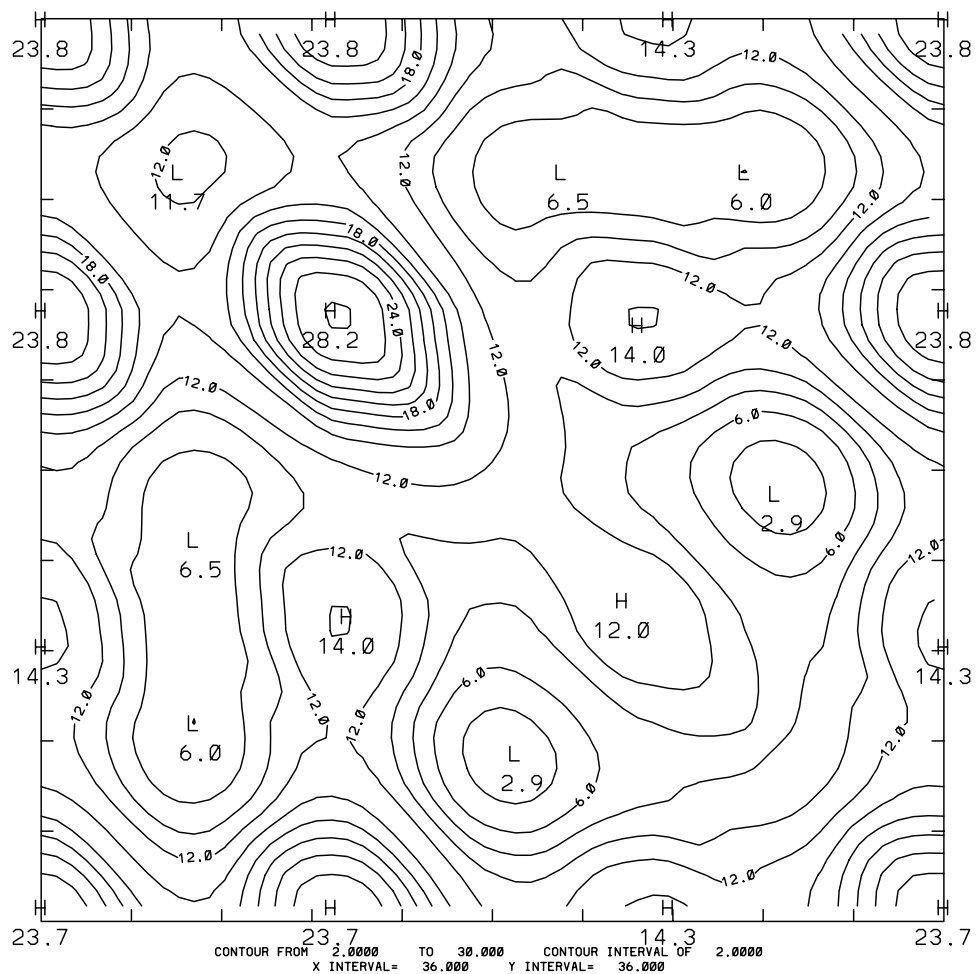


Figure 5.6: One energy quantum calculation of DREIDII adiabatic 2D rotational grids for iPVC

those local minimums, we found the adiabatic quantum rotational energy surface is quite different from the quantum one energy energy surface and the fitted force field energy surface is a very good approximation of the quantum adiabatic energy surface. In molecular dynamics simulations, by using these force fields, we can generate ensembles with the right distribution of thermodynamic density of states and rates of kinetic conformation. These are the general goals of molecular dynamics simulation of amorphous polymer materials.

Table 5.3: Adiabatic QM and FF Energy of iPVC(Kcal/Mol)

Φ_1	Φ_2	QM	FF	Error	Φ_1	Φ_2	QM	FF	Error
30.0	0.0	15.8089	16.9259	-1.1170	120.0	180.0	9.1569	8.2367	0.9202
30.0	30.0	12.2587	10.8467	1.4120	120.0	-150.0	19.5968	19.8119	-0.2151
30.0	60.0	5.3535	4.3767	0.9768	120.0	-120.0	26.8733	27.0582	-0.1849
30.0	90.0	4.8567	3.9588	0.8979	150.0	0.0	15.4643	16.3578	-0.8935
30.0	120.0	6.6466	6.7368	-0.0902	150.0	30.0	10.2474	9.6961	0.5513
30.0	150.0	4.3697	4.2364	0.1333	150.0	60.0	2.9813	2.0368	0.9445
30.0	180.0	5.9952	6.9245	-0.9293	150.0	90.0	5.1055	4.7895	0.3160
30.0	-150.0	12.9656	15.2384	-2.2728	150.0	120.0	7.8812	8.0285	-0.1473
30.0	-120.0	16.3430	17.5058	-1.1628	150.0	150.0	7.3360	5.7343	1.6017
30.0	-90.0	11.7884	12.1166	-0.3282	150.0	180.0	12.1163	9.4241	2.6922
30.0	-60.0	10.2324	10.0156	0.2168	150.0	-150.0	20.3957	19.4888	0.9069
30.0	-30.0	13.8897	16.6105	-2.7208	-180.0	0.0	7.5741	6.6472	0.9269
60.0	0.0	11.7238	11.1711	0.5527	-180.0	30.0	2.8616	1.5604	1.3012
60.0	30.0	8.6727	7.1191	1.5536	180.0	60.0	-0.0022	-0.0358	0.0336
60.0	60.0	4.6264	3.3410	1.2854	-180.0	90.0	1.9730	1.6901	0.2829
60.0	90.0	3.5980	2.9226	0.6754	-180.0	120.0	4.5211	4.1976	0.3235
60.0	120.0	3.0753	2.5728	0.5025	180.0	150.0	5.5894	4.4283	1.1611
60.0	150.0	1.6799	1.2631	0.4168	-180.0	180.0	9.2475	8.2669	0.9806
60.0	180.0	3.5127	4.9334	-1.4207	-150.0	0.0	7.2965	6.5904	0.7061
60.0	-150.0	8.9573	9.6582	-0.7009	-150.0	30.0	5.1871	5.3257	-0.1386
60.0	-120.0	12.2733	11.3416	0.9317	-150.0	60.0	2.3515	3.2187	-0.8672
60.0	-90.0	12.4939	9.8360	2.6579	-150.0	90.0	3.3844	3.2679	0.1165
60.0	-60.0	10.8743	10.0077	0.8666	-150.0	120.0	6.2348	6.8345	-0.5997
90.0	0.0	15.8782	15.6215	0.2567	-150.0	150.0	5.7531	6.1719	-0.4188
90.0	30.0	14.4794	14.9324	-0.4530	-120.0	0.0	10.1112	9.3951	0.7161
90.0	60.0	9.7829	10.6419	-0.8590	-120.0	30.0	8.1835	7.2439	0.9396
90.0	90.0	5.8841	4.8120	1.0721	-120.0	60.0	4.3682	3.8054	0.5628
90.0	120.0	6.1094	6.8685	-0.7591	-120.0	90.0	5.9861	5.0890	0.8971
90.0	150.0	7.1577	6.5007	0.6570	-120.0	120.0	8.5262	8.6714	-0.1452
90.0	180.0	4.5196	5.7023	-1.1827	-90.0	0.0	8.4273	6.0696	2.3577
90.0	-150.0	10.3909	10.4891	-0.0982	-90.0	30.0	6.9850	5.2317	1.7533
90.0	-120.0	19.4740	18.8056	0.6684	-90.0	60.0	4.0977	3.2817	0.8160
90.0	-90.0	19.7082	19.1725	0.5357	-90.0	90.0	4.9734	4.2445	0.7289
120.0	0.0	20.6485	21.8841	-1.2356	-60.0	0.0	10.7522	9.3181	1.4341
120.0	30.0	17.5388	18.0534	-0.5146	-60.0	30.0	9.7813	9.9098	-0.1285
120.0	60.0	9.9411	10.1102	-0.1691	-60.0	60.0	6.3744	7.8857	-1.5113
120.0	90.0	7.2198	6.9026	0.3172	-30.0	0.0	17.0207	17.2469	-0.2262
120.0	120.0	10.1880	11.5163	-1.3283	-30.0	30.0	15.4823	17.1395	-1.6572
120.0	150.0	8.3365	9.0547	-0.7182	0.0	0.0	20.3605	22.4211	-2.0606

Table 5.4: QM and FF Local Minimums of iPVC(Kcal/Mole)

Φ_1	Φ_2	QM	FF	Error	Φ_1	Φ_2	QM	FF	Error
44.9	73.7	3.1331	2.0201	1.1130	56.7	154.1	1.6149	1.3076	0.3073
52.8	-52.8	10.4863	10.8417	-0.3554	-179.5	60.8	0.0000	0.0000	0.0000
-155.9	156.7	5.4815	5.4049	0.0766	-79.2	79.5	4.3209	4.7272	-0.4063

Table 5.5: QM Energy of FF Grids for iPVC(Kcal/Mol)

Φ_1	Φ_2	QM	Φ_1	Φ_2	QM
0.00	0.00	23.8185	120.00	60.00	12.7771
0.00	60.00	13.4073	120.00	120.00	14.0325
0.00	120.00	14.2352	120.00	180.00	11.6897
0.00	180.00	11.8722	120.00	240.00	28.1188
0.00	240.00	23.7898	180.00	0.00	11.8706
0.00	300.00	14.4002	180.00	60.00	3.2899
0.00	360.00	23.8185	180.00	120.00	7.5693
60.00	0.00	14.3980	180.00	180.00	11.8400
60.00	60.00	6.7944	240.00	0.00	14.2382
60.00	120.00	6.6391	240.00	60.00	7.1715
60.00	180.00	7.4092	240.00	120.00	11.8510
60.00	240.00	14.0671	300.00	0.00	13.4102
60.00	300.00	11.7026	300.00	60.00	8.6857
120.00	0.00	23.7916	360.00	0.00	23.8185

