Theor Chem Account (2008) 121:147–153
DOI 10.1007/s00214-008-0457-0

REGULAR ARTICLE

Theoretical investigation of the electronic absorption spectrum of Piceatannol in methanolic solution

T. Andrade-Filho · **Hardiney S. Martins** ·
Jordan Del Nero

Received: 24 March 2008 / Accepted: 14 May 2008 / Published online: 30 May 2008

Abstract In the current work, we use a combination of Monte Carlo (MC) simulation and the Intermediate Neglect of Differential Overlap/Spectroscopic-Configuration Interaction (INDO/S–CI) scheme to investigate the solvent effects on the electronic absorption spectrum of piceatannol molecule in methanolic solution. The investigation was conducted by carrying out a posteriori INDO/S–CI calculations on 125 statistically relevant configurations produced by the MC simulation. Furthermore, a careful study of hydrogen bonds formed in the course of the MC simulation was performed. In general, our results are in very good agreement with the available experimental result.

Keywords Piceatannol · Absorption spectrum · Monte Carlo simulation · Solvent effects

1 Introduction

Piceatannol (3, 5, 3′, 4′-tetrahydroxy-trans-stilbene) (PC) (Fig. 1) is a stilbenoid phytoalexin found in peanuts, berries, red wine and in the skin of certain varieties of grapes [1]. Stilbenes, flavonoids, tanins, terpenes and steroids are fundamental secondary metabolites of plants with a range of beneficial biological activities [2]. Some studies have suggested that PC is an effective antioxidant, anti-platelet, anti-inflammatory and anticancer agent [3–6]. Due to its stilbenoid core, piceatannol is formed by two phenyl rings linked by a non-saturated carbon bridge with four hydroxyl groups substituted on the phenyl rings. Piceatannol, even though structurally very close, is a biomedical agent more potent than resveratrol (RS) [7]. Although the biological activities of PC have been much less investigated than the biological activities of RS, the details of the antioxidative properties of both molecules are completely unclear.

Some works have stated that it is suitable to correlate intrinsic parameters such as molecular size, molecular shape and electronic properties of organic compounds to their specific biological activity [8,9]. In many cases, the unique way to experimentally study the electronic properties of organic compounds is done in liquid solution. For this reason, in the current work, in order to gain some insight into the electronic properties of piceatannol in alcoholic solution, we used the hybrid sequential Monte Carlo/quantum mechanical (S-MC/QM) approach [10] to calculate the electronic absorption spectrum of piceatannol in methanolic solution.

Alcohols form a class of compounds with useful technological and scientific applications [11–15]. In fact, it is known that the physicochemical features of alcohols are directly related with their hydroxyl functional group and capability to form strong hydrogen bond networks [16–18]. The hydrogen bond network of methanol has been the main subject of many publications [19–22]. This simplest alcohol molecule is widely used as solvent in solutions to identify phenolic compounds by high-performance liquid chromatography (HPLC) method [7,23–25].

Here, we investigated how the solvation affects the $\pi \rightarrow \pi^*$ transition energy of PC including explicitly the methanol solvent molecules within the hydrogen bond and first solvation shells in the quantum mechanical (QM) calculations [26–29]. Through this procedure all the polarization and electrostatic interactions were considered [26,27].

T. Andrade-Filho (✉) · H. S. Martins · J. Del Nero
Programa de Pós-Graduação em Física,
Instituto de Ciências Exatas e Naturais,
Universidade Federal do Pará,
66075-110 Belém, Pará, Brazil
e-mail: tarciso@ufpa.br

J. Del Nero
e-mail: jordan@ufpa.br

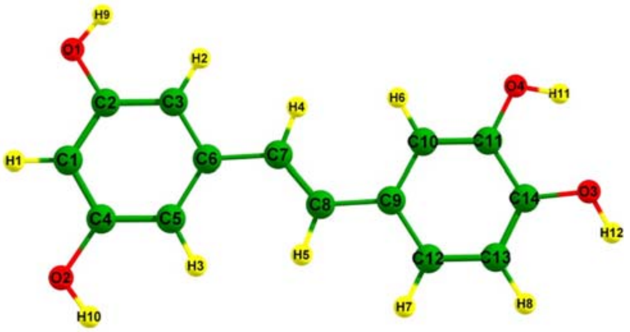

Fig. 1 The structure of piceatannol and the definition of the atomic indices used in Table 1

It is important to emphasize that for the sake of validation of the theoretical results obtained in this work, a direct comparison with the experimental result of the absorption spectrum of PC in methanolic environment is performed.

