RELATIVE POLARITY OF 1,3-DIOXANE AND 1,4-DIOXANE STUDIED BY THE REACTION FIELD THEORY AND *VIA* COMPUTER SIMULATIONS

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Abstract - We show that neither the dipole moment of a molecule nor the static dielectric constant of a solvent are satisfactory descriptors of polarity. According to the usual definition of molecular polarity, 1,3-dioxane is polar while 1,4-dioxane is not. The electric fields at the center of a 1,3-dioxane molecule dissolved in 1,4-dioxane and in 1,3-dioxane (pure liquid) were estimated by means of Monte Carlo statistical mechanics simulations and were found to be similar. This led us to emphasize and discuss one aspect of the limitations of the reaction field theory. Finally, we make use of the relationship between the polarity of solvent and the magnetic relaxation rate of dissolved monoatomic ^{131}Xe to corroborate our conclusions. The relaxation rates of ^{131}Xe dissolved in 1,3-dioxane and 1,4-dioxane were measured and were also found to be similar.

I Introduction.

By definition a polar molecule possesses a permanent electric dipole moment.[1] This definition has always led and, indeed, still leads to a lot of misinterpretations. Indeed, any charge distribution except the neutral and spherical distribution (typically a rare gas atom) is characterized by an infinite series of multipole moments.[1-3] The first non-zero moment is the monopole for CN^-, the dipole for HCl, the quadrupole for CO_2, the octupole for CCl_4, and the hexadecapole for SF_6, but all these charge distributions can interact with any other charge distribution (except for the neutral and spherical distribution since, for the moment, we are not discussing interactions involving induced moments). The first non-zero moment is a poor description of the full charge distribution to the extent that we are interested in electrostatic interactions in the liquid state. Indeed, the so-called multipolar series converges slowly and, in many cases, higher terms are far from negligible in relation to lower terms.[4] Moreover, the use of molecular multipolar expansions in the description of electrostatic interactions is only valid as far as the intermolecular distances (typically the distance between the centres of mass of the interacting molecules) are larger than the inter-charge (or interatomic) distances inside each molecule. This condition can be considered as satisfactorily fulfilled for globular molecules like those studied in this work, but in many cases it becomes necessary to describe the molecular charge distribution *via* a set of multipole series localized at particular positions (atomic positions for instance).[5-7] The truncation of these series at the level of the monopoles leads to the classical description in terms of localized (atomic) partial charges, which is generally used in molecular mechanics (MM), Monte Carlo statistical mechanics (MC), or molecular dynamics (MD) simulations. Unfortunately, the atomic partial charges and other localized multipole moments cannot be either measured or rigourously calculated; they are not observable quantities in the sense of quantum mechanics. Various semi-empirical partitioning procedures have been suggested (Del Re, Mulliken, Löwdin) which generally give satisfactory partial charges for semiquantitative treatments.

