ISSN 1009 - 3095 *Journal of Zhejiang University SCIENCE* V.4, No.1, P.69 - 75, Jan. - Feb., 2003
http://www.periodicals.com.cn; http://www.zju.edu.cn/English
http://www.zjupress.com; http://lib.zju.edu.cn/eindex.htm; jzu_s@mail.hz.zj.cn

Molecular dynamics simulation study on behaviors of liquid 1,2-dichloroethane under external electric fields

DU Zhi-qiang (杜志强)[1†], CHEN Cheng-long (陈正隆)[2]

([1] *Department of Chemistry, Zhejiang University, Hangzhou 310027, China*)
([2] *Department of Chemistry, National Sun Yat-Sen University, Kaohsiung 80424, Taiwan, China*)

[†]E-mail: duzq@css.zju.edu.cn

Received Dec.7.2001; revision accepted June 30, 2002

Abstract: Molecular dynamics simulation was carried out to study the behavior of liquid 1,2-dichloroethane molecules under external electric fields including direct current field, alternating current field and positive-half-period cosin field. The maximum applied field strength was 10^8 V/m, the maximum frequency of the alternating current field and that of the positive-half-period cosine field was 10^{12} Hz. The simulation revealed that the field type and field strength act on the population of the molecular configuration. In the strong direct current field, all trans forms converted completely into gauche forms. Order parameter and the correlation of the system torsion angle were also investigated. The results suggested that these two dynamical parameters depended also on the field type and the field strength. The maximum of order parameter was found to be at 0.6 in the strong direct current field.

Key words: Molecular dynamics, Simulation, External electric field, Liquid 1,2-dichloroethane
Document code: A **CLC number:** O6-39

INTRODUCTION

Molecular dynamics (MD) simulation was found to be an important methodology for study of condensed matter (Tsuzuki et al., 1996). Kiselev and Heinzinger reported MD simulation of a chloride ion in water system under an external electric field (Kiselev and Heinzinger, 1996). They discovered that water structure is sensitive to the strength of the applied direct current (DC) field. In addition to this, the liquid structure of the system, which was reflected in the radius distribution function, as well as the self-diffusion constant of water were also relatived with the applied field. Green and Lu (1997) and Xia and Berkowitz (1995) reported their work on simulation of the liquid water system and platinum surface water under external electric fields by Monte Carlo (MC) method and MD method. They showed that polar molecules system's physical properties are dependent on the external electric field.

Fig.1 shows the torsion angle, ϕ, and three major states i.e., trans, cis and gauche (gauche(+) and gauche(−) in more detail) forms. For the molecule of 1,2-dichloroethane, the magnitude of dipole moment, $|\mu|$, depends mainly on ϕ. For the trans form ($\phi = 180°$) μ is 0, while for the cis form ($\phi = 0°$) μ has its maximum magnitude. Jorgensen et al. (1981) reported MC simulation of liquid 1,2-dichloroethane by TIPS potential. Millot and Rivail (1992) simulated the same system with TIPS potential plus electrostatic interactions between molecules by MD. It was interesting to study how the external electric field influence the population of configurations, hence the liquid

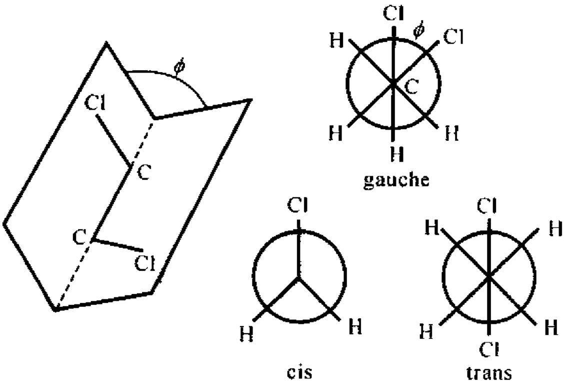


Fig.1 The molecule structure of 1,2-dichloroethane and its cis, trans and gauche forms

polarity and other physical properties of the system. In this study, MD simulation was carried out to study a polar molecular liquid system, 1,2-dichloroethane molecules, under external electric field.

METHOD

1. Molecular dynamics

To simplify the calculation, the bond lengths and bond angles of the 1,2-dichloroethane molecule were constrained. The only unconstrained internal coordinate of the molecule was the torsion angle. The individual potentials of the molecule can be expressed as :

$$U = U_{\mathrm{vdw}} + U(\phi) + U_{\mathrm{int}} \tag{1}$$

, where U_{vdw} is the van der Waals potential, $U(\phi)$ is the torsion potential and U_{int} is the interaction potential with external field.