2 Computational methodology

The Monte Carlo (MC) simulation was carried out for the molecular liquid composed of one PC molecule as solute surrounded by 1,000 methanol solvent molecules in a cubic box. Standard procedures for the Metropolis MC importance sampling scheme and periodic boundary conditions implemented with the minimum image method [30] were used in the canonical (NVT) ensemble. The cubic box with dimensions $40.84 \times 40.84 \times 40.84$ Å^3 was defined by the density of the liquid methanol $\rho = 0.7866$ g/cm^3 at 298.15 K [31]. The intermolecular non-bonded interactions were modeled by the Lennard-Jones plus Coulomb potential.

The united atom optimized potential model for liquid simulations (OPLS-UA) [32] was used as a force field of methanol molecule. The geometry of methanol was taken from the OPLS force field [33]. Since X-ray crystallographic data are not available in the literature for PC, we will resort to geometry optimization to acquire the fundamental information. It was treated quantum mechanically at the B3LYP/6–31+G(d,p) level of theory. Also, for PC we used the all atom optimized potential model for liquid simulations (OPLS-AA) [34] force field with the atomic charges calculated by the CHELPG procedure [35] at the B3LYP/6–311++G(d,p) level of theory (Table 1). The molecular geometries of PC and methanol were kept rigid in the course of the simulation.

The intermolecular non-bonded interactions were truncated with a spherical cutoff radius of 20.42 Å associated with the long range correction scheme for the potential energy [30]. In the current simulation, we performed 4.0×10^7 and 1.0×10^8 MC steps in the thermalization and equilibrium stages, respectively. The simulation was initiated with a random configuration of the molecular liquid under study. New configurations were sequentially generated after 1.0×10^3 MC steps by randomly translating all the methanol solvent molecules along the three Cartesian coordinate directions and rotating them by $\delta\theta = \pm 15°$ around a randomly chosen axis.

Table 1 Lennard-Jones parameters and charge distribution for PC molecule

Site	ε (kcal/mol)	σ (Å)	q (a.u)
C1	3.550	0.070	−0.406
C2	3.550	0.070	0.512
C3	3.550	0.070	−0.511
C4	3.550	0.070	0.495
C5	3.550	0.070	−0.498
C6	3.550	0.070	0.349
C7	3.550	0.076	−0.191
C8	3.550	0.076	−0.169
C9	3.550	0.070	0.220
C10	3.550	0.070	−0.390
C11	3.550	0.070	0.405
C12	3.550	0.070	−0.253
C13	3.550	0.070	−0.195
C14	3.550	0.070	0.194
O1	3.070	0.170	−0.642
O2	3.070	0.170	−0.634
O3	3.070	0.170	−0.633
O4	3.070	0.170	−0.632
H1	2.420	0.030	0.218
H2	2.420	0.030	0.161
H3	2.420	0.030	0.167
H4	2.420	0.030	0.100
H5	2.420	0.030	0.099
H6	2.420	0.030	0.218
H7	2.420	0.030	0.135
H8	2.420	0.030	0.126
H9	0.000	0.000	0.429
H10	0.000	0.000	0.424
H11	0.000	0.000	0.456
H12	0.000	0.000	0.444

In order to calculate the electronic absorption spectrum of the PC molecule in methanolic solution we adopted the hybrid S-MC/QM procedure. This procedure developed by Coutinho and Canuto [10] allows that the electronic spectrum of a molecule be calculated in solution through the application of QM calculations on the molecular liquid structures produced by the MC simulation [27]. In our case, we used the QM Intermediate Neglect of Differential Overlap/Spectroscopic-Configuration Interaction (INDO/S-CI) scheme. Only the hydrogen bond and first solvation shells were used in these INDO/S-CI calculations due to the very good results given by these shells in the theoretical absorption spectrum compared to the experimental result.