The recent literature[8-16] shows an increasing interest in the quantum mechanics calculation of the electrostatic properties of molecular systems. In the "simple" case of an isolated molecule, only an extended basis set and a proper estimation of correlation effects are able to give reliable results.[8] It is consequently obvious that the description of the solvent influence on the solute electrostatic properties is a very difficult task. It is more and more common to see the simultaneous use of *ab initio* quantum mechanics with various classical tools such as MM, MC or MD simulations.[9-11] Quantum mechanics calculations are also frequently associated with classical reaction field theory.[12-18] Reaction field theory, which allows the calculation of solute-solvent electrostatic interaction energy for instance, was developed more than half a century ago.[19] It describes the solute as a charge distribution or as a multipole series enclosed in a cavity and the solvent as a continuum whose electric properties are characterized by means of the static dielectric constant ε. The solute polarizes its surrounding and an non-homogeneous electric potential consequently appears in the cavity. The charge distribution interacts with this potential or, if the multipolar description is adopted, the solute dipole moment interacts with the electric field (the so-called reaction field), the quadrupole moment with the reaction field gradient, and the higher multipole moments with the higher derivatives of the reaction field. Previously, we used the reaction field model in order to estimate the solute-solvent electrostatic interaction energies of 1,3-dioxane and 1,4-dioxane in various solvents.[20] In Table 1 we illustrate our conclusions through the case of 1,3- and 1,4-dioxane dissolved in acetone. It is clear that both solutes interact similarly with acetone even if, according to the usual definition of a polar molecule, 1,3-dioxane is polar (μ=2.15±0.03 D[21]) while 1,4-dioxane is not. This led us to conclude that the dipole moment is definitively not a satisfactory descriptor of the molecular polarity of the solute (it must be pointed out that these conclusions were drawn from comparisons between systems made up of different solutes in the same solvent, a factor which should minimize the incidence of the rather crude reaction field theory description of the solvent; these conclusions were also born out by heat of dissolution measurements). Since it has been established that μ is not a satisfactory descriptor of the polarity of a molecule, it is worth wondering whether ε is a satisfactory macroscopic descriptor of the polarity of a solvent.

Solute	$H_{dip.}$ (kcal mol^{-1})	$H_{quad.}$ (kcal mol^{-1})	$H_{oct.}$ (kcal mol^{-1})	Sum (kcal mol^{-1})
1,3-dioxane	-1.10	-0.45	-0.72	-2.27
1,4-dioxane	0.00	-2.08	0.00	-2.08

Table 1: Dipolar, quadrupolar and octupolar contributions to the solute-solvent electrostatic interaction enthalpy for 1,3- and 1,4-dioxane dissolved in acetone at 298K.[20]

II Electric field a the centre of a dipolar molecule dissolved in dipolar and non-dipolar solvents

Comparison between the electric fields estimated from MC simulations and the reaction fields calculated by the Kirkwood-Onsager theory

While the static dielectric constant of a solvent, ε, is a function of the electric dipole moment and the dipolar polarizability of the constituting molecules, higher electric moments are not taken into account. This can easily be illustrated by comparing the dielectric constants of liquid benzene and cyclohexane. The benzene and cyclohexane molecules are not dipolar, they have similar polarisabilities but their electric quadrupole moments are very different; the dielectric constants of these solvents are nevertheless similar (Table 2). Therefore, the characterization of the solvent polarity by means of the dielectric constant only neglects contributions due to quadrupoles and higher electric moments, and might constitute a severe limitation of the reaction field theory.

In this chapter, our aim is to establish whether solvent molecular electric moments higher than the dipole can lead to a substantial average electric field at the centre of a dipolar solute. In order to reach this goal we have considered the particular case of 1,3-dioxane dissolved in 1,4-dioxane and, for purposes of comparison, pure liquid 1,3-dioxane. We are thus interested in a comparison between systems made up of the same (dipolar) solute dissolved in different solvents.

Solvent	α ($Å^3$)	Θ_{zz}[#] ($10^{-40}Cm^2$)	$\varepsilon/\varepsilon_0$ (20°C)
benzene	10.4[22]	-29 ± 2[22]	2.284[23]
cyclohexane	11.2[24]	3 ± 1[24]	2.023[23]

Table 2: Dipolar polarisability (α), electric quadrupole moment (Θ) and static dielectric constant relative to vacuum permitivity ($\varepsilon/\varepsilon_0$) of benzene and cyclohexane.

[#] In both cases the quadrupole tensor is axially symmetrical ($\Theta_{zz}=-2\Theta_{xx}=-2\Theta_{yy}$); the z axis corresponds to the C_6 and C_3 symmetry axes of benzene and cyclohexane respectively.

