

Quantum chemical studies of Li^+ cation binding to polyalkyloxides[☆]

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Abstract

A quantum chemical study of the binding of Li^+ cation to polyalkyloxides has been carried out. The lithium cation interaction with three polyalkyloxides (polyethylene oxide (PEO), polytrimethylene oxide (PTMO), and polypropylene oxide (PPO)) has been investigated using ab initio molecular orbital theory at the HF/6-31G* level with molecular models for the polymers. Coordination by one to six oxygens was considered. In addition, higher level calculations were carried out using G3(MP2) theory for coordination of Li^+ by one oxygen. For coordination of lithium by one oxygen, the binding energy ordering is PTMO > PPO > PEO, with PTMO having the largest lithium cation affinity. The same ordering is found for larger coordination numbers with the exception of coordination by six oxygens, where the ordering changes due to the steric interactions.

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1. Introduction

There has been much interest in lithium polymer electrolytes for their potential applications in fuel cells, secondary battery systems, and other electrochemical devices. Polymer electrolytes [1,2] are generally composites of a polyethylene oxide (PEO) or another modified polyether and a salt such as LiCF_3SO_3 or $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$. The ion–polymer and ion–ion interactions in these materials play an important role in the ion transport mechanism. There have been theoretical studies of lithium cation–polymer interactions [3–15] and most of them have focused on PEO. We have reported studies based on a molecular model of $\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3$ for PEO [3,4]. The results indicated that the binding energies of Li^+ –PEO complexes increase with increasing coordination of Li^+ by oxygen, but the average binding energy per Li–O bond decreases. In this paper, we report on a comparative study of the interaction of lithium cation with two other polyalkyloxides for comparison with polyethylene oxide. The two polyalkyloxides are polytrimethylene oxide

(PTMO) and polypropylene oxide (PPO). Coordination by one to six oxygens was considered. The lithium cation binding energies of these polymers are of interest in finding polymer electrolytes with higher ionic conductivities and to help understand the conductivity mechanism. It has been speculated that smaller binding energies may result in smaller lithium cation migration barriers, and thus, higher ionic conductivities [16]. In Section 2, the theoretical methods are described. In Section 3, the lithium cation binding energies for a series of polyalkyoxide– Li^+ complexes are presented, and the results are discussed.

2. Theoretical methods

All of the chemical species considered in this paper were fully optimized at the HF/6-31G* level of theory [17]. Vibrational frequencies were calculated to verify that the structures corresponded to local minima. The lithium cation binding energies of the complexes are defined relative to the corresponding all-trans neutral molecule. However, in some cases other conformers have lower energies; and this is noted in those cases. The single oxygen coordination complex was further studied at higher levels of theory including use of larger basis sets (6-31+G*, 6-311G (2df, p), G3MP2Large [8]) at the second-order perturbation level (MP2) and G2(MP2) theory [8] to assess the effect on the binding energies. All of the calculations were done with the Gaussian 98 [19] computer program.

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3. Results and discussion

3.1. Polymer models

PTMO is modeled by $\text{CH}_3(\text{OCH}_2\text{CH}_2\text{CH}_2)_n\text{OCH}_3$ ($n = 2-5$), PEO is modeled by $\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3$ ($n = 2-5$), and PPO is modeled by $\text{CH}_3(\text{OCH}(\text{CH}_3)\text{CH}_2)_n\text{OCH}_3$ ($n = 2-5$). The structures of the $n = 2$ models are shown in Fig. 1. The $n = 2$ species are used for lithium cation coordination with one, two, and three oxygens, the $n = 3$ species for four-coordinated Li^+ , the $n = 4$ model for five-coordinated Li^+ , and the $n = 5$ model for six-coordinated Li^+ . The diglyme model ($n = 2$) for PEO was previously [3,4] used to model one-, two-, and three-coordinated Li.