Precisely, 1,000 configurations were produced by the MC simulation. However, several configurations obtained in the current simulation are dependent or correlated and they do not provide important extra information on the calculated average values [26,28,36]. In fact, these correlated configurations can be excluded without loss of statistical information using the concept of autocorrelation function of energy [26–28,36]. One important property obtained from the integration (from zero to infinity) of the autocorrelation function of the energy is the correlation step τ [28,36]. The correlation step plays a fundamental role in determining the interval between the relevant configurations [26,36]. One can ensure that configurations are relevant when structures separated by $n > 2\tau$ are indeed selected [36]. Through this procedure, we obtained a number of 125 relevant configurations separated by 8.0×10^5 MC steps. The statistical correlation between these 125 configurations was less than 18%.

The electronic absorption spectrum was computed by the INDO/S-CI scheme [37] implemented in the ZINDO package [38]. Several methodologies have been combined with the INDO/S-CI scheme in order to model the solvatochromic shifts of several molecules in different liquid environments. Using the S-MC/QM methodology, Canuto et al. satisfactorily applied the INDO/S-CI scheme to determine the solvatochromic shifts on the $\pi \rightarrow \pi^*$ transition energy of β-carotene in apolar (isopentane) and polar (acetone, methanol and acetonitrile) solvents [39]. Using this same methodology, Rocha et al. successfully determined the spectroscopy shifts on the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transition energies of formamide in aqueous solution [27]. Broo et al. [40] applied the INDO/S-CI and self-consistent reaction field schemes in order to calculate the solvatochromic shifts on the electronic spectrum of uracil and 1, 3-dimethyluracil. Their results are according to the experimental data. The study of ethanolic solvation of C_{60} fullerene reported by Malaspina et al. [41] succeed in reproducing the experimental data using a combined molecular dynamics and INDO/S-CI approach.

In this modelling, the average values of the $\pi \rightarrow \pi^*$ transition energies were safely calculated as a simple average of the values produced by each relevant configuration because the Boltzmann factor was indeed considered in the Metropolis MC importance sampling scheme [27]. All the DFT calculations were carried out by Gaussian 98 program [42] and the MC statistical mechanics simulation was carried out by DICE program [43].

3 Results and discussion

3.1 Hydrogen bond

Hydrogen bonds (HBs) are of fundamental importance in regulating the structure and interactions of biomolecules [16, 44]. HBs avoid phenolic compounds becoming free radicals when these compounds donate a hydrogen atom to free radicals [45]. Figures 2 and 3 illustrate the radial distribution functions between the hydroxyl oxygens of PC and the methanol hydroxyl hydrogen, g_{O1-H}(r), g_{O2-H}(r), g_{O3-H}(r) and g_{O4-H}(r) and the radial distribution functions between the hydroxyl hydrogens of PC and the methanol oxygen, g_{H9-O}(r), g_{H10-O}(r), g_{H11-O}(r) and g_{H12-O}(r), respectively.

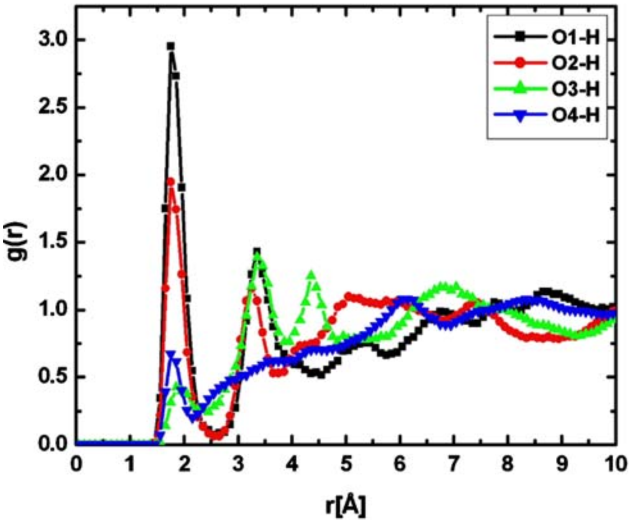

Fig. 2 Radial distribution functions between the hydroxyl oxygens of PC and the hydroxyl hydrogen of methanol