MC simulations have been performed in the N,V,T ensemble at 298 K for pure liquid 1,3-dioxane (125 molecules) and for 1,3-dioxane dissolved in 1,4-dioxane (1 and 124 molecules respectively). Both dioxane molecules were considered as unpolarizable rigid bodies and modelled as six interaction sites (implicit hydrogens) centered at the oxygen and carbon positions. The intermolecular interaction potentials consist of Lennard-Jones and Coulomb terms. The partial charges were estimated by *ab initio* calculations; in the case of 1,3-dioxane, our molecular model and the *ab initio* partial charges lead to a dipole moment of 2.16 D in very good agreement with the experimental value. Potential parameters and computational details are given in the appendix. In the following, we focus on some electric properties of the simulated systems; an extensive analysis of the simulations will be the subject of a subsequent publication.

The average electric field at the 1,3-dioxane molecule centre of mass, <E>, was calculated in the molecular frame defined in Figure 1. The results are quoted in Table 3 and represented in graph form in Figure 2. For reasons of symmetry, the x component of the average electric field must vanish (cf. Figure 1). In accordance with the way of estimating the errors (cf. the appendix), this constraint must be considered as fulfilled in both simulations. From the results displayed in Table 3 we can see that the average electric field in the non-dipolar 1,4-dioxane solvent is far from negligible in comparison to the value in the dipolar 1,3-dioxane solvent.

Solvent	$\langle E_x\rangle$ ($10^9 Vm^{-1}$)	$\langle E_y\rangle$ ($10^9 Vm^{-1}$)	$\langle E_z\rangle$ ($10^9 Vm^{-1}$)	$|\langle E\rangle|$ ($10^9 Vm^{-1}$)	Θ[#] (deg.)
1,3-dioxane	-0.007 ± 0.005	-0.647 ± 0.005	1.08 ± 0.01	1.26 ± 0.01	10.0 ± 0.1
1,4-dioxane	-0.02 ± 0.04	-0.50 ± 0.05	0.85 ± 0.07	0.99 ± 0.07	10 ± 2

Table 3: Average electric field calculated in the molecular frame at the centre of mass of a 1,3-dioxane molecule in the pure liquid phase and dissolved in 1,4-dioxane (results obtained from MC simulations; contributions of the solvent molecules are taken into account whose centres are up to 12.5 Å from the solute centre of mass).

[#] angle between the electric field and the permanent electric dipole (cf. Figure 2).

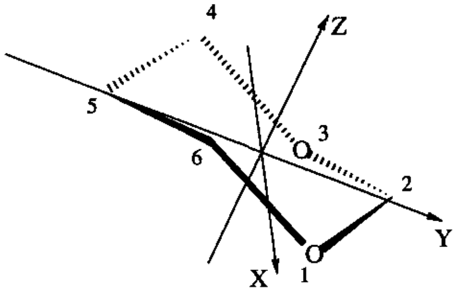

Figure 1:Representation of the 1,3-dioxane molecular frame. The origin corresponds to the centre of mass of the molecule. The X axis is parallel to the O_3-O_1 vector, the Y axis is parallel to the C_5-C_2 vector, and the Z axis is perpendicular to both X and Y axes.

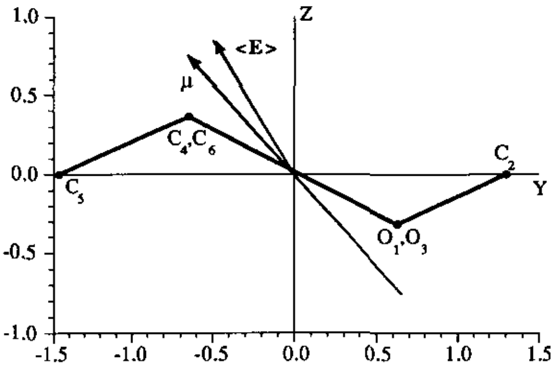

Figure 2: Graph showing the results quoted in Table 3 for the case of 1,3-dioxane in 1,4-dioxane. The scale corresponds to Å for atomic coordinates, D for the dipole moment and $10^9 Vm^{-1}$ for the average electric field. The dipole moment is represented according to the definition used in physics; its direction is then opposite to the direction with wich chemists are familiar.