The van der Waals interaction in the system is calculated by

$$U_{\mathrm{vdw}} = \left(\frac{A}{r_{ij}}\right)^{12} - 2.0\left(\frac{B}{r_{ij}}\right)^{6} \tag{2}$$

where A and B are the constants adopted from TRIPOS 5.2 force field (Clark et al., 1989), r_{ij} is the distance between ith and jth atom. In this force field the electrostatic interactions between any two molecules are implicitly included in the van der Waals term.

The torsion potential in the TIPS force field is expressed in detail as:

$$U(\phi) = \sum_{i=0}^{3} c_i(\cos\phi)^i \tag{3}$$

where c_i is the constant obtained from *ab initio* calculation on the isolated molecule.

The interaction potential among the molecules and external field can be written as

$$U_{\mathrm{int}} = -\sum_{i=1}^{N} \boldsymbol{\mu}_i \cdot \boldsymbol{E} = -\sum_{i=1}^{N}\sum_{j=1}^{n} q_j^i \boldsymbol{r}_{ij} \cdot \boldsymbol{E} \tag{4}$$

where N is the number of molecules, n is the number of atoms in the molecule, $\boldsymbol{\mu}_i$ is the dipole moment of the molecule, $\boldsymbol{E}$ is the external electric field, q_j^i and $\boldsymbol{r}_{ij}$ are the partial charge and the position vector between the jth atom and the mass center of the ith molecule respectively. In Jorgensen et al. (1981) and Millot et al. (1992), the methylene groups (CH_2) in 1,2-dichloroethane were treated as points, and the partial charges on the methylene group and the chlorine atom were fixed at 0.25 and −0.25 proton charge. In this simulation three different charge systems were employed. In the fixed charge system the partial charges on the carbon atom and the chlorine atom were assigned 0.25 and −0.25 proton charge. In the PM3 charge system and the 6-31G charge system, the partial charge on each atom was obtained from quantum mechanism calculation by using PM3 and *ab initio* 6-31G . The atomic charges were calculated for each configuration from $\phi = 0°$ to $180°$ with $10°$ increment. These charges were then fitted as functions of the torsion angle in the form

$$q(\phi) = q^{o} + \sum_{i=1}^{8} a_i(\cos\phi)^i \tag{5}$$

where q^{o} and a_i' s are constants listed in Table 1.

Table 1 The constants, q^0 and a_i, of atomic charges of 1,2-dichloroethane obtained by PM3 and *ab initio* 6-31G methods

Method	*ab initio* 6-31G				PM3			
Atom	H_1	H_2	C	Cl	H_1	H_2	C	Cl
$q^{0\dagger}$	0.2383	0.2588	−0.4396	−0.0575	0.1467	0.1634	−0.2533	−0.0567
a_1	−0.0024	−0.0255	0.0034	0.0245	0.00244	−0.0117	−0.0043	0.0136
a_2	0.0023	−0.0039	−0.0065	0.0082	0.0042	−0.0082	−0.0043	0.0084
a_3	−0.0098	0.0211	−0.0126	0.0016	−0.0108	0.0117	0.0008	−0.0017
a_4	0.0097	−0.0323	0.0031	0.0191	0.0022	−0.0151	0.0046	0.0077
a_5	0.0265	−0.0175	−0.0076	−0.0008	0.0154	−0.0232	0.0072	0.0008
a_6	−0.0271	0.0434	0.0076	−0.0237	−0.0088	0.0158	−0.0018	−0.0046
a_7	−0.0196	0.0154	0.0047	−0.0010	−0.0127	0.0168	−0.0040	−0.0002
a_8	0.0197	−0.0223	−0.0080	0.0106	0.0053	−0.0061	0.0004	0.0001

"†": q^0 is in the unit of proton's charge

2. Simulation systems

Constant-temperature MD method was adopted to run the simulation， and 125 molecules of 1，2-dichloroethane were chosen for the simulation system. The density of the system was supposed to be 1.24 g/cm^3， which matched with experimental data. The temperature was fixed at 300 K. SHAKE algorithm（Anderson，1983）was used to constrain the bond lengths and three-atom-angles of the 1，2-dichloroethane molecule. All systems were pre-equilibrated before the external field was applied. Then 40 ps trajectories were collected for analysis in all simulations.