5.3.2 Syndiotactic Polyvinyl Chloride

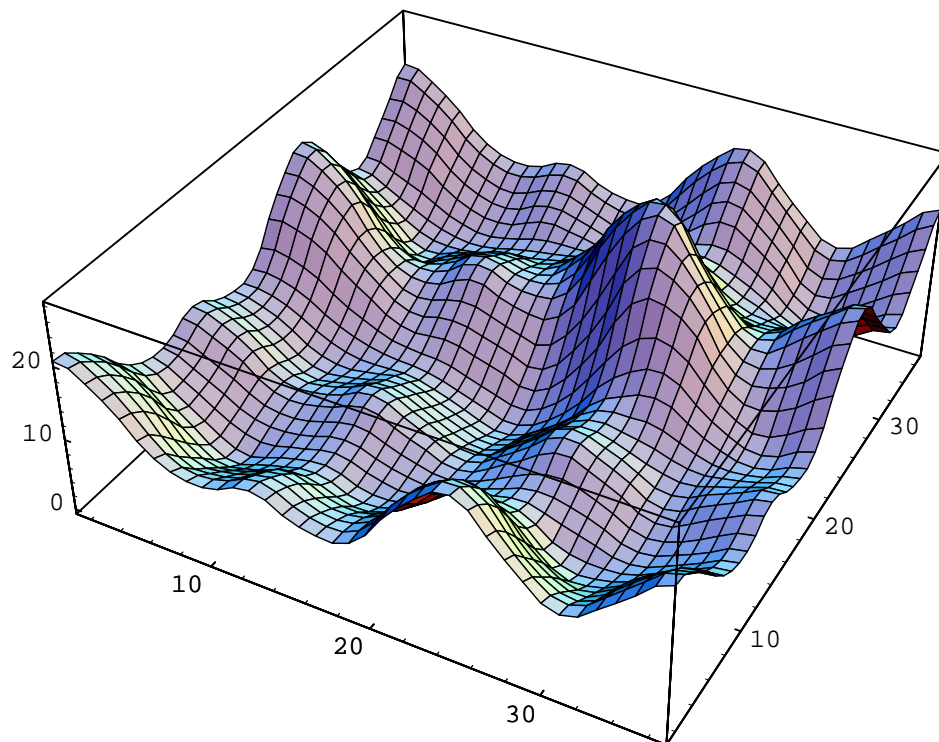


Figure 5.7: 3D plot of adiabatic 2D rotational surface for sPVC, z-axis is the energy with unit kcal/mol. x-axis and y-axis correspond to the two backbone dihedral angles with unit 10°

Similar to iPVC, there is also a reflection plane on the 2D rotational space for sPVC. The reflection axis is perpendicular to that of iPVC. 76 grid points are required for an angle increment of 30° . The 3D plot of quantum adiabatic rotational energy surface is in Fig. 5.7, while the 2D contour map is in Fig. 5.8. Figure 5.9 is the 2D contour map of adiabatic rotational energy surface, based on optimized force field. The quantum and force field energies at the grid points are tabulated in Table 5.6, and those of the six local minimums are in Table 5.7. As a comparison, we calculated the quantum one energy on force field generated grids. The 2D contour map is in

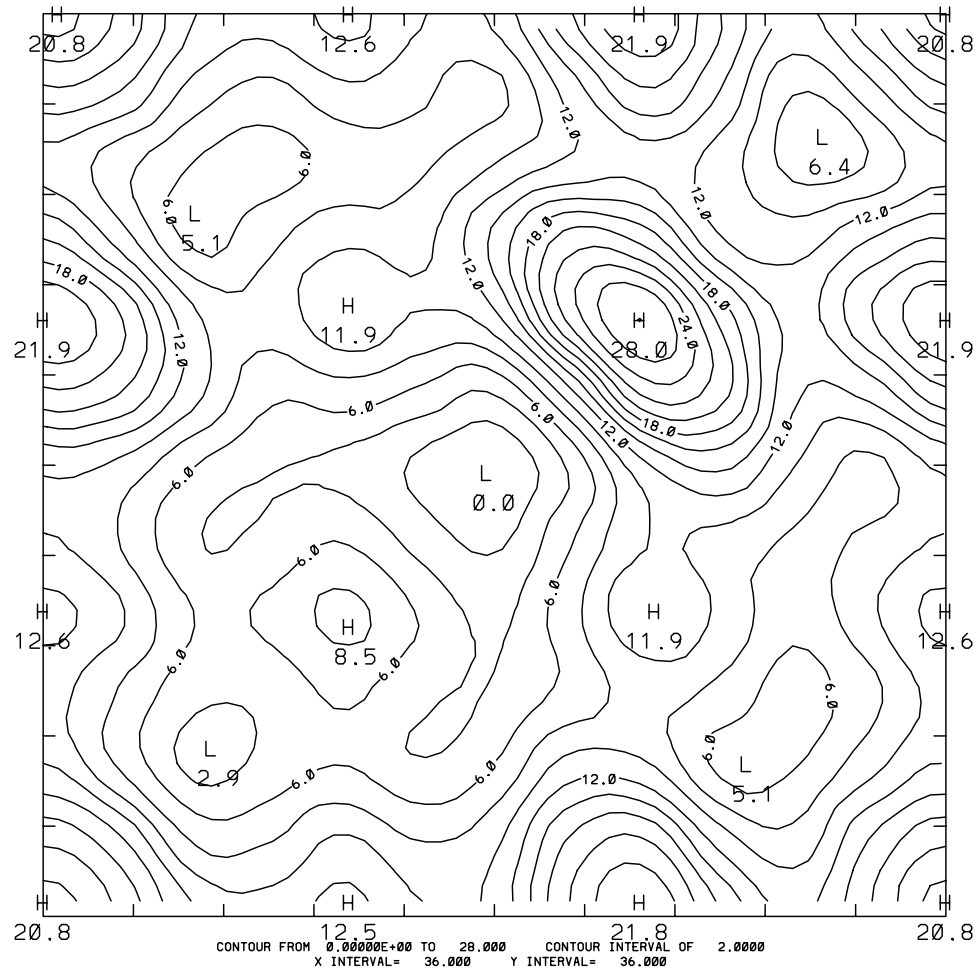


Figure 5.8: Quantum adiabatic 2D rotational surface for sPVC

Fig. 5.10. The energies are tabulated in Table [5.8].

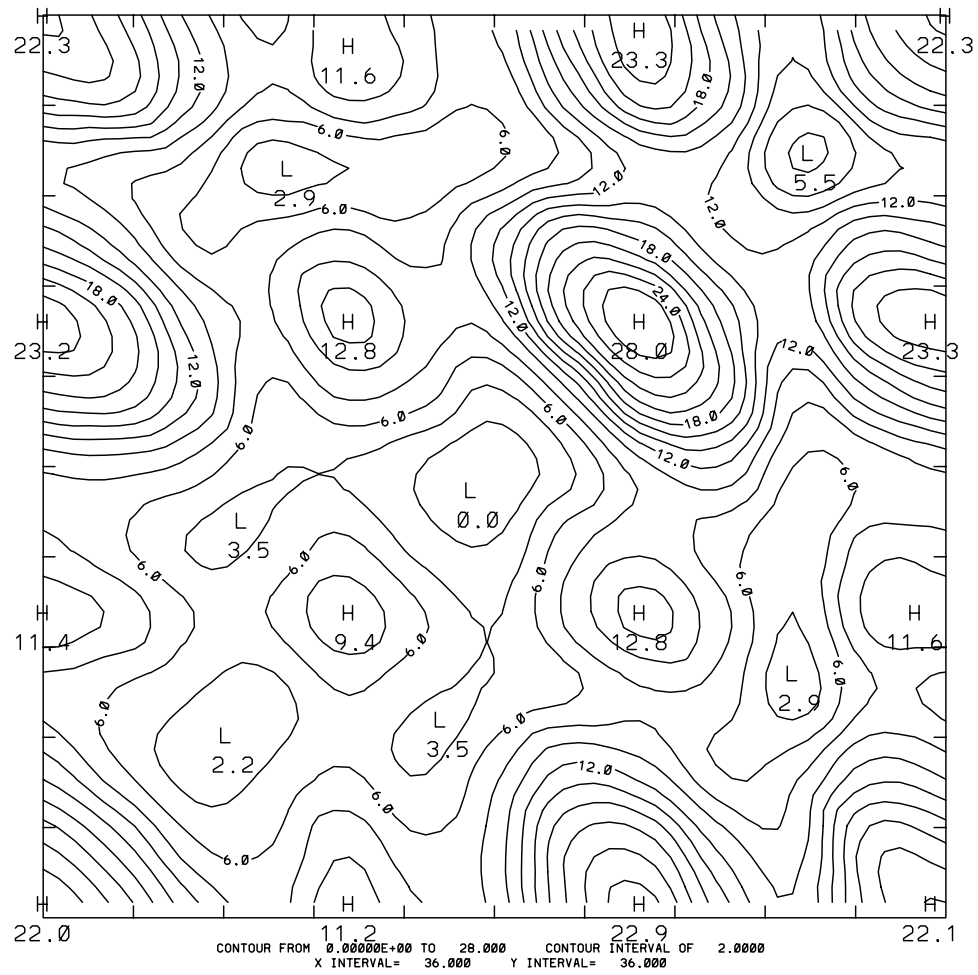


Figure 5.9: Force field adiabatic 2D rotational surface for sPVC

Table 5.6: Adiabatic QM and FF Energy of sPVC(Kcal/Mol)