Viscometric studies [20–22] show that PTMO is unusually compact presumably due to a preference for the gauche conformation about CC bonds, leading to small random coil dimensions (conformational randomness). From our calculations, the $n = 2$ model for PTMO rotation about a CC bond to form a gauche conformation results in an increased favorable interaction between an oxygen atom (partial negative charge) and a CH_2 group (partial positive charge) which are separated by three bonds. On the other hand, rotation about a CO bond results in the unfavorable

interaction between two large partially positively charged CH_2 groups. This ttgg conformation, trans about CO bonds and gauche about CC bonds, is responsible for the conformational randomness of PTMO when averaged over the repeat unit. At the HF/6-31G* level, the ttggtgg conformation of $\text{CH}_3(\text{OCH}_2\text{CH}_2\text{CH}_2)_2\text{OCH}_3$ is 3.2 kcal/mol lower in energy than the all-trans species. The optimized ttggtgg structure contains four OCH_2 interactions so each gauche interaction contributes about 0.8 kcal/mol to the enhanced stability of the structure. In the following results, the binding energies for the Li^+ –PTMO complexes were calculated by comparing the energy of the complex with the energies of the corresponding all-trans model for PTMO and Li^+ . The all-trans conformer was used in the binding energy calculations because it would be extremely difficult to locate the most stable conformer for the different PTMO models. Similarly, the binding energies for the Li^+ –PEO and Li^+ –PPO complexes were calculated by comparing the energy of the complex with the energies of the corresponding all-trans model for PEO and PPO. As in the case of PTMO, there are gauche containing conformers of the $n = 2$ molecular models of PEO and PPO that are lower in energy than the all-trans conformer, although the energy difference is much smaller (less than 1 kcal/mol) [23–25].

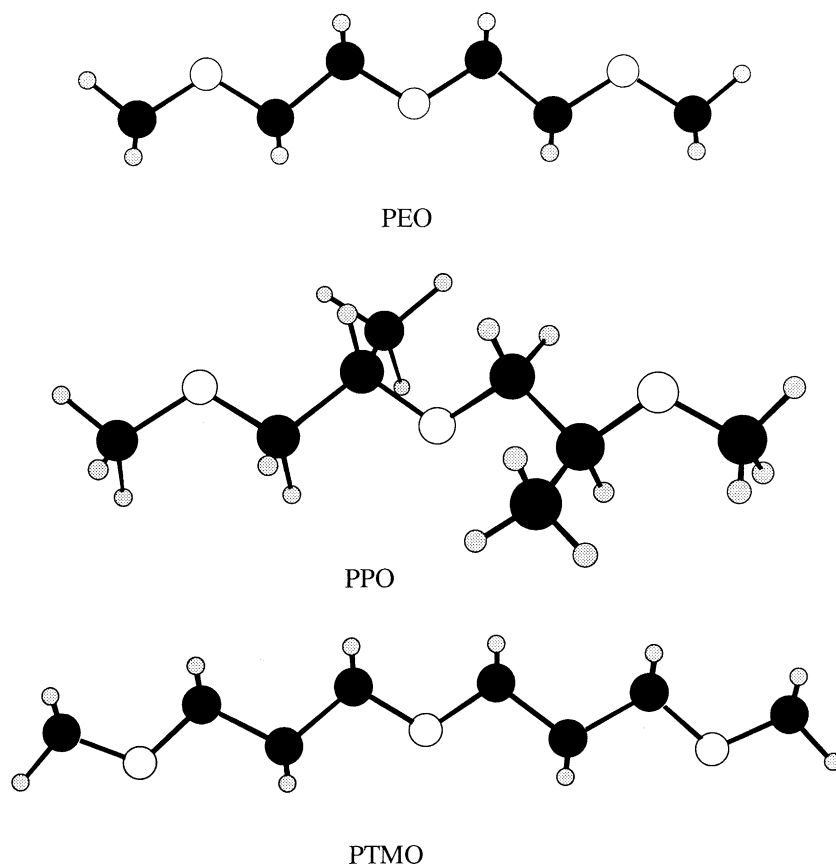


Fig. 1. Structures of $\text{CH}_3(\text{OCH}_2\text{CH}_2)_2\text{OCH}_3$, $\text{CH}_3(\text{OCH}(\text{CH}_3)\text{CH}_2)_2\text{OCH}_3$ and $\text{CH}_3(\text{OCH}_2\text{CH}_2\text{CH}_2)_2\text{OCH}_3$ used as models for PEO, PPO, and PTMO, respectively. The black atoms are carbon, the white atoms are oxygen, and the small shaded atoms are hydrogen.