Table 2 lists the definitions of the simulated systems under no external electric fields and different external electric fields for the fixed charge system， the PM3 charge system and the 6-31G charge system. Three types of external fields were applied:

direct current（DC）field， i.e.

$$E = aE_0 \qquad (6)$$

alternative current（AC）field， i.e.

$$E = aE_0\cos(\omega t) \qquad (7)$$

and "positive-half -period-cosin"（PHPC）field， i.e.

$$E = \begin{cases} aE_0\cos(b\omega t), & 0 \leqslant \omega t \leqslant \pi \\ 0 & \pi < \omega t < 2\pi \end{cases} \qquad (8)$$

Table 2 Definitions of systems of MD simulations and the population percent of the torsional angle

System	External field		Type of atom's charge	The population percent（%）		
				0 – 120°	120 – 240°	240 – 360°
I(a)	$E = 0$		6 – 31G	6.94	79.73	13.32
I(b)	$E = 0$		Fixed charge	12.64	79.24	8.12
I(c)	$E = 0$		PM3	16.20	64.24	19.55
I(d)	$E = 25E_0^{\dagger}$	(DC)	6-31G	8.34	80.61	11.04
I(e)	$E = 25E_0$	(DC)	Fixed charge	10.86	79.79	9.35
I(f)	$E = 25E_0$	(DC)	PM3	37.82	20.85	41.33
II(a)	$E = 5E_0$	(DC)	6-31G	3.71	88.33	7.97
II(b)	$E = 15E_0$	(DC)	6-31G	5.39	83.99	10.62
II(c)	$E = 25E_0$	(DC)	6-31G	8.34	80.10	11.04
II(d)	$E = 40E_0$	(DC)	6-31G	18.49	57.21	24.30
II(e)	$E = 50E_0$	(DC)	6-31G	37.44	29.51	33.05
II(f)	$E = 75E_0$	(DC)	6-31G	52.73	2.09	45.18
II(g)	$E = 100E_0$	(DC)	6-31G	51.54	0.71	47.75
III(a)	$E = 25E_0\cos(\omega t)^{\ddagger}$	(AC)	6-31G	4.61	88.51	6.88
III(b)	$E = 25E_0\cos(\omega t)$	(AC)	6-31G	3.41	88.85	7.74
III(c)	$E = 50E_0\cos(\omega t)$	(AC)	6-31G	7.04	83.83	9.13
IV(a)	$E = 5E_0\cos(\omega t)$	(PHPC)	6-31G	2.35	91.88	5.77
IV(b)	$E = 25E_0\cos(\omega t)$	(PHPC)	6-31G	4.38	90.40	5.22
IV(c)	$E = 50E_0\cos(\omega t)$	(PHPC)	6-31G	10.44	76.70	12.87
IV(d)	$E = 50E_0\cos(0.1\omega t)$	(PHPC)	6-31G	17.13	67.83	15.04
IV(e)	$E = 50E_0\cos(0.05\omega t)$	(PHPC)	6-31G	14.33	70.51	15.16

"†": $E_0 = 10^8$ V/m， "‡": $\omega = 10^{12}$ Hz where aE_0 is the strength of the field, a is a constant, and $E_0 = 10^8$ V/m, $b\omega$ is the frequency of the field, b is a constant and $\omega = 10^{12}$ Hz, respectively. In all the simulations, the external field directs along the space fixed X-axis. The strength of the applied field varies from 5 to 100 × 10^8 V/m, these were smaller than the field strength (0.5 – 2 × 10^{10} V/m) used by Kiselev and Heinzinger (1996) in their simulation of water. The frequency of applied AC and PHPC field varied from 0.05 to 1 × 10^{12} Hz. Table 2 lists Systems I(d) to I(g) and Systems II(a) to II(g) corresponding to the simulation of the field strengths under DC fields, Systems III(a) to III (c) corresponding to the simulation against the field strengths and the frequencies under AC fields, Systems IV(a) to IV(e) corresponding to the simulation against the field strengths under PHPC fields.