Φ_1	Φ_2	QM	FF	Error	Φ_1	Φ_2	QM	FF	Error
0.0	0.0	20.7512	22.2526	-1.5014	-120.0	90.0	8.7270	7.8848	0.8422
30.0	0.0	17.7018	17.9686	-0.2668	-120.0	120.0	11.7605	12.7938	-1.0333
30.0	30.0	14.5433	12.7143	1.8290	-120.0	150.0	9.9155	9.4261	0.4894
60.0	0.0	12.1369	11.0654	1.0715	-120.0	180.0	11.6682	9.5211	2.1471
60.0	30.0	7.8451	6.2442	1.6009	-120.0	-150.0	22.8654	21.9387	0.9267
60.0	60.0	3.0885	2.3345	0.7540	-120.0	-120.0	27.8581	27.7586	0.0995
90.0	0.0	10.5627	7.4305	3.1322	-90.0	0.0	16.0561	15.3750	0.6811
90.0	30.0	7.9213	5.8571	2.0642	-90.0	30.0	11.2363	11.2502	-0.0139
90.0	60.0	4.6914	4.1180	0.5734	-90.0	60.0	5.5801	5.9376	-0.3575
90.0	90.0	4.7283	3.2885	1.4398	-90.0	90.0	7.5104	7.1264	0.3840
120.0	0.0	12.5809	11.3823	1.1986	-90.0	120.0	9.6502	8.6833	0.9669
120.0	30.0	10.3198	9.5264	0.7934	-90.0	150.0	9.4032	6.9806	2.4226
120.0	60.0	6.0037	6.0117	-0.0080	-90.0	180.0	14.5115	11.9499	2.5616
120.0	90.0	6.3292	6.0386	0.2906	-90.0	-150.0	20.9291	19.4929	1.4362
120.0	120.0	8.5405	9.4207	-0.8802	-90.0	-120.0	19.2815	17.7766	1.5049
150.0	0.0	10.1142	8.2782	1.8360	-90.0	-90.0	12.2225	12.5022	-0.2797
150.0	30.0	8.0092	6.2557	1.7535	-60.0	0.0	11.4476	10.2491	1.1985
150.0	60.0	4.1812	3.7861	0.3951	-60.0	30.0	8.7952	9.0983	-0.3031
150.0	90.0	4.5879	4.3093	0.2786	-60.0	60.0	5.9185	7.2621	-1.3436
150.0	120.0	5.8998	6.2568	-0.3570	-60.0	90.0	5.1630	2.9834	2.1796
150.0	150.0	3.2461	3.1074	0.1387	-60.0	120.0	6.5757	3.9887	2.5870
180.0	0.0	10.4632	8.3690	2.0942	-60.0	150.0	7.6877	4.5708	3.1169
180.0	30.0	9.5698	8.8535	0.7163	-60.0	180.0	10.0187	5.9194	4.0993
180.0	60.0	6.1067	7.2761	-1.1694	-60.0	-150.0	12.4385	8.7992	3.6393
180.0	90.0	4.1773	4.2475	-0.0702	-60.0	-120.0	13.4105	12.6881	0.7224
180.0	120.0	3.5704	3.9085	-0.3381	-60.0	-90.0	11.0617	12.0989	-1.0372
180.0	150.0	1.6332	2.0600	-0.4268	-60.0	-60.0	7.3634	5.8632	1.5002
180.0	180.0	0.2216	0.3691	-0.1475	-30.0	0.0	15.7345	18.5026	-2.7681
-150.0	0.0	17.7869	18.0511	-0.2642	-30.0	30.0	14.2055	18.9437	-4.7382
-150.0	30.0	16.2873	17.9934	-1.7061	-30.0	60.0	9.3602	12.5579	-3.1977
-150.0	60.0	10.8166	12.3405	-1.5239	-30.0	90.0	7.5116	7.8856	-0.3740
-150.0	90.0	6.5821	5.6859	0.8962	-30.0	120.0	9.6724	10.5458	-0.8734
-150.0	120.0	7.2955	8.4953	-1.1998	-30.0	150.0	8.4496	8.8431	-0.3935
-150.0	150.0	5.7584	7.0988	-1.3404	-30.0	180.0	7.5589	6.5552	1.0037
-150.0	180.0	4.3716	3.7380	0.6336	-30.0	-150.0	12.9275	13.9545	-1.0270
-150.0	-150.0	11.6940	10.0056	1.6884	-30.0	-120.0	17.9070	21.5364	-3.6294
-120.0	0.0	21.8825	23.1340	-1.2515	-30.0	-90.0	14.0468	16.7854	-2.7386
-120.0	30.0	18.1823	18.8285	-0.6462	-30.0	-60.0	8.1658	8.9191	-0.7533
-120.0	60.0	10.3347	10.5278	-0.1931	-30.0	-30.0	11.4063	14.9270	-3.5207

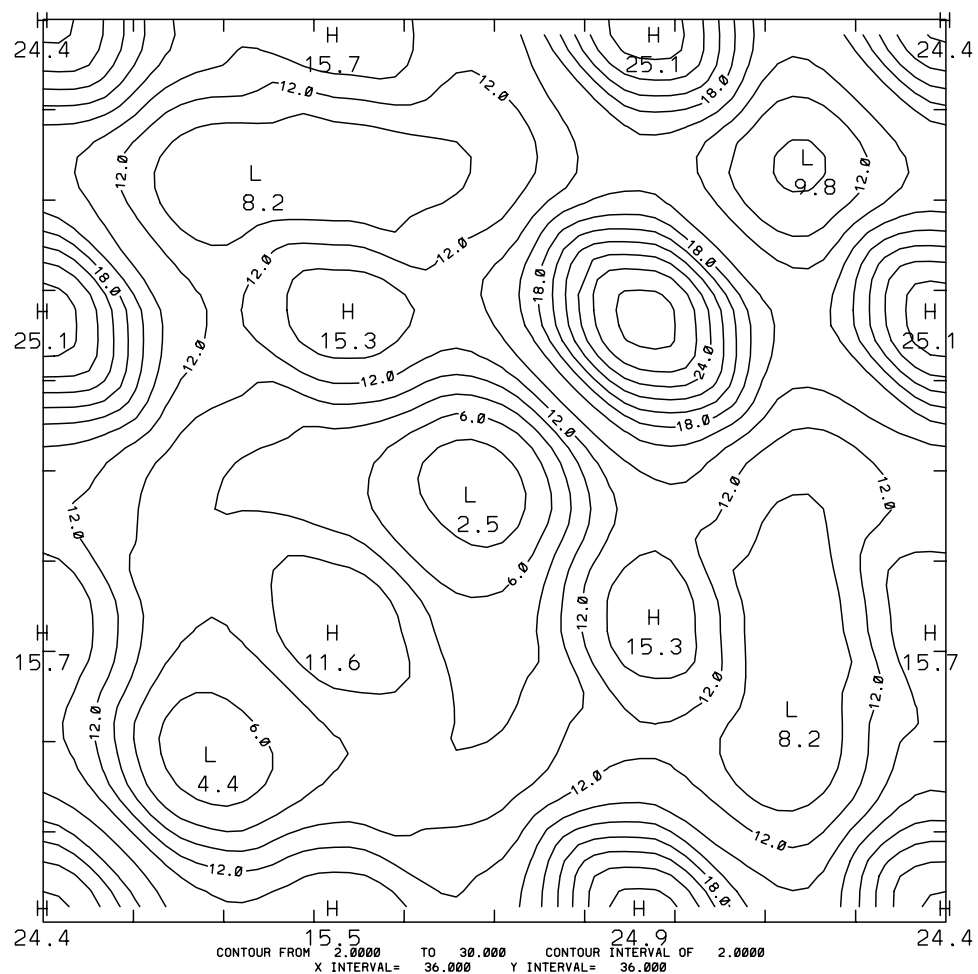


Figure 5.10: Quantum one energy calculation of DREIDII adiabatic 2D rotational grids for sPVC

Table 5.7: Local Minimums for sPVC(Kcal/Mole)

Φ_1	Φ_2	QM	FF	Error	Φ_1	Φ_2	QM	FF	Error
64.2	64.3	2.9916	2.3713	0.6203	160.7	79.1	3.7644	3.5273	0.2371
173.4	173.4	0.0000	0.0000	0.0000	-69.3	71.5	5.1593	5.0076	0.1517
-32.1	171.3	7.2982	6.1663	1.1319	-48.0	-48.0	6.4601	6.1377	0.3224

Table 5.8: QM Energy of FF Grids for sPVC(Kcal/Mole)

Φ_1	Φ_2	QM	Φ_1	Φ_2	QM
360.00	360.00	24.4116	120.00	120.00	28.7529
360.00	300.00	15.2077	360.00	60.00	14.4116
300.00	300.00	5.0835	300.00	60.00	8.8213
360.00	240.00	15.6601	240.00	60.00	8.5839
300.00	240.00	8.0973	180.00	60.00	10.5997
240.00	240.00	11.5547	120.00	60.00	15.4012
360.00	180.00	13.0037	60.00	60.00	9.7703
300.00	180.00	8.7231	360.00	0.00	24.4132
240.00	180.00	6.5478	300.00	0.00	15.1999
180.00	180.00	3.1852	240.00	0.00	15.6611
360.00	120.00	25.0846	180.00	0.00	13.0042
300.00	120.00	12.3637	120.00	0.00	25.0842
240.00	120.00	15.1657	60.00	0.00	14.4159
180.00	120.00	14.1483	0.00	0.00	24.4116

5.3.3 Polyvinylidene Chloride

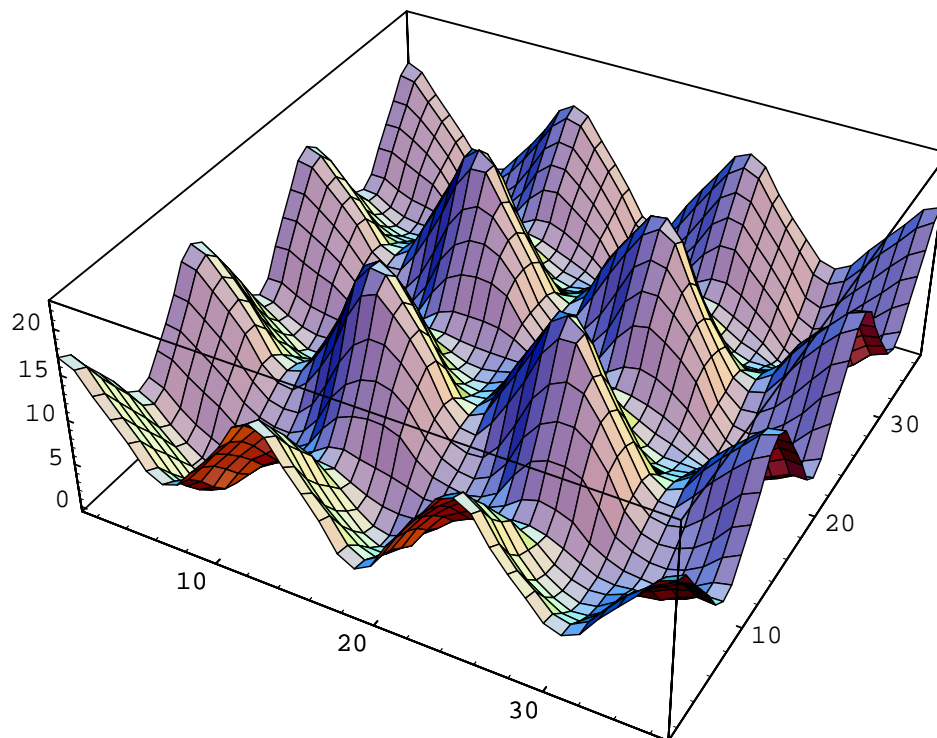


Figure 5.11: 3D plot of adiabatic 2D rotational surface for PVDC (Angle in 10°)

Polyvinylidene Chloride has higher symmetry than that of iPVC and sPVC. For interval of 30° , we used 50 grid points that covers one quarter of the 2D space, plus four local minimums. Figure 5.11 is the 3D plot of quantum adiabatic energy surface, while the 2D contour map is in Fig. 5.12. The results from optimized force field are plotted in Fig. 5.13. Comparison of energies at each point are tabulated in Table 5.9.