In order to properly compare the average electric field estimated from the MC simulations and *via* the reaction field theory, it is worth noting that in the latter approach the polarizability of the solvent molecules is taken into account. In our MC simulations, nothing prevented the inclusion of molecular polarizabilities, but the computational times would have been much longer. Obviously, the dielectric constant of an unpolarizable and non-dipolar solvent is 1. Therefore, the reaction field calculated at the centre of a 1,3-dioxane molecule dissolved in the unpolarizable 1,4-dioxane solvent is zero, a value which must be compared with the $(0.99\pm0.07)\ 10^9 Vm^{-1}$ quoted in Table 3. The disagreement is obviously far from negligible.

The Kirkwood-Onsager reaction fields calculated on the basis of the experimental static dielectric constants (and taking molecular polarisabilities into account) are given in Table 4. The similarity is purely fortuitous between the reaction field at the centre of mass of a 1,3-dioxane molecule dissolved in polarizable 1,4-dioxane and the $|\langle E\rangle|$ value estimated by MC simulation for 1,3-dioxane in unpolarizable 1,4-dioxane. Since the refractive indexes and the densities of 1,3- and 1,4-dioxane are very similar (n_D^{20} = 1.4165 and 1.4224, $d^{20/4}$ = 1.0342 and 1.0337, for 1,3- and 1,4-dioxane respectively), the molecular polarizability of these molecules must be alike (from the Clausius-Mossotti equation: 8.5 $Å^3$ and 8.6 $Å^3$ respectively). The difference between the reaction field values quoted in Table 4 cannot therefore be ascribed to polarizability effects, but is directly related to the fact that 1,3-dioxane solvent is dipolar while 1,4-dioxane is not, and that ε does not take electric moments higher than the dipole into account.

Solvent	$\varepsilon/\varepsilon_0$ (25°C)#	$|\mathbf{R}|$$ (10^9Vm^{-1})
1,3-dioxane	13.57	1.70
1,4-dioxane	2.209	0.85

Table 4: Kirkwood-Onsager reaction field, $|\mathbf{R}|$, at the centre of mass of a 1,3-dioxane molecule in pure liquid phase dissolved in 1,4-dioxane.

static dielectric constant relative to vacuum permitivity.

$ $\mathbf{R} = \frac{1}{4\pi\varepsilon_0}\frac{2(\varepsilon/\varepsilon_0-1)}{1+2\varepsilon/\varepsilon_0}\frac{\mu}{a^3}$; where $|\mu|$=2.16D and a=3.24Å (evaluated from the molar volume of pure liquid 1,3-dioxane at 298K, cf. the appendix).

In the Kirkwood-Onsager theory, the electronic and, possibly, the orientational polarization of the medium arises in such a way that the solute dipole and the reaction field are co-linear. In our MC simulations the polarization was only orientational, i.e. preferential orientations of the (unpolarizable) solvent molecules around the solute. In order to substantiate the extent of the role of solute-solvent electrostatic interactions in the existence of an average electric field at the centre of a 1,3-dioxane molecule dissolved in 1,4-dioxane, we undertook the MC simulation of a system made up of an "apolar 1,3-dioxane molecule" (the atomic partial charges were set up to zero) and 124 1,4-dioxane molecules. The components of the average electric field at the centre of the "apolar 1,3-dioxane molecule" which we calculated in the molecular frame were (0.00±0.07,-0.01±0.05,-0.10±0.08) 10^9Vm^{-1}. This result clearly indicates that the average electric fields quoted in Table 3 arose from electrostatic solute-solvent interactions or, equivalently, that the structuration of the solvation shell due to the van der Waals interactions did not lead to significant average electric fields: this is a particularly interesting conclusion since the van der Waals contribution to the total solute-solvent interaction energy exceeded 90% (Table 5).