RESULT AND DISCUSSION

1. Populations of the torsion angle

Table 2 also gives the population percent of the torsion angle of the systems by MD simulation. For the population percent of the torsion angle, $P(\phi)$, of systems I(d) to I(g), Table 2 and Fig. 2 indicate that three partial charge distribution (Fixed, PM3 and 6-31G) give qualitatively the same trend under the DC field ($E = 25 \times 10^8$ V/m). The trans population, P_{trans} (in the range $150° \leqslant \phi \leqslant 210°$), decreased and gauche populations, P_{gauche} (in the range $30° \leqslant \phi \leqslant 90°$ and $270° \leqslant \phi \leqslant 330°$) increased. Both P_{trans} and P_{gauche} were slightly different for the 6-31G and the Fixed systems. However, in the PM3 system, the P_{gauche} was larger than the P_{trans} under the same DC field. The 6-31G result agreed well with that of Millot and Rivail (1992), so 6-31G partial charges were adapted for all the other simulations.

Fig. 3a of $P(\phi)$ of the system II(a) to II(g) against the field strengths under external DC field suggests that P_{trans} decreases inversely with the field strength. When the external field strength is over 75 × 10^8 V/m, all trans forms were converted into gauche configurations.

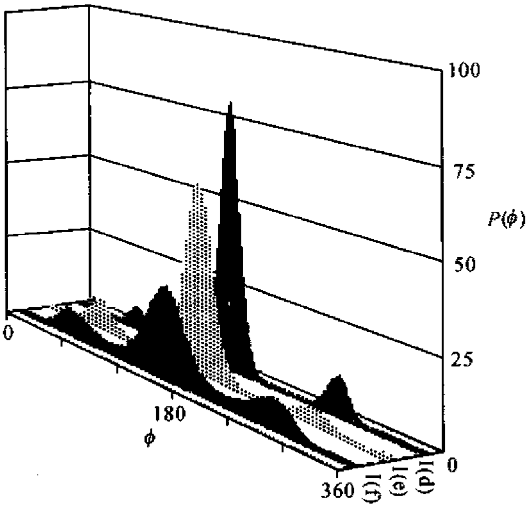


Fig. 2 Population of torsion angles with use of fixed charges, PM3 charges and 6-31 G charges

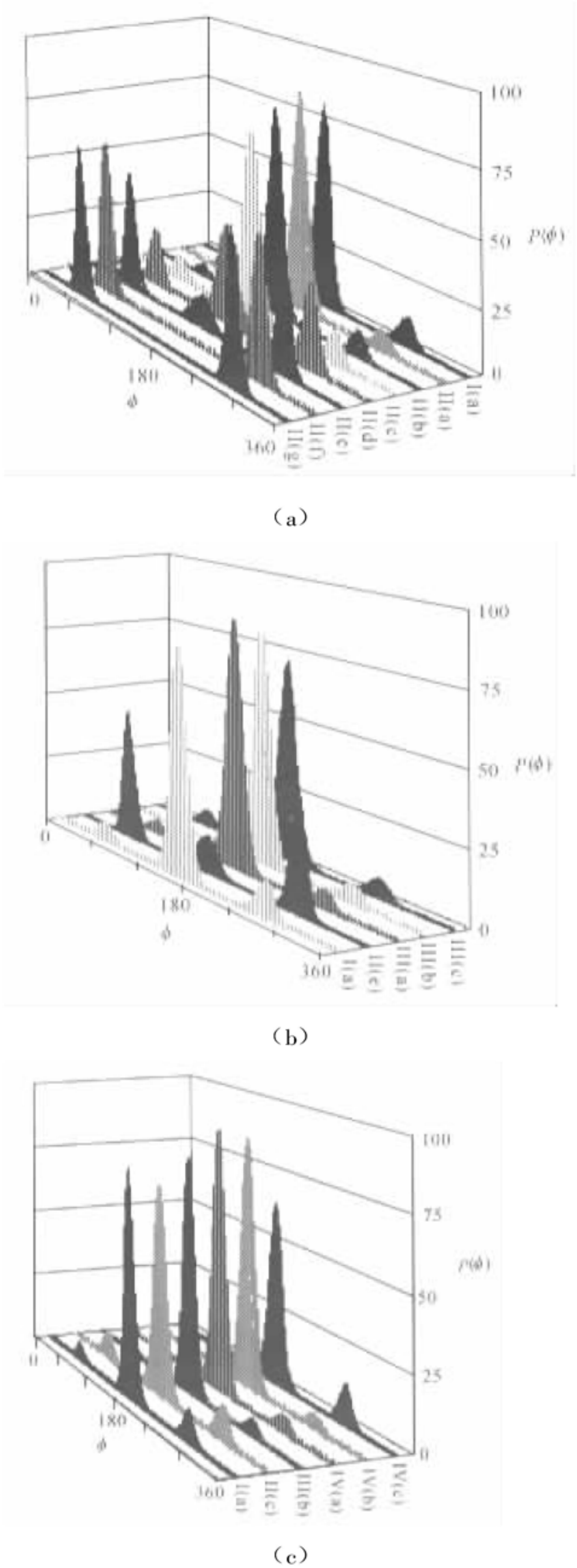
Fig. 3b gives the $P(\phi)$ of the system III against the field strengths under same frequency ($\omega = 10^{12}$ Hz) external AC fields. The $P(\phi)$ of the system without external field and the system under the DC field ($E = 50 \times 10^8$ V/m) are shown for comparison showing that P_{trans} decreases very slowly (compared to that in the DC field) while the field strength increases.