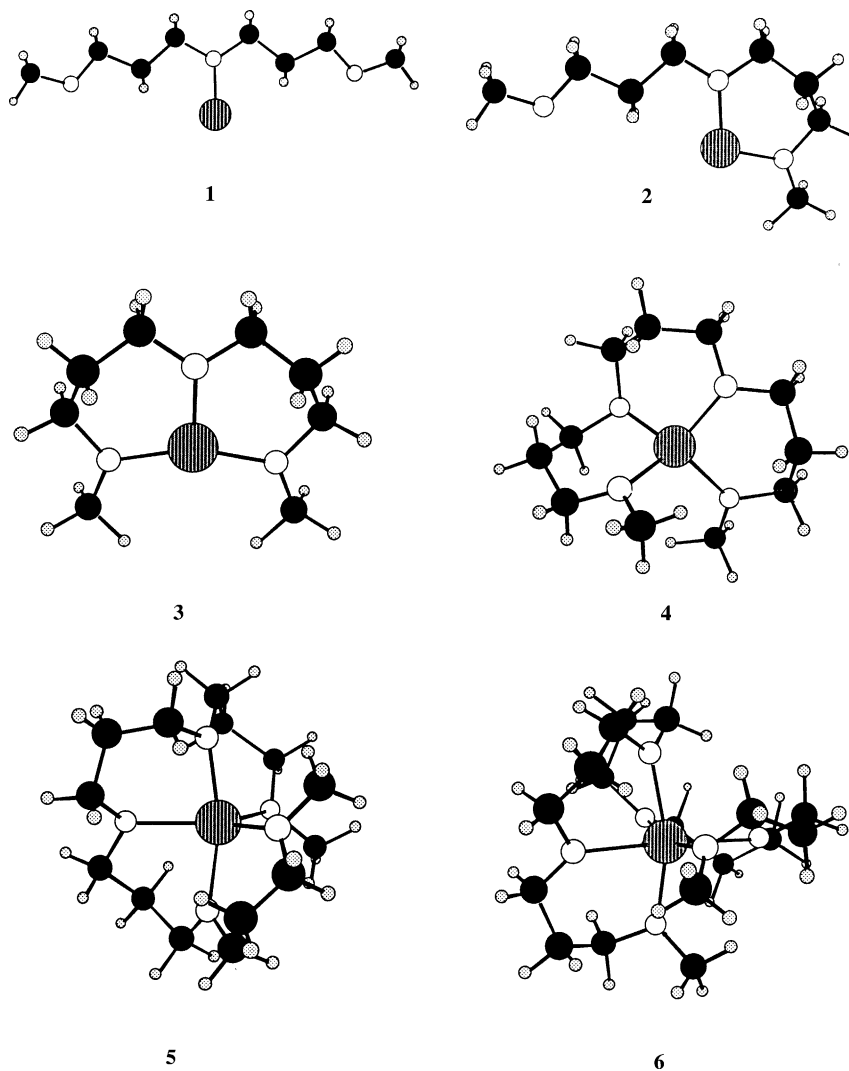


Fig. 2. Structures of one-, two-, three-, four-, five-, and six-coordinated Li^+ -PTMO complexes. The black atoms are carbon, the white atoms are oxygen, the large shaded atoms are lithium, and the small shaded atoms are hydrogen.

3.2. Binding energies of the Li^+ -PTMO, Li^+ -PEO, and Li^+ -PPO complexes

One-, two-, three-, four-, five-, and six-coordinated complexes of Li^+ with PTMO and PEO were investigated. While we have not done an exhaustive search of the potential energy surface for conformers, we have tried to choose the conformers that are likely to be lowest in energy. The geometries of these structures were fully optimized. The structures of the PTMO- Li^+ complexes are shown in Fig. 2. The structures of the PEO and PPO complexes are similar.