We also did quantum one energy calculation on grids generated based on DREIDII force field. The 2D contour map of rotational energy surface is plotted in Fig. 5.14, and tabulated in Table [5.10].

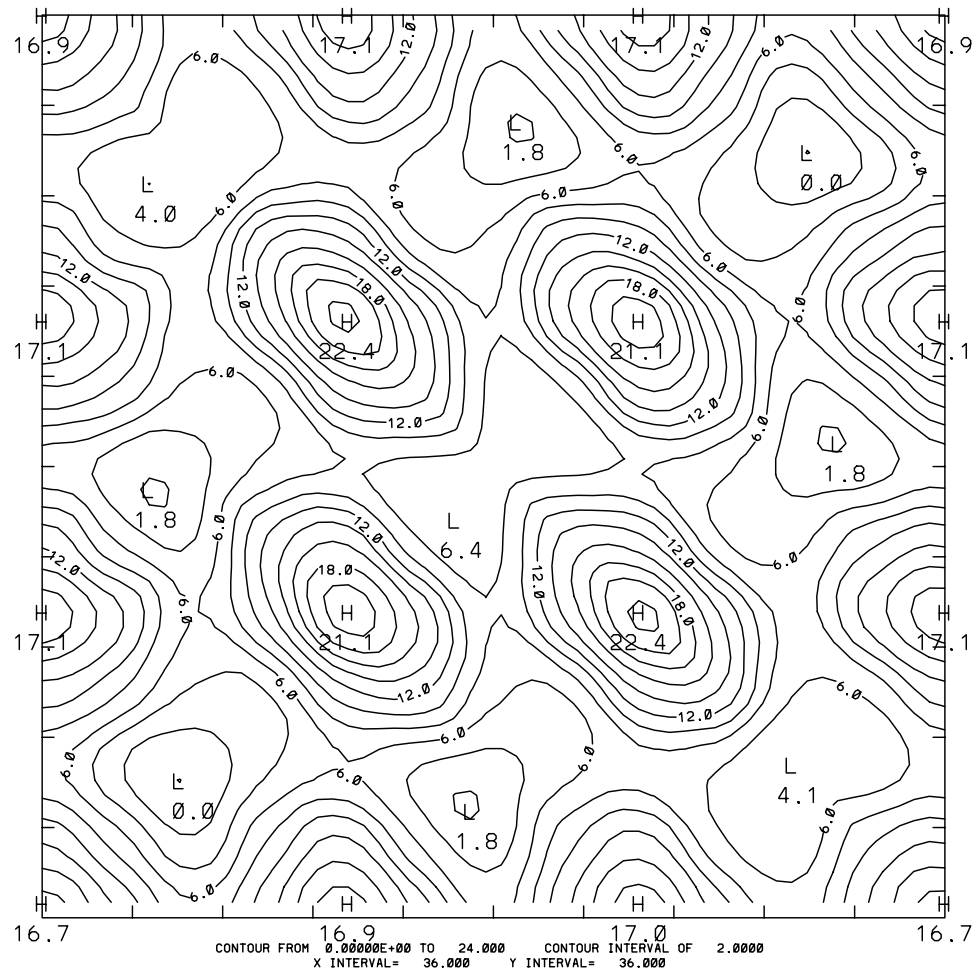


Figure 5.12: Quantum adiabatic 2D rotational surface for PVDC

Table 5.9: Adiabatic QM and FF Energy of PVDC (Kcal/Mole)

Φ_1	Φ_2	QM	FF	Error	Φ_1	Φ_2	QM	FF	Error
0.0	0.0	16.9396	17.7674	-0.8278	90.0	-180.0	6.5771	6.6309	-0.0538
0.0	30.0	11.9382	11.3183	0.6199	120.0	-180.0	7.9857	7.2809	0.7048
30.0	30.0	7.0920	7.2073	-0.1153	150.0	180.0	7.4874	6.7613	0.7261
0.0	60.0	6.6058	7.0085	-0.4027	-180.0	-180.0	7.3741	7.4003	-0.0262
30.0	60.0	2.3499	1.0767	1.2732	0.0	-150.0	11.5447	11.9868	-0.4421
60.0	60.0	0.3630	1.6444	-1.2814	30.0	-150.0	9.4859	10.6921	-1.2062
0.0	90.0	11.1026	10.4971	0.6055	60.0	-150.0	5.5174	5.2661	0.2513
30.0	90.0	8.1697	8.6125	-0.4428	90.0	-150.0	6.3921	6.1841	0.2080
60.0	90.0	3.7732	4.7668	-0.9936	120.0	-150.0	14.5706	14.6971	-0.1265
90.0	90.0	4.0411	4.9931	-0.9520	150.0	-150.0	14.8181	15.6382	-0.8201
0.0	120.0	17.1286	17.6353	-0.5067	0.0	-120.0	17.1280	17.6352	-0.5072
30.0	120.0	12.4872	13.1084	-0.6212	30.0	-120.0	12.7333	12.7494	-0.0161
60.0	120.0	5.9531	5.6287	0.3244	60.0	-120.0	7.2256	5.9681	1.2575
90.0	120.0	11.2123	11.9355	-0.7232	90.0	-120.0	14.2035	14.5203	-0.3168
120.0	120.0	20.8974	21.5827	-0.6853	120.0	-120.0	22.4389	22.8679	-0.4290
0.0	150.0	11.5615	11.9933	-0.4318	0.0	-90.0	11.1122	10.4849	0.6273
30.0	150.0	5.9401	6.0794	-0.1393	30.0	-90.0	6.4651	6.7689	-0.3038
60.0	150.0	3.9551	3.2074	0.7477	60.0	-90.0	6.0472	4.9345	1.1127
90.0	150.0	12.3129	12.9045	-0.5916	90.0	-90.0	13.8084	12.7514	1.0570
120.0	150.0	15.8376	16.4206	-0.5830	0.0	-60.0	6.5967	7.0067	-0.4100
150.0	150.0	8.1747	6.7956	1.3791	30.0	-60.0	4.6666	3.4726	1.1940
0.0	-180.0	5.2519	6.1510	-0.8991	60.0	-60.0	4.3747	4.4720	-0.0973
30.0	180.0	3.0201	2.9148	0.1053	0.0	-30.0	11.9398	11.3198	0.6200
60.0	180.0	3.2468	4.2251	-0.9783	30.0	-30.0	9.7730	10.4496	-0.6766
Local Minimums									
52.4	52.4	0.0000	0.0000	0.0000	42.6	167.2	1.8653	1.9294	-0.0641
180.0	179.9	7.3696	7.4012	-0.0316	56.7	-56.5	4.2612	4.3652	-0.1040

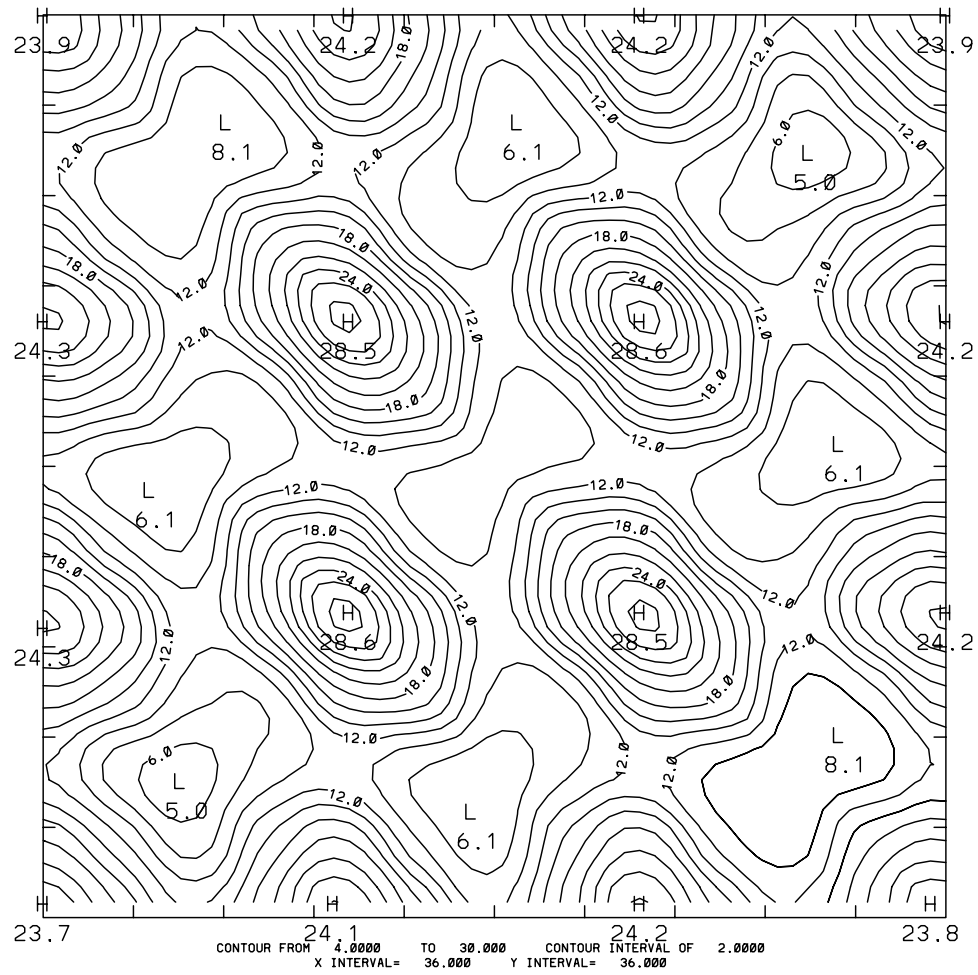


Figure 5.14: Quantum one energy calculation of DREIDII adiabatic 2D rotational grids for PVDC