Fig. 3c gives the $P(\phi)$ of the system IV against the field strengths under PHPC fields. The $P(\phi)$ of the system without external field, that under DC field and that under AC field are all shown for comparison. Table 2(IV) shows that P_{trans} was larger than that of the system without external field and larger than that of the system under AC field with same field strength, when the strength of the PHPC field was less than 25 × 10^8 V/m. On the other hand, when the strength of the PHPC field was over 50 × 10^8 V/m, the P_{trans} was less than that of the system without external field and less than that of the system under AC field with same field strength (Fig. 3 in the next page).

2. Order parameter

The order parameter (Bohm et al., 1984), $S(t)$, of the system in all the cases is defined as

$$S(t) = \frac{1}{2}(3 < \cos^2\theta > - 1) \qquad (9)$$

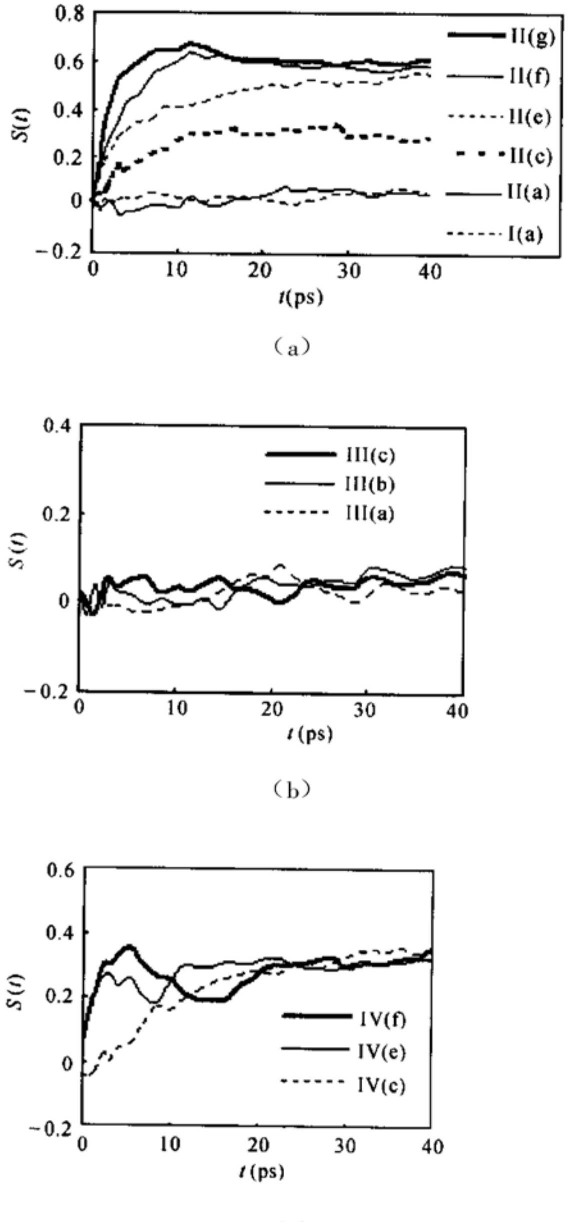


（a）

（b）

（c）

Fig.3 Population of torsion angles of systems under
（a）DC field;（b）AC field;（c）PHPC field