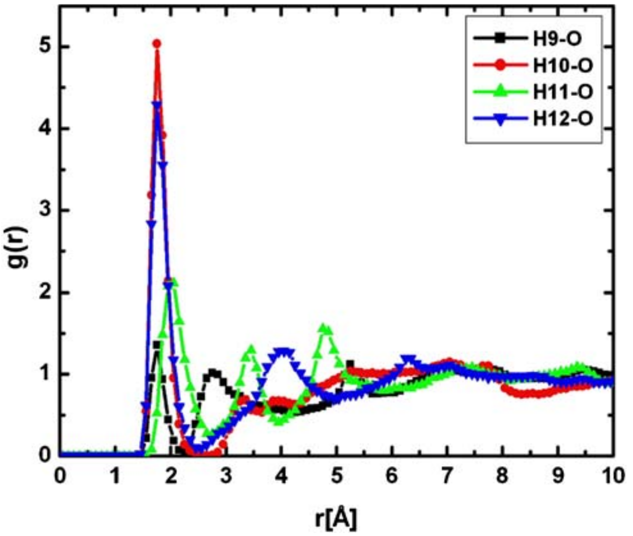

Fig. 3 Radial distribution functions between the hydroxyl hydrogens of PC and the oxygen of methanol

As one can note, the $g_{O-H}(r)$ distribution functions ($g_{O1-H}(r)$, $g_{O2-H}(r)$, $g_{O3-H}(r)$ and $g_{O4-H}(r)$) start at 1.39, 1.31, 1.43 and 1.39 Å and go up to 2.61, 2.57, 2.44 and 2.11 Å, respectively. Integration of these respective peaks yields 0.8, 0.5, 0.2 and 0.2 methanol nearest neighbors. The