Table 5.10: QM Energy of FF Grids for PVDC (Kcal/Mole)

Φ_1	Φ_2	QM	Φ_1	Φ_2	QM
360.0	360.0	23.9285	180.0	270.0	9.6934
330.0	360.0	18.1459	180.0	240.0	11.0720
330.0	330.0	12.5615	180.0	210.0	10.1891
300.0	360.0	12.0579	180.0	180.0	9.3368
300.0	330.0	7.0202	150.0	360.0	16.8153
300.0	300.0	5.1921	150.0	330.0	14.7447
270.0	360.0	17.4350	150.0	300.0	9.6692
270.0	330.0	14.3536	150.0	270.0	10.2060
270.0	300.0	8.8495	150.0	240.0	19.7465
270.0	270.0	9.0098	150.0	210.0	18.5852
240.0	360.0	24.2266	120.0	360.0	24.2014
240.0	330.0	18.2955	120.0	330.0	19.2246
240.0	300.0	10.5900	120.0	300.0	12.0979
240.0	270.0	17.9293	120.0	270.0	19.1709
240.0	240.0	28.6327	120.0	240.0	28.5145
210.0	360.0	16.7986	90.0	360.0	17.4333
210.0	330.0	10.0442	90.0	330.0	11.3092
210.0	300.0	8.1266	90.0	300.0	9.7406
210.0	270.0	17.5767	90.0	270.0	18.2809
210.0	240.0	19.2904	60.0	360.0	12.0661
210.0	210.0	10.5292	60.0	330.0	9.0761
180.0	360.0	9.6271	60.0	300.0	8.1909
180.0	330.0	6.9211	30.0	360.0	18.1512
180.0	300.0	6.7819	30.0	330.0	15.7161

5.3.4 Mixture of Polyvinyl Chloride and Polyvinylidene Chloride

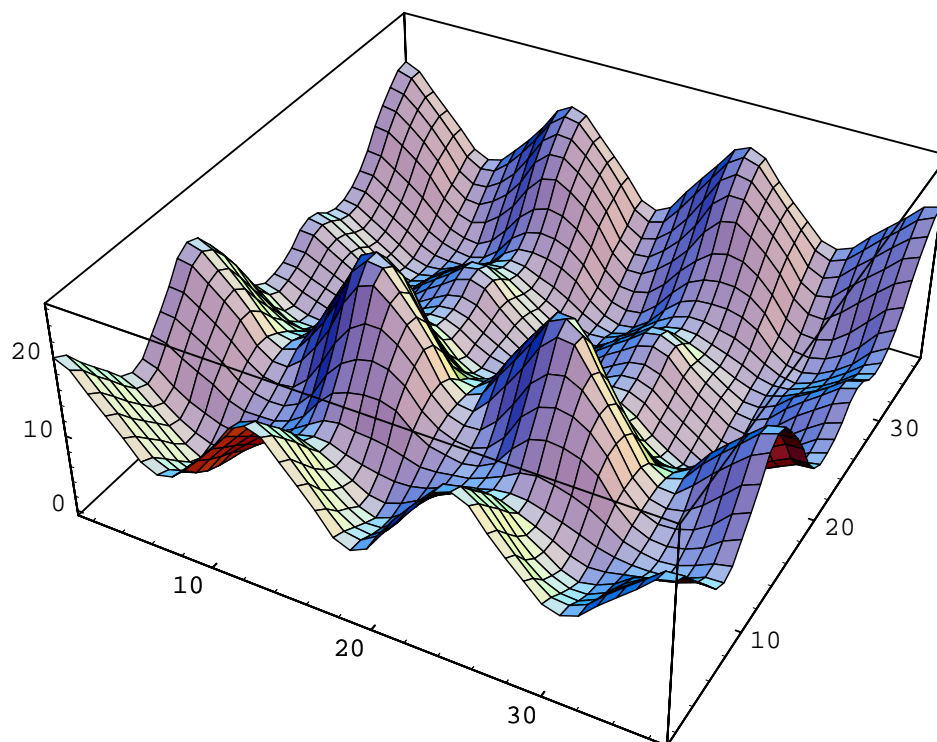


Figure 5.15: 3D plot of adiabatic 2D rotational surface for PVC-PVDC (Angle in 10°)

In the case of the mixture of Polyvinyl Chloride and Polyvinylidene Chloride, there is no reflection symmetry. For an interval of 30° , 144 grid points plus 9 local minimums are calculated. The 3D quantum adiabatic energy surface is plotted in Fig. 5.15, while the 2D contour map plot is in Fig. 5.16. Figure 5.17 is the 2D contour map based on optimized force field. The energies at grid points are tabulated in Table 5.11 and Table 5.12. The 9 local minimums are tabulated in Table 5.14.

Figure 5.18 is the 2D contour map of quantum one energy calculations on DREI-

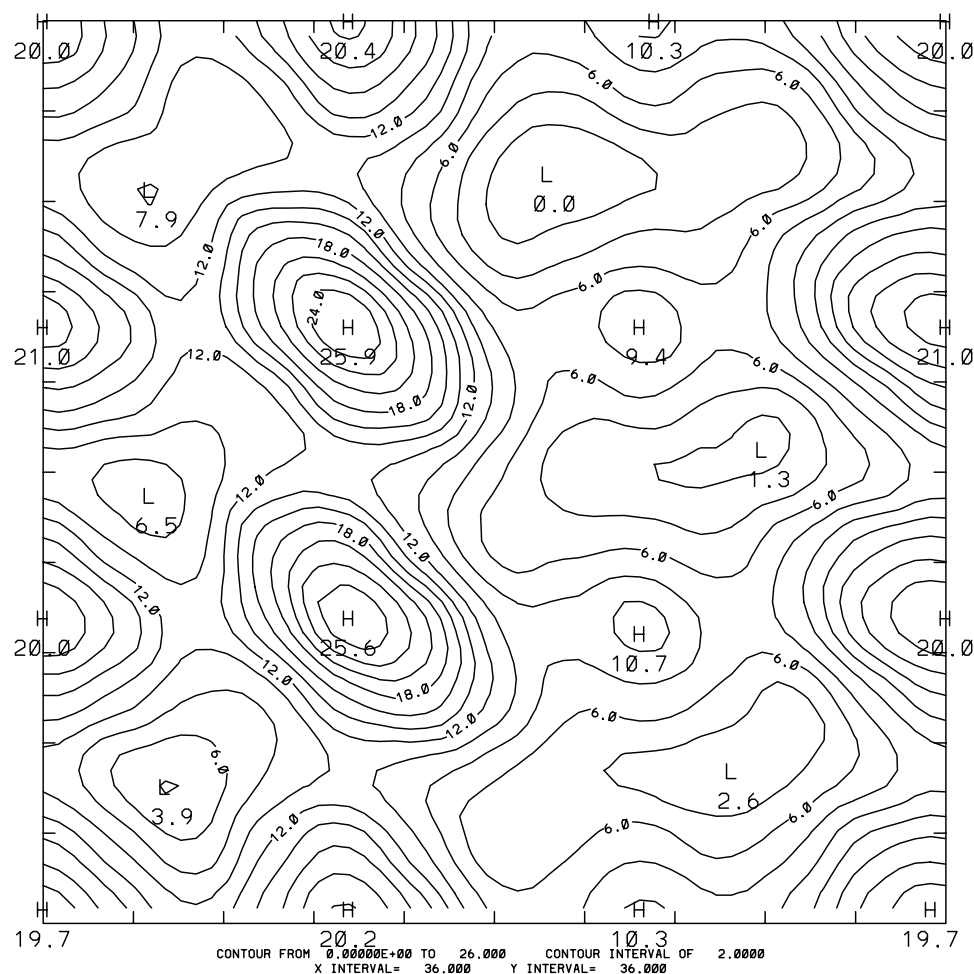


Figure 5.16: Quantum adiabatic 2D rotational surface for PVC-PVDC

IDII force field generated grids. The energies are listed in Table 5.14.