（a）

（b）

（c）

Fig.4 Order parameters of systems under
（a）DC field;（b）AC field;（c）PHPC field

where “ $< \cos^2\theta >$ ” means the average of $\cos^2\theta$, with θ being the angle between the dipole moment of the molecule and the direction of the external field. Fig.4a of the plots of $S(t)$ of the systems under DC fields shows that for all systems, $S(t)$ tend to some specific values; and that these specific values increase with the strength of the external field. The maximum value of $S(t)$ stayed around 0.6 when the field strength was above 75×10^8 V/m. This indicated that the dipole moments of 1, 2-dichloroethane molecules oriented along the direction of the external field with the value of $S(t)$ limited around 0.6. Fig.4b and Fig.4c are the $S(t)$ of the systems under AC field and PHPC field respectively. The former shows that $S(t)$ is very small for all the AC fields, indicating that the dipole moment of 1,2-dichloroethane molecule apparently has no order under the AC field. The latter shows that $S(t)$ of the system under PHPC field behaves like $S(t)$ of the system under DC field. $S(t)$ increases with frequency under PHPC field. The maximum of $S(t)$ converges at 0.32 when the field strength is 50×10^8 V/m and the frequency is 10^{12} Hz under PHPC field. This value is much smaller than the corresponding value (0.6) of the system under the DC field with the same field strength.

3. Correlation function

The correlation function (Bohm et al., 1984), $M(t)$, of torsion angle was defined as

$$M(t) = \frac{< \cos\phi(t)\cdot\cos\phi(0) > - < \cos\phi(0) >^2}{< \cos\phi(0)\cdot\cos\phi(0) > - < \cos\phi(0) >^2} \qquad (10)$$

where the " < > " means the average of each term. Fig.5a shows that $M(t)$ falls more rapidly when the strength of the DC field increases. When the strength of the DC field is over 75×10^8 V/m, $M(t)$ tend to zero within 5 ps. Fig. 5b shows that $M(t)$ falls more rapidly when the strength of the AC field increases. As a result, $M(t)$ falls faster in the AC field than that in the DC field at same field strength. Fig. 5c shows that $M(t)$ falls very slowly under the PHPC field compared to $M(t)$ of the corresponding DC or AC field with same field strength.

The order parameters in Fig. 4 shows how fast and to what extent the molecule orients its dipole along the direction of the applied field. The correlation function of the torsion angle in Fig. 5 shows how fast the molecule is unrelated to its original structure. Since the dipole moment of 1,2-dichloroethane is the function of the torsion angle, this correlation function also indicates how fast the molecule changes its dipole under the external field.