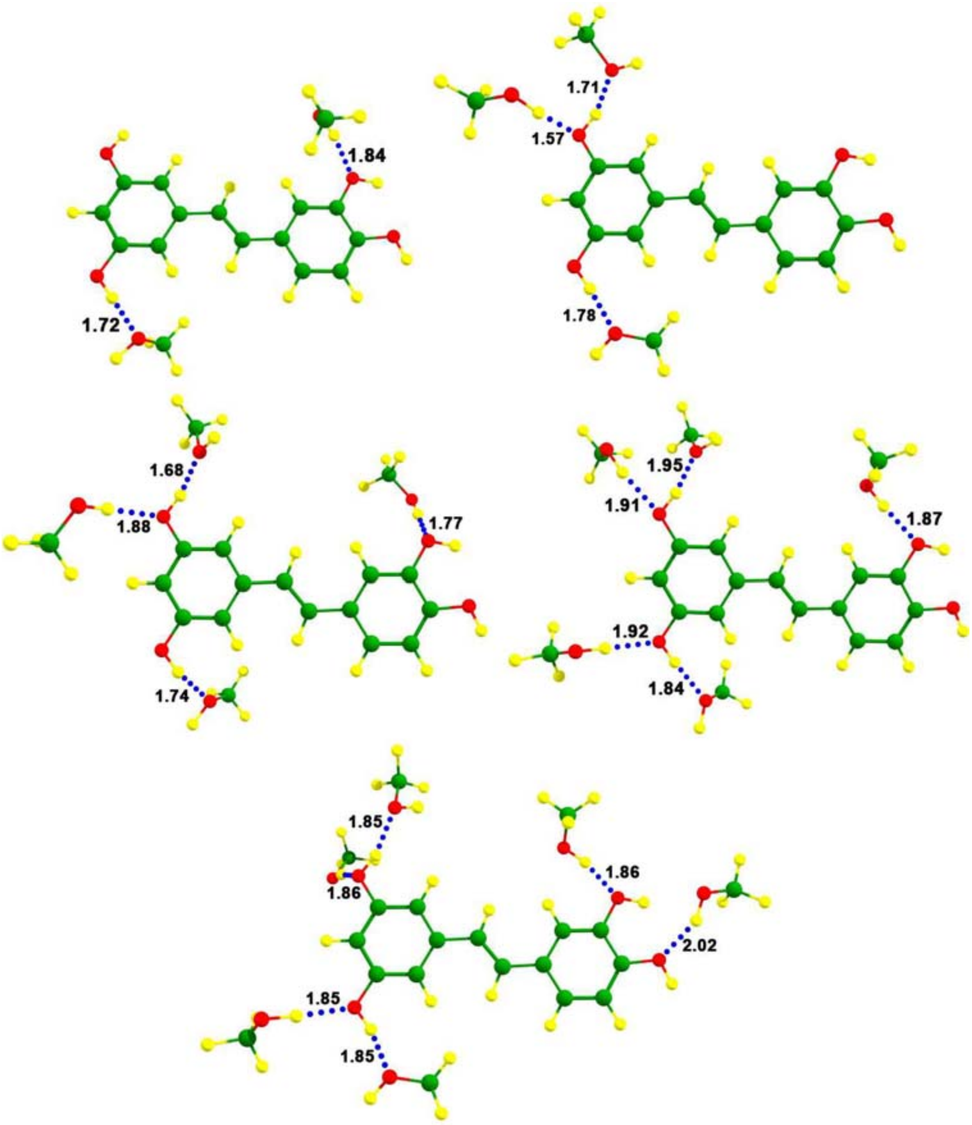

Fig. 4 Snapshots of the hydrogen bond interactions between PC and methanol molecules. Distance in Å

$g_{H-O}(r)$ distribution functions ($g_{H9-O}(r)$, $g_{H10-O}(r)$, $g_{H11-O}(r)$ and $g_{H12-O}(r)$) start at 1.35, 1.39, 1.48 and 1.31 Å and go up to 2.23, 2.57, 2.65 and 2.49 Å, respectively. Integration of these respective peaks yields 0.2, 1.0, 0.9 and 1.0 methanol nearest neighbors.

In several works, the definition of HBs have been based only on geometric criteria [46–50]. In these works, the criterion for the interatomic distances is obtained from the radial distribution functions. However, it is showed in Refs. [26–28] that the most suitable method to characterize the HBs in liquids must be based simultaneously on geometric and energetic criteria. Further details can be found elsewhere [51,52]. Therefore, the methanol molecules are hydrogen-bonded to PC molecule if and only if all the following three criteria are satisfied: (1) the R_{DA} distance is smaller than 3.8 Å; (2) the AHD angle is smaller than 40°; and finally (3) the binding energy is larger than 4.0 kcal mol^{-1} [26–28].

With all these three conditions satisfied, 485 hydrogen bonds in 125 relevant configurations are formed. This yields an average of 3.9 hydrogen bonds formed between PC and methanol nearest neighbors. PC molecule is able to form two to six hydrogen bonds with the methanol nearest neighbors (Fig. 4). The statistical data on the occurrence of the HBs formed is summarized in Table 2. It can be seen from this table that four to six hydrogen bonds constitute 80.3% of the relevant configurations and two to three hydrogen bonds account for a combined total of 19.7% of the relevant configurations.

3.2 Electronic spectrum

In the following we show the calculated results for the electronic absorption spectrum of PC in gas phase and in

Table 2 Statistics of the hydrogen bonds (HBs) formed between PC and methanol and their $\pi \rightarrow \pi^*$ average transition energies

Number of HBs	Occurrence (%)	$\pi \rightarrow \pi^*$ (nm)
2	1.2	317.9 ± 0.71 [0.79]
3	18.5	316.7 ± 0.67 [0.81]
4	51.1	318.3 ± 0.32 [0.83]
5	21.6	316.0 ± 0.57 [0.80]
6	7.6	316.2 ± 0.92 [0.79]
Total (HB shell)	100	317.1 ± 0.58 [0.83]