5.4 Summary

The quality of force fields for amorphous polymers are mainly determined by two factors; one is the relative energy difference between the local minimums of torsional conformations, which dictates the equilibrium distributions of torsional states thermodynamically; the other factor is the energy barriers between various local optimum conformations, which determines the rate of conformation transitions, i.e., the rigidity of polymer chains. Compared to the usual one-energy quantum potential based on

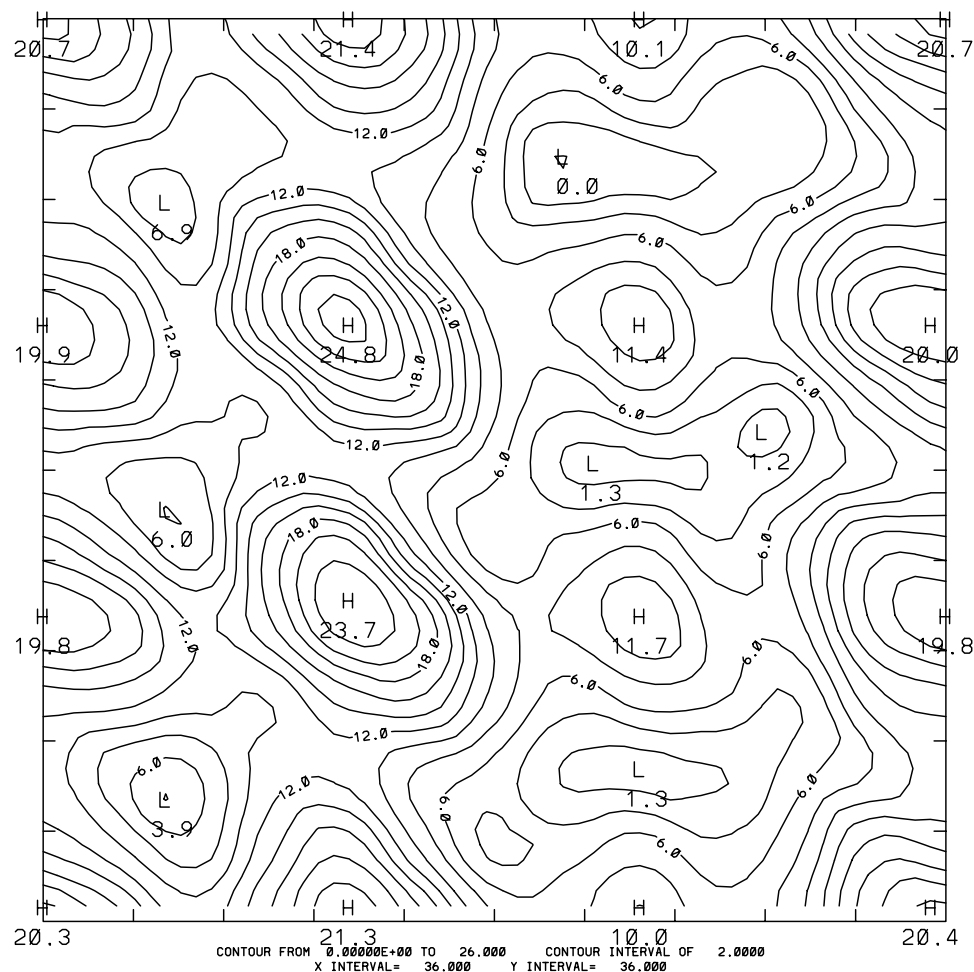


Figure 5.17: Force field adiabatic 2D rotational surface for PVC-PVDC

one torsion angle, adiabatic 2D quantum potential calculations are a big step forward, the new approach included the correlation of adjacent torsion angles.

Adiabatic molecular simulation force field (MSFF) suitable for carrying out molecular dynamics simulations of amorphous polymers (polyvinyl chloride, polyvinylidene chloride) are developed. These force fields can be used in molecular dynamics simulations to study physical properties of amorphous polymers such as glass transition temperature and diffusivity of gas molecules.

The force fields are based on adiabatic 2D (two adjacent backbone torsions) rotational energy surfaces generated by using *ab initio* calculations. Clusters with five-backbone carbon atoms are used to mimick the polymer chains. These 2D grids

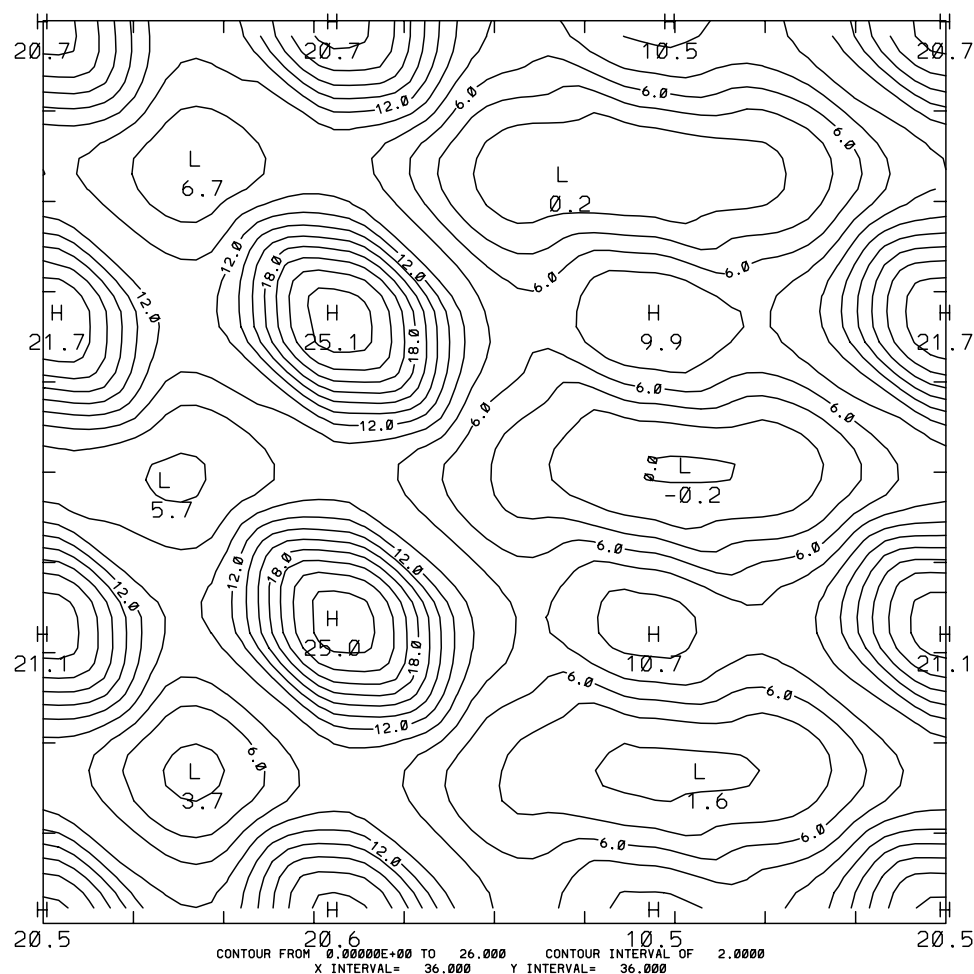


Figure 5.18: Quantum one energy calculation of DREIDII adiabatic 2D rotational grids for PVC-PVDC

are based on rotating two backbone torsions with increment of 30° . For each conformation (symmetry properties are being used to reduce the number of points), we optimize the whole structure while the two backbone torsions are constrained. These grid points plus local minimum points (fully optimized) are used to generate the 2-D adiabatic potential energy surfaces. Force fields are fitted so that the adiabatic force field potential energy surfaces match to that of quantum adiabatic potential surface. These force fields will be used in molecular dynamics simulations of glass transition and gas diffusions.

5.5 References

1. R.G. Parker, G.A., Martello, "Chemical Modifications: Chlorinated PVC," *Encyclopedia of PVC*, 1986, 619-654.
2. A.K. Rappe, W.A. Goddard III, "Charge equilibration for molecular-dynamics simulations," *J. Phys. Chem.* **95(8)**, 1991, 3358-3363.
3. S.L. Mayo, B.D. Olafson, W.A. Goddard III, "DREIDING - a generic force-field for molecular simulations," *J. Phys. Chem.* **94(26)**, 1990, 8897-8909.

Table 5.11: Adiabatic QM and FF Energy of PVC-PVDC(I)(Kcal/Mol)

Φ_1	Φ_2	QM	FF	Error	Φ_1	Φ_2	QM	FF	Error
0.0	0.0	19.9762	20.7012	-0.7250	0.0	90.0	13.8179	13.2234	0.5945
30.0	0.0	15.0481	16.5916	-1.5435	30.0	90.0	11.3239	13.1494	-1.8255
60.0	0.0	10.5482	10.9257	-0.3775	60.0	90.0	7.9540	10.9207	-2.9667
90.0	0.0	14.8661	15.6856	-0.8195	90.0	90.0	8.7855	10.2082	-1.4227
120.0	0.0	20.3736	21.3788	-1.0052	120.0	90.0	15.8084	15.0014	0.8070
150.0	0.0	15.6739	16.6426	-0.9687	150.0	90.0	17.7785	16.0937	1.6848
-180.0	0.0	7.8042	8.0675	-0.2633	-180.0	90.0	11.5137	9.3888	2.1249
-150.0	0.0	7.5416	7.2500	0.2916	-150.0	90.0	6.6511	5.0241	1.6270
-120.0	0.0	10.3352	10.1168	0.2184	-120.0	90.0	7.3163	7.0918	0.2245
-90.0	0.0	8.4622	6.5329	1.9293	-90.0	90.0	5.4951	6.2457	-0.7506
-60.0	0.0	10.6236	8.9141	1.7095	-60.0	90.0	3.5514	4.0861	-0.5347
-30.0	0.0	16.7263	16.9315	-0.2052	-30.0	90.0	9.2279	11.0936	-1.8657
0.0	30.0	14.7441	13.5445	1.1996	0.0	120.0	19.9609	19.7939	0.1670
30.0	30.0	10.1531	10.2035	-0.0504	30.0	120.0	15.6855	17.5523	-1.8668
60.0	30.0	6.4123	6.7368	-0.3245	60.0	120.0	10.6193	11.7889	-1.1696
90.0	30.0	12.2198	13.2206	-1.0008	90.0	120.0	16.1165	15.8059	0.3106
120.0	30.0	16.1147	17.2455	-1.1308	120.0	120.0	25.3444	23.2912	2.0532
150.0	30.0	10.3590	9.7034	0.6556	150.0	120.0	20.9443	19.8328	1.1115
-180.0	30.0	4.6262	3.5206	1.1056	-180.0	120.0	10.2243	9.1277	1.0966
-150.0	30.0	5.7643	5.0507	0.7136	-150.0	120.0	8.6180	8.4162	0.2018
-120.0	30.0	7.4031	6.8218	0.5813	-120.0	120.0	10.6005	11.6716	-1.0711
-90.0	30.0	5.5573	4.3182	1.2391	-90.0	120.0	7.4051	7.1531	0.2520
-60.0	30.0	7.8903	7.5299	0.3604	-60.0	120.0	8.9009	7.5315	1.3694
-30.0	30.0	13.2516	14.4476	-1.1960	-30.0	120.0	16.4946	16.1500	0.3446
0.0	60.0	9.3778	10.6221	-1.2443	0.0	150.0	14.7990	14.7035	0.0955
30.0	60.0	5.6312	6.8451	-1.2139	30.0	150.0	10.0124	10.7370	-0.7246
60.0	60.0	4.4995	5.8291	-1.3296	60.0	150.0	9.1348	6.6505	2.4843
90.0	60.0	8.1241	10.9316	-2.8075	90.0	150.0	17.3892	16.4785	0.9107
120.0	60.0	10.1993	11.4540	-1.2547	120.0	150.0	20.3033	20.6689	-0.3656
150.0	60.0	8.8769	7.8059	1.0710	150.0	150.0	11.7127	10.7140	0.9987
-180.0	60.0	6.3909	5.2834	1.1075	180.0	150.0	5.5250	4.4776	1.0474
-150.0	60.0	4.3370	1.7162	2.6208	-150.0	150.0	5.5422	6.5779	-1.0357
-120.0	60.0	3.5902	1.3247	2.2655	-120.0	150.0	5.8219	7.8685	-2.0466
-90.0	60.0	2.6454	1.9353	0.7101	-90.0	150.0	4.6442	4.1449	0.4993
-60.0	60.0	3.8330	4.9469	-1.1139	-60.0	150.0	8.3645	8.4462	-0.0817
-30.0	60.0	6.8525	7.9980	-1.1455	-30.0	150.0	13.3523	14.8192	-1.4669