Solvent	$\langle U_{elec}\rangle$ (kcal mol^{-1})	$\langle U_{vdw}\rangle$ (kcal mol^{-1})
1,3-dioxane	-1.49 ± 0.01	-15.15 ± 0.01
1,4-dioxane	-1.19 ± 0.07	-14.92 ± 0.10

Table 5: Electrostatic and van der Waals contributions to the solute-solvent interaction energy of a 1,3-dioxane molecule in a pure liquid phase and dissolved in 1,4-dioxane (results obtained from MC simulations; contributions of the solvent molecules are taken into account whose centres are up to 12.5 Å from the solute centre of mass).

Table 5 also shows that the electrostatic interactions of 1,3-dioxane with 1,3-dioxane (pure liquid phase) and with 1,4-dioxane (diluted solution) are similar. Once again, such a result would never have been obtained using reaction field theory (the electrostatic solute-solvent interaction energy for a dipolar solute in an unpolarizable non-dipolar solvent is zero).

III The nuclear magnetic relaxation of ^{131}Xe dissolved in 1,3-dioxane and 1,4-dioxane

The study of relaxation phenomena in nuclear magnetic resonance (nmr) is one of the best sources of information on molecular translational and rotational motions in the liquid state. Monoatomic ^{131}Xe can be visualized as a "spin-spy" able to give information on the motion of the surrounding solvent molecules. We have devoted a few papers[25-28] to this problem, to which the interested reader is referred. Here, we would like to insist on the link between the magnetic relaxation rate of dissolved ^{131}Xe and polarity of the solvent.

In nmr, quadrupolar nuclei like ^{131}Xe are generally characterized by a very fast relaxation rate in solution. This behaviour is explained by the efficiency of the so-called quadrupolar mechanism resulting from the interaction between the nuclear electric quadrupole moment and the fluctuating electric field gradients. In the case of monoatomic xenon, the electric field gradients are of intermolecular origin and, therefore, depend on the electric properties of the solvent molecules. In an isotropic environment, the average electric field gradient felt by the xenon atom vanishes, but the fluctuations are definitely different from zero

Whereas in 1984, Stengle *et al.* observed that the spin-lattice relaxation of ^{131}Xe is fast in polar solvents like acetone or water and much slower in solvents like n-hexane or methylcyclohexane, they also found that the relaxation rate in benzene is similar to the value in acetone and concluded: "*benzene is an exception among the nonpolar liquids*".[29] Taking into account the fact that the benzene molecule is quadrupolar, we had previously performed MD simulations of the mixture xenon/benzene (1/124) in order to calculate the autocorrelation function of the electric field gradient at the xenon nucleus and its associated spectral density.[28] This allowed us to estimate the spin-lattice relaxation rate of ^{131}Xe: we obtained (150±20) s^{-1} while experimental determination led to 188,[30] 198,[27] and 227[29] s^{-1}. The agreement between the experimental and calculated values is the proof that benzene is not an exception among the non-polar liquid because benzene is a (quadru)polar.

In the framework of the present study, we measured the relaxation rate of ^{131}Xe dissolved in 1,3- and 1,4-dioxane at 298K (see below); we found 420 s^{-1} and 380 s^{-1} respectively. An interpretation of these results based on MD simulations is currently in progress; in this paper we limit ourselves to observing that these relaxation rates are nearly the same and to pointing out that this experimental fact cannot be explained as far as unlike 1,3-dioxane, 1,4-dioxane is called a nonpolar solvent or, in the same way, as far as the polarity of these solvents is described by means of their dielectric constants.

IV Conclusions.