The HF/6-31G* binding energies of the PTMO- Li^+ , PEO- Li^+ , and PPO- Li^+ complexes ($n = 2-5$) are given in Table 1. The binding energies given in Table 1 are relative to the all-trans conformer. The Li-O distances are given in Table 2. For coordination of the lithium cation with a single oxygen in the polymer model the ordering of the binding

Table 1
HF/6-31G* binding energies (kcal/mol) Li^+ -PTMO, Li^+ -PTMO, and Li^+ -PTMO complexes^a

n	Oxygen coordination	Structure	PEO	PPO	PTMO
2	1	1	39.4	42.9	48.6
	2	2	66.0	68.3	75.0
	3	3	87.1	89.4	97.4
3	4	4	103.0	103.0	110.4
4	5	5	110.1	110.2	115.6
5	6	6	115.4	115.3	112.7

^a Using $\text{CH}_3(\text{OCH}_2\text{CH}_2\text{CH}_2)_n\text{OCH}_3$ ($n = 2-5$) as a model for PTMO, $\text{CH}_3(\text{OCH}_2\text{CH}_2)_n\text{OCH}_3$ ($n = 2-5$) as a model for PEO, $\text{CH}_3(\text{OCHCH}_2\text{CH}_2)_n\text{OCH}_3$ ($n = 2-5$) as a model for PPO. The binding energy is the energy of the complex relative to the Li^+ cation and the all-trans conformer. It does not include zero-point energies.

Table 2
Summary of Li–O bond distances (in Angstroms) in PEO–Li⁺, PPO–Li⁺, and PTMO–Li⁺ complexes

<i>n</i>	Coordination number	PEO	PPO	PTMO
2	1	1.835	1.831	1.830
		1.876	1.868	1.851
	3	1.880	1.887	1.860
		1.918	1.912	1.876
		1.938	1.919	1.897
		1.938	1.923	1.897
3	4	2.006	1.952	1.937
		2.007	2.001	1.954
		2.014	2.036	1.968
	5	2.014	2.049	2.004
		2.069	2.062	2.042
		2.071	2.076	2.047
4	6	2.110	2.086	2.093
		2.130	2.109	2.103
		2.175	2.109	2.181
		2.089	2.091	2.074
		2.154	2.127	2.074
		2.162	2.135	2.207
		2.215	2.287	2.208
		2.227	2.316	2.426
		2.233	2.317	2.426

energies is PTMO > PPO > PEO. The Li⁺–PTMO binding energy of 48.6 kcal/mol is 9.2 kcal/mol larger than that of Li⁺–PEO. The Li⁺–PPO binding energy is 42.9 kcal/mol. The ordering does not change if the ttggttg conformer is used for the *n* = 2 model of PTMO. This conformer is 3.2 kcal/mol lower in energy than the all-trans conformer.

The binding energies of the singly-coordinated oxygen complex at several higher levels of theory (MP2/6-31+G(d), MP2(6-311G(2df, p), G3(MP2) theory) are given in Table 3. The results at the higher levels give binding energies similar in magnitude and order as HF/6-31G*. The binding energies differ by only several kcal/mol. The stronger Li⁺ binding in PTMO compared to PEO can be partially be rationalized by examination of the electron distributions. The atomic charges (Mulliken populations with hydrogens summed into

Table 3
Binding energies (in kcal/mol) of PEO–Li⁺, PPO–Li⁺, and PTMO–Li⁺ complexes at different levels of theory

Method	PEO	PPO	PTMO
HF/6-31G(d) ^a	39.4	42.9	48.6
MP2/6-31+G(d) ^a	38.5	42.9	47.2
MP2/6-311G(2df, p) ^a	41.9	45.8	49.8
MP2/G3MP2Large ^{a,b}	37.7	42.3	46.5
G3(MP2) w/o ZPE ^c	37.9	42.7	46.6
G3(MP2)w ZPE ^d	37.1	41.6	45.4

^a At the HF/6-31G(d) geometries, no zero-point energies included.