Table 5.12: Adiabatic QM and FF Energy of PVC-PVDC(II)(Kcal/Mol)

Φ_1	Φ_2	QM	FF	Error	Φ_1	Φ_2	QM	FF	Error
0.0	180.0	9.0038	9.3985	-0.3947	0.0	-90.0	15.3252	13.1480	2.1772
30.0	180.0	7.4941	7.8429	-0.3488	30.0	-90.0	10.7678	11.7926	-1.0248
60.0	180.0	8.5738	7.7518	0.8220	60.0	-90.0	10.9056	8.2794	2.6262
90.0	-180.0	11.9431	11.2798	0.6633	90.0	-90.0	17.9846	16.5977	1.3869
120.0	-180.0	12.4131	11.2679	1.1452	120.0	-90.0	17.5892	18.1186	-0.5294
150.0	180.0	10.7086	9.1172	1.5914	150.0	-90.0	8.3351	9.3409	-1.0058
-180.0	180.0	6.5415	6.3632	0.1783	180.0	-90.0	2.6204	5.7277	-3.1073
-150.0	-180.0	2.8567	1.7441	1.1126	-150.0	-90.0	3.2942	5.7955	-2.5013
-120.0	180.0	2.0276	1.7430	0.2846	-120.0	-90.0	4.8173	6.6368	-1.8195
-90.0	180.0	1.8371	2.2851	-0.4480	-90.0	-90.0	4.9843	4.4986	0.4857
-60.0	-180.0	2.8055	3.9525	-1.1470	-60.0	-90.0	9.2510	8.6804	0.5706
-30.0	-180.0	6.1274	7.0730	-0.9456	-30.0	-90.0	14.1032	13.4640	0.6392
0.0	-150.0	15.2027	15.1317	0.0710	0.0	-60.0	10.7323	11.2059	-0.4736
30.0	-150.0	13.6714	14.9507	-1.2793	30.0	-60.0	8.6991	8.7833	-0.0842
60.0	-150.0	10.6847	10.9255	-0.2408	60.0	-60.0	8.8575	8.2889	0.5686
90.0	-150.0	11.7029	10.6855	1.0174	90.0	-60.0	10.3158	10.2313	0.0845
120.0	-150.0	18.8750	17.4005	1.4745	120.0	-60.0	10.3322	10.3552	-0.0230
150.0	-150.0	18.3598	17.5461	0.8137	150.0	-60.0	7.3471	9.0164	-1.6693
-180.0	-150.0	9.7425	8.4954	1.2471	-180.0	-60.0	1.8799	4.7822	-2.9023
-150.0	-150.0	5.1060	4.8177	0.2883	-150.0	-60.0	0.0747	0.0218	0.0529
-120.0	-150.0	6.0248	7.7307	-1.7059	-120.0	-60.0	1.8095	0.9662	0.8433
-90.0	-150.0	3.9297	4.7020	-0.7723	-90.0	-60.0	2.7045	2.0198	0.6847
-60.0	-150.0	2.7288	2.1862	0.5426	-60.0	-60.0	3.7672	3.2004	0.5668
-30.0	-150.0	9.8623	10.5394	-0.6771	-30.0	-60.0	7.7909	6.9672	0.8237
0.0	-120.0	20.9759	19.8901	1.0858	0.0	-30.0	15.5042	13.9469	1.5573
30.0	-120.0	16.6697	16.3663	0.3034	30.0	-30.0	13.1547	14.5027	-1.3480
60.0	-120.0	12.2783	11.0088	1.2695	60.0	-30.0	8.8985	9.7063	-0.8078
90.0	-120.0	18.9684	18.3175	0.6509	90.0	-30.0	10.3416	10.8283	-0.4867
120.0	-120.0	25.9434	24.8339	1.1095	120.0	-30.0	15.7328	15.2951	0.4377
150.0	-120.0	18.1441	16.9945	1.1496	150.0	-30.0	12.6513	13.8533	-1.2020
-180.0	-120.0	7.5578	7.5011	0.0567	-180.0	-30.0	5.4405	6.5088	-1.0683
-150.0	-120.0	7.1104	8.5841	-1.4737	-150.0	-30.0	3.8506	3.8065	0.0441
-120.0	-120.0	9.3474	11.3717	-2.0243	-120.0	-30.0	6.4863	6.4622	0.0241
-90.0	-120.0	6.5526	6.6365	-0.0839	-90.0	-30.0	4.7655	3.5549	1.2106
-60.0	-120.0	9.6881	9.5182	0.1699	-60.0	-30.0	5.1556	3.2032	1.9524
-30.0	-120.0	17.7739	17.9179	-0.1440	-30.0	-30.0	12.1162	10.3788	1.7374

Table 5.13: Local Minimums for PVC-PVDC(Kcal/Mole)

Structure	Φ_1	Φ_2	QM	FF	Error
1	48.9	52.2	3.9428	3.9824	-0.0396
2	-171.7	37.2	4.2132	4.1230	0.0902
3	-72.8	69.3	2.8813	3.0163	-0.1350
4	38.3	168.0	6.6523	6.6592	-0.0069
5	-101.5	178.2	1.7873	1.6719	0.1154
6	-69.5	-165.9	1.4099	1.3183	0.0916
7	37.5	-71.1	8.0181	7.4327	0.5854
8	-155.2	-60.7	0.0000	0.0000	0.0000
9	-74.4	-48.4	2.5129	2.3245	0.1884

Table 5.14: QM Energy of FF Grids for PVC-PVDC(Kcal/Mole)

Φ_1	Φ_2	QM	Φ_1	Φ_2	QM
0.0	0.0	20.6882	180.0	0.0	7.8939
0.0	60.0	8.7936	180.0	60.0	4.1968
0.0	120.0	21.0308	180.0	120.0	8.7877
0.0	180.0	7.2674	180.0	180.0	3.8761
0.0	240.0	21.6684	180.0	240.0	7.6463
0.0	300.0	9.9833	180.0	300.0	1.2937
60.0	0.0	10.1944	240.0	0.0	10.4056
60.0	60.0	3.6692	240.0	60.0	1.6462
60.0	120.0	9.7714	240.0	120.0	10.6799
60.0	180.0	5.8693	240.0	180.0	0.0000
60.0	240.0	11.2843	240.0	240.0	9.8981
60.0	300.0	6.7427	240.0	300.0	0.4488
120.0	0.0	20.6304	300.0	0.0	10.3548
120.0	60.0	9.0058	300.0	60.0	2.7670
120.0	120.0	25.0148	300.0	120.0	9.1315
120.0	180.0	9.0668	300.0	180.0	1.1101
120.0	240.0	25.0629	300.0	240.0	8.7192
120.0	300.0	8.8143	300.0	300.0	2.3128

5.6 Appendix

Listed in the tables are the geometry of optimized local minimums for iPVC, sPVC, PVDC, and PVC-PVDC.

Table 5.15: Bonds and Angles of iPVC Local Optimums

Structure	1	2	3	4	5	6
Bond Distances (Å)						
C_2—C_1	1.515	1.517	1.519	1.516	1.520	1.517
C_2—C_3	1.526	1.525	1.529	1.524	1.526	1.532
C_3—C_4	1.529	1.524	1.529	1.523	1.526	1.532
C_4—C_5	1.517	1.515	1.519	1.517	1.520	1.517
C_2—Cl_1	1.912	1.913	1.894	1.906	1.893	1.907
C_4—Cl_2	1.908	1.916	1.894	1.908	1.894	1.907
C_2—H_1	1.075	1.075	1.077	1.074	1.077	1.078
C_4—H_2	1.076	1.076	1.077	1.076	1.077	1.078
C_3—H_3	1.085	1.085	1.091	1.082	1.082	1.079
C_3—H_4	1.081	1.084	1.082	1.086	1.088	1.083
C_1—H_5	1.081	1.080	1.081	1.080	1.080	1.080
C_1—H_6	1.081	1.082	1.078	1.083	1.082	1.082
C_1—H_7	1.082	1.085	1.085	1.084	1.085	1.082
C_5—H_8	1.081	1.079	1.078	1.082	1.082	1.082
C_5—H_9	1.085	1.084	1.085	1.085	1.085	1.082
C_5—H_10	1.080	1.081	1.081	1.080	1.080	1.080
Angles (<i>degree</i>)						
C_3—C_2—C_1	117.05	113.28	118.79	115.75	112.66	117.38
C_4—C_3—C_2	117.03	117.32	124.49	115.08	117.28	113.88
C_5—C_4—C_3	116.51	117.87	118.79	113.10	112.69	117.40
Cl_1—C_2—H_1	101.59	102.56	100.99	102.53	102.73	102.05
Cl_1—C_2—C_1	107.52	107.24	108.16	107.91	107.26	106.71
Cl_1—C_2—C_3	106.01	109.62	112.01	106.39	111.37	106.65
Cl_2—C_4—H_2	100.86	101.46	106.09	102.28	102.69	102.05
Cl_2—C_4—C_3	111.33	108.22	112.01	109.43	111.35	106.63
Cl_2—C_4—C_5	108.25	108.16	108.16	107.90	107.23	106.73
H_4—C_3—H_3	106.72	106.58	106.10	107.18	106.57	107.10
Backbone Torsion Angles (<i>degree</i>)						
C_1—C_2—C_3—C_4	44.9	56.7	52.8	-179.5	-155.9	-79.2
C_2—C_3—C_4—C_5	73.7	154.1	-52.8	60.8	156.7	79.5
Minimum Energy (<i>Kcal/Mol</i>)						
Energy	3.1331	1.6149	10.4863	0.0000	5.4815	4.3209
HF (6-31G**) <i>ab initio</i> PS-GVB Constraint Minimizations						