On the basis of Monte Carlo statistical mechanics simulations of liquid systems made up of two isomeric heterocycles, it has been easy to demonstrate the poverty of the description of the molecular or macroscopic polarity by means of the electric dipole moment or the dielectric constant, and its unsatisfactory nature if the ability of a molecule to give rise to significant electrostatic interactions is concerned. To be more precise, it has been shown that it can be misleading to use ε as a measure of solvent polarity even if the solute is described by a set of localized partial charges or a multipolar series not restricted to the electric dipole moment. The reaction field theory is certainly a good model to obtain semiquantitaive results very easily or to systematically compare the behaviour of different solutes dissolved in the same solvent. Nevertheless the use of the reaction field theory in conjunction with sophisticated *"ab initio"* calculations is perhaps not so easily justified.

EXPERIMENTAL SECTION

Whereas 1,4-dioxane was distilled and dried on molecular sieve, 1,3-dioxane was Aldrich product of the highest available purity and was used without any further purification. The samples contained 3 ml of solvent in a 10 mm nmr tube and were atlernatively degassed and saturated with xenon through cycles involving sonication and bubbling with xenon at normal temperature. After the last bubbling, the samples were sealed under a xenon atmosphere. The spectra were recorded on a Bruker AMX 600 spectrometer at 298 K; ^{131}Xe was observed at a centerband frequency of 49.217 MHz. The pulse duration was 30 10^{-6} s, the frequency width was 20000 Hz, the memory size was 4096 points, and the acquisition time was 0.1024 s. The delay between the end of the data acquisition and the start of the next pulse was 1 10^{-3} s, and the number of scans was 16384. The spectra were recorded without lock and the nmr tube was not spinning. We adopted the linewidth procedure to determine T_1 on the basis of the assumption that T_1=T_2; the linewidth were obtained from a lorentzian fit of the signal.

ACKNOWLEDGEMENTS

The authors thank the "Communauté Française de Belgique-Direction Generale de l'Enseignement Supérieur et de la Recherche Scientifique" for its financial support. We wish to acknowledge Dr. J. Lievin for the *ab initio* calculations of atomic partial charge distributions, Professor S. Wodak for providing computer time and Dr. D. van Belle for valuable discussions. Gratitude is expressed to Dr. D. Zimmermann, Dr. P.G. Scherer and Spectrospin-Bruker for their contribution to the determination of the ^{131}Xe relaxation rates.

Appendix: Computer simulations of dioxane systems

A. Molecular models and potential functions

Both dioxane molecules were considered as unpolarizable rigid bodies and modelled as six interaction sites (implicit hydrogens) centered on the C and O, whose Cartesian coordinates were obtained from the equilibrium geometries given by Remerie *et al.*[31] The intermolecular interaction potentials consisted of Lennard-Jones plus Coulomb terms (Table A1). The partial charges were estimated by *ab initio* calculations by means of the GAMESS package.[32] We used the Dunning-Hay basis set augmented with 1 set of 6d-polarization functions on C and O and with 1 set of p functions on H. Atomic partial charges were obtained from a Löwdin population analysis of the closed-shell self-consistent field wave function (without geometry optimization). Partial charges on CH_2 interaction sites were obtained by summing up H and C atomic partial charges. The OPLS (optimized potentials for liquid simulations) Lennard-Jones parameters for ethers[33] have been slightly modified in such a way that MC simulations of pure liquid 1,3- and 1,4-dioxane lead to reasonable pressure and reproduce heats of vaporization satisfactorily (Table A2).

Molecule	Site	Centered on	ε/R (K)	σ (Å)	q (e)
1,3-dioxane	O	O1,O3	85.59	3.000	-0.328
	CH_2	C2	59.41	3.850	0.281
	CH_2	C4,C6	59.41	3.850	0.182
	CH_2	C5	59.41	3.905	0.011
1,4-dioxane	O	O1,O4	85.59	3.000	-0.348
	CH_2	C2,C3,C5,C6	59.41	3.850	0.174

Table A1: Interaction parameters for 1,3-dioxane and 1,4-dioxane. ($R=1.986$ cal $mol^{-1}K^{-1}$, $e=1.6021\ 10^{-19}$ C)

Pure liquid	Pressure (atm)	$\Delta H_{vap.}$ (kcal mol^{-1})	exp. $\Delta H_{vap.}$ (kcal mol^{-1})
1,3-dioxane	-140±10	9.25±0.01	9.34
1,4-dioxane	-30±10	8.87±0.01	9.24

Table A2: Pressure and heat of vaporization of pure liquid 1,3- and 1,4-dioxane.