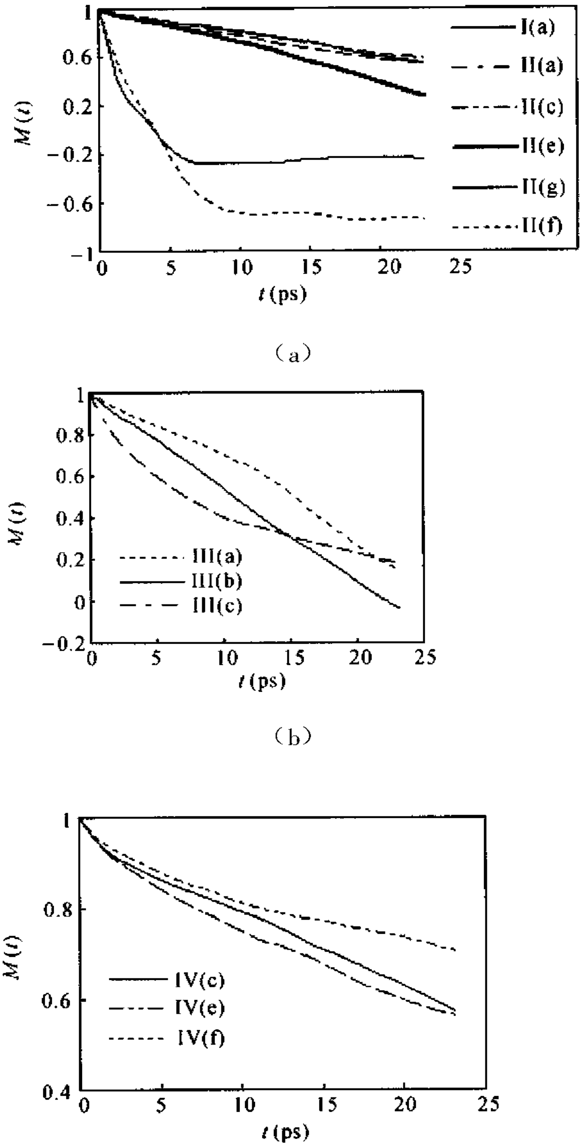


Fig.5 Correlation functions of torsion angle of systems under

(a) DC field; (b) AC fields (c) PHPC field

CONCLUSIONS

MD simulation showed that the populations of the trans and gauche forms could either increase or decrease when different polarity molecules interacted with different external fields. This meant that it is possible to control the population of the specific configuration of the 1,2-dichloroethane molecule by properly selecting the type and strength of the external field. The trans forms could convert to gauche forms under strong DC field. Similar conversion was observed under AC field, but at much slower conversion rate than under DC field. Small magnitude PHPC field can cause the increase of the trans configuration, while strong PHPC field has the same effect as the DC field. Investigation of the order parameter of the systems showed that the dipole moment of 1,2-dichloroethane molecule tended to align along the direction of the DC and PHPC field. The larger the strength of the DC field or PHPC field, the higher was the value of the order parameter. The maximum of the order parameter of the system under the DC field was found at 0.6. The system had no order under AC fields independent of the field strength. The torsion angle was not correlated with time under AC field and PHPC field, and the torsion angle decreased faster with time under AC field than that under PHPC field.

References

Anderson, H. C., 1983. Rattle: a "velocity" version of the shake algorithm for molecular dynamics calculations. *J. Comp. Phys.*, **52**: 24 – 34.

Bohm, H. J., Lynden-Bell, R. M., Madden, P. A. and McDonald, I. R., 1984. Molecular motion in a model of liquid acetonitrile. *Molecular Physics*, **51**(3): 761 – 777.

Clark, M., Cramer. III, R. D. and Van Opdenbosch, N., 1989. Validation of the general purpose Tripos 5.2 force field. *J. Comp. Chem.* **10**(8): 982 – 1012.

Green, M. E. and Lu, J., 1997, Simulation of water in a small pore : effect of electric and density. *J. Phys. Chem. B*, **101**:6512 – 6524.

Jorgensen, W. L., Binning, R. C. Jr. and Bigot, B., 1981, Structures and property of organic liquids: n-Butane and 1,2-dichloroethane and their conformational equilibrium. *J. Am. Chem. Soc.*, **103**(15): 4393 – 4399.

Kiselev, M. and Heinzinger, K., 1996. Molecular dynamics simulation of a chloride ion in water under the influence of an external electric field. *J. Chem. Phys.*, **105**(2): 650 – 657.

Millot, C. and Rivail, J. L., 1992. Molecular dynamics simulation of the TIPS model of 1,2-dichloroethane in the liquid phase. *Mol. Phys.*, **77**(1): 157 – 175.

Tsuzuki, S., Uchimaru, T., Mikami, M., Tanabe, K., Sako, T., Kuwajima, S., 1996. Molecular dynamics simulation of supercritical carbon dioxide fluid with the model potential from ab initio molecular orbital calculations. *Chemical Physics Letters*, **255**: 347 – 349.

Xia, X.F. and Berkowitz, M. L., 1995. Electric-field induced restructuring of water at a platinum-water interface: A molecular dynamics computer simulation. *Phys. Rev. Lett.*, **74**(16): 3193 – 3196.

International Peer Review System for Scientific Papers Published in the English-language *Journal of Zhejiang University SCIENCE*

The characteristics and requirements of world-class journal were considered in establishing a rigid peer review system for scientific papers submitted for publication in the English-language *Journal of Zhejiang University SCIENCE* from 2002 onward. We sent the over 408 contributions received from January to December in 2002 to the U.S.A., the U.K., Ireland, France, Canada, Australia, Austria, Germany, New Zealand, the Netherlands, Finland, Poland, Portugal, Italy, Israel, Spain, Belgium, Sweden, Switzerland, Denmark, Japan, Singapore, Slovak, India, Greece, Czech, Mexico, Hong Kong, Macao, Taiwan, etc., for pre-publication review by topnotch international scientists there in their respective specialties. Experience in scientific papers publication has shown that an international peer review system plays an important part in ensuring the high quality of a journal's contents and helping it to be known by worldwide.

Every little improvement of this journal depends on the strong support from the reviewers. We take this opportunity to give our heartfelt thanks to reviewers in China and abroad for their help since the establishment of the journal.