Table 5.16: Bonds and Angles of sPVC Local Optimums

structure	1	2	3	4	5	6
Bond Distances (Å)						
C_2—C_1	1.517	1.515	1.516	1.516	1.520	1.516
C_3—C_2	1.528	1.527	1.519	1.527	1.522	1.526
C_4—C_3	1.528	1.527	1.519	1.531	1.530	1.526
C_4—C_5	1.517	1.519	1.516	1.518	1.517	1.516
C_2—Cl_1	1.901	1.912	1.911	1.913	1.894	1.917
C_4—Cl_2	1.901	1.907	1.911	1.906	1.898	1.916
C_2—H_1	1.076	1.077	1.075	1.074	1.076	1.076
C_4—H_2	1.076	1.077	1.075	1.077	1.076	1.076
C_3—H_3	1.081	1.084	1.085	1.081	1.081	1.085
C_3—H_4	1.081	1.082	1.085	1.086	1.089	1.085
C_1—H_5	1.080	1.081	1.080	1.080	1.080	1.081
C_1—H_6	1.082	1.081	1.082	1.082	1.082	1.078
C_1—H_7	1.085	1.081	1.085	1.082	1.085	1.083
C_5—H_8	1.085	1.085	1.085	1.085	1.086	1.083
C_5—H_9	1.082	1.082	1.082	1.078	1.080	1.078
C_5—H_10	1.080	1.080	1.080	1.081	1.080	1.081
Angles (<i>degree</i>)						
C_1—C_2—C_3	115.54	117.24	113.55	117.57	112.27	118.73
C_2—C_3—C_4	112.61	115.34	116.08	118.25	119.25	121.73
C_3—C_4—C_5	115.54	112.82	113.55	118.71	116.52	118.72
Cl_1—C_2—H_1	102.02	101.86	102.46	102.28	102.55	100.37
Cl_1—C_2—C_1	107.85	107.37	107.88	106.92	107.60	108.41
Cl_1—C_2—C_3	106.89	106.51	108.56	105.57	111.45	110.02
Cl_2—C_4—H_2	102.02	102.34	102.46	101.51	100.83	100.39
Cl_2—C_4—C_3	106.89	111.00	108.56	109.73	111.28	110.02
Cl_2—C_4—C_5	107.85	107.04	107.88	108.30	108.51	108.42
H_3—C_3—H_4	107.30	106.87	107.08	106.80	106.49	106.17
Backbone Torsion Angles (<i>degree</i>)						
C_1—C_2—C_3—C_4	64.2	160.7	173.4	-69.3	-32.1	-48.0
C_2—C_3—C_4—C_5	64.3	79.1	173.4	71.5	171.3	-48.0
Minimum Energy (<i>Kcal/Mol</i>)						
Energy	2.9916	3.7644	0.0000	5.1593	7.2982	6.4601
HF (6-31G**) <i>ab initio</i> PS-GVB Constraint Minimizations						

Table 5.17: Bonds and Angles of PVDC Local Optimums

structure	1	2	3	4
Bond Distances (Å)				
C_2—C_1	1.513	1.512	1.523	1.515
C_3—C_2	1.533	1.533	1.531	1.536
C_4—C_3	1.533	1.531	1.531	1.536
C_4—C_5	1.513	1.518	1.523	1.514
C_2—Cl_1	1.880	1.887	1.860	1.888
C_4—Cl_2	1.880	1.879	1.860	1.856
C_2—Cl_3	1.873	1.865	1.860	1.856
C_4—Cl_4	1.873	1.857	1.860	1.888
C_3—H_3	1.080	1.081	1.084	1.079
C_3—H_4	1.080	1.081	1.084	1.083
C_1—H_5	1.079	1.079	1.079	1.079
C_1—H_6	1.080	1.080	1.082	1.082
C_1—H_7	1.079	1.079	1.082	1.078
C_5—H_8	1.079	1.082	1.082	1.082
C_5—H_9	1.080	1.082	1.082	1.078
C_5—H_10	1.079	1.079	1.079	1.079
Angles (<i>degree</i>)				
C_1—C_2—C_3	119.05	118.85	109.30	118.52
C_2—C_3—C_4	120.24	122.23	127.97	122.21
C_3—C_4—C_5	119.05	110.61	109.30	118.54
Cl_1—C_2—Cl_3	105.47	105.19	107.55	105.81
Cl_1—C_2—C_1	107.54	107.61	106.74	106.61
Cl_1—C_2—C_3	104.73	104.79	113.06	103.64
Cl_2—C_4—Cl_4	105.47	107.01	107.55	105.81
Cl_2—C_4—C_3	104.72	110.02	113.06	112.57
Cl_2—C_4—C_5	107.54	106.97	106.74	108.63
Cl_3—C_2—C_1	108.62	109.05	106.75	108.63
Cl_3—C_2—C_3	110.50	110.40	113.06	112.59
Cl_4—C_4—C_3	110.51	114.10	113.07	103.64
Cl_4—C_4—C_5	108.62	107.83	106.75	106.62
H_3—C_3—H_4	106.93	106.92	106.99	106.85
Backbone Torsion Angles (<i>degree</i>)				
C_1—C_2—C_3—C_4	52.4	42.6	180.0	56.7
C_2—C_3—C_4—C_5	52.4	167.2	179.9	-56.5
Minimum Energy (<i>Kcal/Mol</i>)				
Energy	0.0000	1.8653	7.3696	4.2612

HF (6-31G**) *ab initio* PS-GVB Constraint Minimizations

Table 5.18: Bonds and Angles of PVC-PVDC Local Optimums

Property	opt1	opt2	opt3	opt4	opt5	opt6	opt7	opt8	opt9
Bond Distances (Å)									
C_2-C_1	1.512	1.512	1.514	1.517	1.515	1.516	1.516	1.511	1.513
C_2-C_3	1.520	1.530	1.531	1.527	1.525	1.527	1.530	1.524	1.530
C_3-C_4	1.530	1.525	1.531	1.531	1.532	1.528	1.534	1.526	1.532
C_4-C_5	1.517	1.520	1.517	1.517	1.517	1.515	1.517	1.518	1.516
C_2-Cl_1	1.875	1.859	1.871	1.857	1.872	1.872	1.888	1.875	1.876
C_4-Cl_2	1.910	1.891	1.906	1.904	1.907	1.910	1.898	1.908	1.906
C_2-Cl_3	1.883	1.887	1.877	1.882	1.870	1.871	1.856	1.877	1.871
C_4-H_2	1.076	1.075	1.074	1.077	1.074	1.074	1.077	1.075	1.076
C_3-H_3	1.083	1.080	1.079	1.086	1.080	1.082	1.086	1.082	1.081
C_3-H_4	1.081	1.084	1.083	1.082	1.084	1.083	1.079	1.082	1.080
C_1-H_5	1.079	1.079	1.079	1.079	1.079	1.079	1.079	1.079	1.079
C_1-H_6	1.080	1.083	1.082	1.082	1.082	1.081	1.078	1.080	1.081
C_1-H_7	1.079	1.081	1.078	1.082	1.082	1.082	1.082	1.081	1.083
C_5-H_8	1.079	1.082	1.082	1.078	1.082	1.081	1.080	1.082	1.081
C_5-H_9	1.080	1.080	1.080	1.081	1.080	1.080	1.080	1.080	1.081
C_5-H_{10}	1.083	1.085	1.082	1.083	1.082	1.081	1.085	1.085	1.081
Angles (degree)									
$C_3-C_2-C_1$	118.26	116.44	118.31	111.51	112.75	112.12	117.11	117.83	116.21
$C_4-C_3-C_2$	120.91	118.38	117.26	123.12	116.91	118.80	121.81	116.59	116.21
$C_5-C_4-C_3$	119.74	111.44	117.81	119.46	115.18	117.93	119.69	112.55	117.66
$Cl_3-C_2-Cl_1$	105.39	105.62	106.62	107.18	106.97	107.22	106.59	106.46	105.74
$Cl_1-C_2-C_1$	108.78	108.96	108.57	107.88	107.93	107.25	106.26	108.19	107.93
$Cl_1-C_2-C_3$	110.37	111.35	109.92	113.15	111.16	111.38	104.97	106.36	106.33
$Cl_2-C_4-H_2$	100.62	102.73	102.42	100.49	102.16	102.17	100.74	102.71	101.77
$Cl_2-C_4-C_3$	110.25	112.39	105.10	110.11	107.82	104.80	110.78	109.96	105.38
$Cl_2-C_4-C_5$	108.29	107.50	106.86	108.63	107.08	107.57	108.09	107.35	107.38
$Cl_3-C_2-C_1$	107.73	107.64	106.96	106.84	108.20	107.95	108.81	108.59	108.64
$Cl_3-C_2-C_3$	105.49	106.19	105.81	109.99	109.62	110.71	112.35	108.83	111.41
$H_4-C_3-H_3$	106.58	106.95	107.10	106.53	107.18	107.19	106.44	106.97	107.12
Backbone Torsion Angles (degree)									
$C_1C_2C_3C_4$	48.9	-171.7	-72.8	38.3	-101.5	-69.5	37.5	-155.2	-74.4
$C_2C_3C_4C_5$	52.2	37.2	69.3	168.0	178.2	-165.9	-71.1	-60.7	-48.4
Minimum Energy (Kcal/Mol)									
Energy	3.9428	4.2132	2.8813	6.6523	1.7873	1.4099	8.0181	0.0000	2.5129

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