Correction has been made to the Lennard-Jones contribution due to molecules beyond the cutoff.

B. Simulation procedure

Monte Carlo statistical mechanics (MC) simulations were carried out in the canonical ensemble at 298 K for systems made up of 125 molecules in a periodic cubic cell measuring $(26.104\ \text{Å})^3$; this corresponds to the normal density of pure liquid 1,4-dioxane (1.0280[34]; the normal density of 1,3-dioxane is not available; at 293 K and 1 atm, the densities of 1,3- and 1,4-dioxane are nearly the same: 1.0342 and 1.0337 respectively[23]). A spherical cutoff at 12.5 Å (based on the distance between the centres of mass) was applied to all the potential terms. Metropolis sampling was used; the ranges for translational and rotational motions were adjusted in such a way that an acceptance ratio for new configurations of ca. 50 % was achieved. Each simulation consisted of 2.5 10^6 configurations for the equilibration followed by 5 sets of 1.25 10^6 configurations for the production run (8 sets in the case of mixtures). The statistical errors were estimated from subaverages taken over each set, and these corresponded to the standard deviation of the mean. It must be pointed out that due to the small number of possibly non-totally independent observations (5 or 8), our statistical errors might be slightly underestimated. The computations were performed on a Silicon Graphics 4D/340S computer.

Particular attention was paid to possible artefacts due to the truncation of the electrostatic interactions. Molecular dynamics (MD) simulations of pure liquid 1,3-dioxane, whose results will appear in a subsequent publication, were performed in similar conditions except for the truncation scheme which was based on atomic distances and included the use of a termination function.[35] This function, applied over the entire distance range to the Coulomb interaction terms, removes the discontinuities in the electrostatic potential and force at the cutoff distance. The configurations obtained in such MD simulations lead to average interactions energies, pair distribution functions and other static properties in very good agreement with the MC results. For instance, the norm of the electric field at the 1,3-dioxane centre of mass (pure liquid) is estimated as (1.21±0.02) 10^9 Vm^{-1} while the MC result is (1.26±0.01) $10^9 Vm^{-1}$ (cf. Table 3). This allows us to state that the truncation scheme does not sensitively affect the properties at which we looked.

REFERENCES

1. E. M. Purcell, 'Electricity and Magnetism', Berkeley Physics Course 2, Mc Graw Hill, New York, 1965.
2. C. J. F. Böttcher, 'Theory of Electric Polarisation', Elsevier Pub. Company, Amsterdam, 1952.
3. J. C. Slater and N. H. Frank, 'Electromagnetism', Dover Publication, New York, 1969.
4. M.-L. Stien, M. Claessens, A. Lopez, and J. Reisse, *J. Am. Chem. Soc.*, 1982, **104**, 5902.
5. F. London, *J. Phys. Chem.*, 1942, **46**, 305.
6. E. Gerocco and J. Tomasi, 'Topics in Current Chemistry: Vol. 42, ed. by Springer Verlag, Berlin, Heidelberg, 1973, pp. 95.
7. R. Rein, *Adv. Quant. Chem.*, 1973, 7, 335.
8. S. L. Price, J. S. Andrews, C. W. Murray, and R. D. Amos, *J. Am. Chem. Soc.*, 1992, **114**, 8268.
9. P. A. Kollman and K. M. Merz Jr, *Acc. Chem. Res.*, 1990, **23**, 246.
10. J. Gao, *J. Phys. Chem.*, 1992, **96**, 537.
11. J. Gao and J. Pavelites, *J. Am. Chem. Soc.*, 1992, **114**, 1912.
12. M. M. Karelson, A. R. Katritzky, M. Szafran, and M. C. Zerner, *J. Org. Chem.*, 1989, **54**, 6030.