^b This basis set is equivalent to 6-311++G(2df, 2p) for first-row atoms. See [18].

^c G3(MP2) theory without zero-point energies.

^d G3(MP2) theory with zero-point energies.

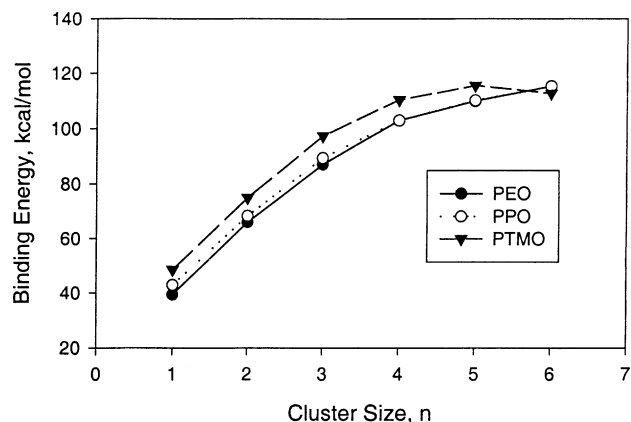


Fig. 3. Plot of the binding energies for the PTMO–Li⁺, PPO–Li⁺, and PEO–Li⁺ complexes as a function of coordination number.

heavy atoms) for the single-coordination structures shows that the CH₂ groups two bonds away from the central oxygen have very different values in the PTMO and PEO complexes (PTMO = −0.04e, PEO = 0.30e). Assuming a system of point charges with hydrogens summed into heavy atoms (at the optimized geometries), the Coulombic interaction energies (*qql/r*) between Li⁺ and the model polymer are −33.2 kcal/mol for the one-coordinated PTMO complex versus −15.5 kcal/mol for the corresponding PEO complex. Although the Coulombic interaction energies are different from the HF/6-31G* results (−48.6 and −39.4 kcal/mol, respectively), the former are consistent with the increased binding of PTMO–Li⁺. This is primarily due to the charge redistribution from the extra CH₂ group in the PTMO repeat unit. The atomic charges of the PPO complex are very similar to that of PEO and, thus, their binding energies are similar.

A plot of the binding energies in Table 1 versus coordination number is given in Fig. 3. The plot indicates that the binding energies of the PTMO–Li⁺ complexes level off between four- and five-coordination whereas they level off at around five- and six-coordination for PEO–Li⁺ and PPO–Li⁺. The only six-coordination structure that we could locate for PTMO–Li⁺ had a smaller binding energy than the five-coordination complex. The large range of Li–O distances (2.07–2.43 Å) for six-coordination PTMO–Li⁺ suggests that the PTMO chain is having some difficulty in forming a six-coordination complex due to steric crowding. The binding energies of the PPO–Li⁺ complexes are very similar to that of the PEO–Li⁺ complexes. This is expected because of the similar atomic charges on the models representing PEO and PPO.

3.3. Conclusions

In this paper, we have reported on an ab initio molecular orbital study of the interaction of a single Li⁺ cation with molecules modeling polyalkyloxides including PEO, PTMO, and PPO. Coordination by one to six oxygens

was considered. For the singly-oxygen coordinated structure at the HF/6-31G(d) level, the PTMO–Li⁺ complex had the largest binding energy followed by PPO–Li⁺ and then PEO–Li⁺. This order was confirmed by high level calculations including G3(MP2) theory. Similarly, for two- through five-coordination, the binding energies of the PTMO–Li⁺ complexes are larger than those of the corresponding PEO complexes. This is due to the differences in the charge distributions in the two systems. Only the six-coordination PEO–Li⁺ complex had a larger binding energy than the corresponding PTMO–Li⁺ complex due to steric hindrance in the latter case. The binding energies of the PPO–Li⁺ complexes for the two- through six-coordination structures are very similar to those for the PEO–Li⁺ complexes. A comparison of Li⁺ migration barriers for these complexes will be reported on in a future publication. A previous study of Li⁺ migration in Li⁺–PEO complexes found that the barriers largely depended on the energy differences between coordination structures [4]. Based on the energy differences in Table 1 the migration barriers for PTMO are likely to be smaller than that of PEO and those of PPO are likely to be very similar to those of PEO.