13. K. W. Mikkelsen, H. Agren, J. Aa Jensen, and T. Helgaker, *J. Chem. Phys.*, 1988, **89**, 3086.

14. F. J. Luque, M. J. Negre, and M. Orozco, *J. Phys. Chem.*, 1993, **97**, 4386.

15. M. W. Wong, M. J. Frisch, and K. B. Wiberg, *J. Am. Chem. Soc.*, 1991, **113**, 4776.

16. J. Tomasi, R. Bonaccorsi, R. Cammi, and F. J. Olivares del Valle, *J. Mol. Struct. (Teochem)*, 1991, **234**, 401.

17. O. Tapia and O. Goscinski, *Molec. Phys.*, 1975, **29**, 1653.

18. J. L. Rivail, B. Terryn, and M. F. Ruiz-Lopez, *J. Mol. Struct. (Theochem)*, 1985, **120**, 387.

19. J. G. Kirkwood, *J. Chem. Phys.*, 1934, **1**, 351.

20. J. Reisse, M. Claessens, O. Fabre, G. Michaux, M.-L. Stien, and D. Zimmermann, *Bull. Soc. Chim. Belg.*, 1983, **92**, 819.

21. R. Walker and D. W. Davidson, *Can. J. Chem.*, 1959, **37**, 492.

22. M. R. Battaglia, A. D. Buckingham, and J. H. Williams, *Chem. Phys. Lett.*, 1981, **78**, 421.

23. R. C. Weast, 'CRC Handbook of Chemistry and Physics' , 58th ed., 1977-1978.

24. I. E. Craven, M. R. Hesling, D. R. Laver, P. B. Lukins, G. L. D. Ritchie, and J. Vrbancich, *J. Phys. Chem.*, 1989, **93**, 627.

25. J. Reisse, *Nouv. J. Chim.*, 1986, **10**, 665.

26. M. Luhmer, A. Dejaegere, and J. Reisse, *Magn. Reson. Chem.*, 1989, **27**, 950.

27. A. Dejaegere, M. Luhmer, M.-L. Stien, and J. Reisse, *J. Magn. Reson.*, 1991, **91**, 362.

28. M. Luhmer, D. van Belle, J. Reisse, M. Odelius, J. Kowalewski, and A. Laaksonen, *J. Chem. Phys.*, 1993, **98**, 1566.

29. T. R. Stengle, N. V. Reo, and K. L. Williamson, *J. Phys. Chem.*, 1984, **88**, 3225.

30. R. K. Mazitov, H. G. Hertz, V. F. Garanin, K. M. Enikeev, A. V. Il'yasov, and Sukhoverkhov, *Dokl. Akad. Nauk. SSSR*, 1983, **273**, 131.

31. K. Remerie, W. F. Van Gunsteren, J. P. M. Postma, and H. J. C. Berendsen, *Molec. Phys.*, 1984, **53**, 1517.

32. M. W. Schmidt, K. K. Baldridge, J. A. Boatz, J. H. Jensen, S. Koseki, M. S. Gordon, K. A. Nguyen, T. L. Windus, and S. T. Elbert, *QCPE Bull.*, 1990, **10**, 52.

33. J. M. Briggs, T. Matsui, and W. L. Jorgensen, *J. Comp. Chem.*, 1990, **11**, 958.

34. J. A. Riddick and W. B. Bunger, 'Organic Solvents. Physical Properties and Methods of Purification.', Techniques of Chemistry 2, Wiley-Interscience, New York, 1970.

35. M. Prévost, D. van Belle, G. Lippens, and S. Wodak, *Molec. Phys.*, 1990, **71**, 587.

Received, 4th October, 1993