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References

- [1] P.G. Bruce, F.M. Gray, *Solid State Electrochemistry*, Cambridge, New York, 1995, p. 119.
- [2] J.R. MacCallum, C.A. Vincent, *Polymer Electrolyte Reviews-I*, Elsevier, London, 1987.
- [3] A. Sutjianto, L.A. Curtiss, *J. Phys. Chem. A* 102 (1998) 968.
- [4] A.G. Baboul, P.C. Redfern, A. Sutjianto, L.A. Curtiss, *J. Am. Chem. Soc.* 121 (1999) 7220.
- [5] S.P. Gejji, P. Johansen, J. Tegenfeldt, J. Lindgren, *Comput. Polym. Sci.* 99 (1995) 5.
- [6] S.P. Gejji, P. Johansen, J. Tegenfeldt, J. Lindgren, *Solid State Ionics* 86/88 (1996) 297.
- [7] M.B. More, E.D. Glendening, D. Ray, D. Feller, P.B. Armentrout, *J. Phys. Chem.* 100 (1996) 1605.
- [8] D.J. Williams, K.B. Hall, *J. Phys. Chem.* 100 (1996) 8224.
- [9] D. Ray, E.D. Glendening, M.B. More, P.B. Armentrout, *J. Phys. Chem.* 100 (1996) 16116.
- [10] G.D. Smith, R.L. Jaffe, H. Partridge, *J. Phys. Chem. A* 101 (1997) 1705.
- [11] P.T. Boinske, L.A. Curtiss, J.W. Halley, B. Lin, A. Sutjianto, *J. Comput.-Aid. Mater. Design* 3 (1996) 385.
- [12] P. Johansson, J. Tegenfeldt, J. Lindgren, *Polymer* 40 (1999) 4399.
- [13] P. Johansson, J. Tegenfeldt, J. Lindgren, *Polymer* 42 (2001) 6573.
- [14] S.P. Gejji, S.R. Gadre, V.J. Barge, *Chem. Phys. Lett.* 344 (2001) 527.
- [15] P. Johansson, *Polymer* 42 (2001) 4367.
- [16] Y.B. Han, J. Hou, J.B. Kerr, K. Kinoshita, J.K. Pugh, C. Leiva-Parades, S.E. Sloop, S. Wang, in: *Proceedings of the Electrochemical Society on Interfaces, Phenomena, and Nanostructures in Lithium Batteries*, 2000, Vol. 36, 2001, p. 340.
- [17] W.J. Hehre, L. Radom, J.A. Pople, P.V.R. Schleyer, *Ab Initio Molecular Orbital Theory*, Wiley, New York, 1987.
- [18] L.A. Curtiss, P.C. Redfern, K. Raghavachari, V. Rassolov, J.A. Pople, *J. Chem. Phys.* 110 (1999) 4703.
- [19] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, *Gaussian 98, Revision A.7*, Gaussian Inc., Pittsburgh, PA, 1998.
- [20] J.E. Mark, D.S.J. Chiu, *Chem. Phys.* 66 (1977) 1901.
- [21] Y. Takahashi, J.E. Mark, *J. Am. Chem. Soc.* 98 (1976) 3756.
- [22] D.S. Chiu, Y. Takahashi, J.E. Mark, *Polymer* 17 (1976) 670.
- [23] R.L. Jaffe, G.D. Smith, D.Y. Yoon, *J. Phys. Chem.* 97 (1993) 12745.
- [24] A. Sutjianto, L.A. Curtiss, *Chem. Phys. Lett.* 264 (1997) 127.
- [25] G.D. Smith, O. Borodin, D. Bedrov, *J. Phys. Chem. A* 102 (1998) 10318.