The numbers in brakets are the average oscillator strengths

methanolic solution. We found a value of 315.3 nm (with oscillator strength = 0.79) for the gas phase $\pi \rightarrow \pi^*$ transition energy. Unfortunately, this transition is not known in the literature neither in the gas phase nor in apolar solvents. In Table 2 we present our computed values for the $\pi \rightarrow \pi^*$ average transition energies of PC due to the hydrogen bond interactions with the methanol solvent molecules. For two, three, four, five and six hydrogen bonds, the $\pi \rightarrow \pi^*$ average transition energy was calculated as 317.9 ± 0.71, 316.7 ± 0.67, 318.3 ± 0.32, 316.0 ± 0.57 and 316.2 ± 0.92 nm, respectively. We calculated a value of 317.1 ± 0.58 nm for the hydrogen bond shell $\pi \rightarrow \pi^*$ average transition energy. This value is in accordance with the experimental result of PC in methanolic solution [7].

The liquid structure of the first solvation shell was obtained by means of the minimum distance distribution function (MDDF) [39,53]. It does not grow in a spherical form, but considers the shape of the PC, and this nearest neighbor radial distribution function was calculated using the smallest distance between all the PC atoms and all methanol atoms [39,53]. As can be seen later, the first solvation shell can be easily located.

The minimum distance distribution function is shown in Fig. 5. The first solvation shell starts at 1.41 Å and goes up to 4.55 Å. Integration of this peak yields 36 methanol molecules in the first solvation shell of PC. A snapshot of a random configuration of the first solvation shell of PC molecule is illustrated in Fig. 6. A number of 125 INDO/S–CI calculations of the $\pi \rightarrow \pi^*$ transition were carried out and their computed values were averaged [27–29]. The statistical convergence of the $\pi \rightarrow \pi^*$ transition energy calculated for the first solvation shell is illustrated in Fig. 7. It can be seen in this Fig. 7 that the $\pi \rightarrow \pi^*$ average transition energy is calculated as 320.5 ± 0.41 nm (with average oscillator strength = 0.87), which is in better accordance with the experimental result of 320.0 nm [7] than that obtained for the hydrogen bond shell. In fact, for this calculated value, there is an excellent agreement between theory and experiment within the statistical noise. The statistical noise is attributed to the uncertainty introduced when the $\pi \rightarrow \pi^*$ transition energy is calculated using a finite number of configurations [54]. In Fig. 7, it is worth noting that the $\pi \rightarrow \pi^*$ average transition energy converges with only 70 INDO/S-CI calculations [29,55]. As discussed before by Georg et al. [29] and Ludwig et al. [55], the fast convergence is achieved principally due to sampling only the configurations that are statistically uncorrelated.

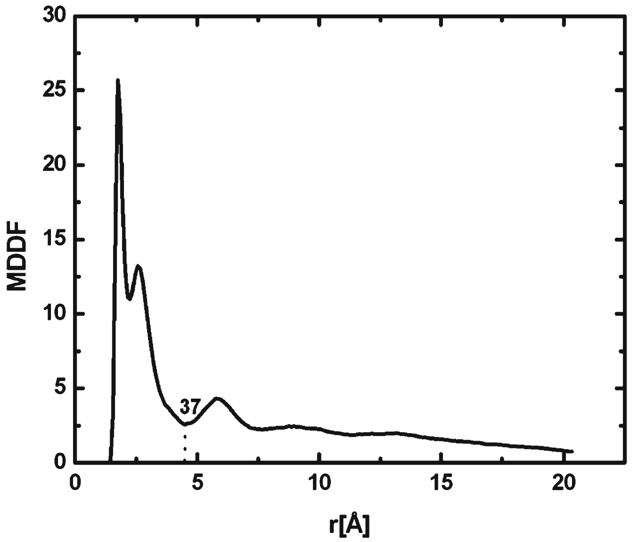

Fig. 5 Minimum-distance distribution function (MDDF) between the smallest distance of all PC atoms and all methanol atoms

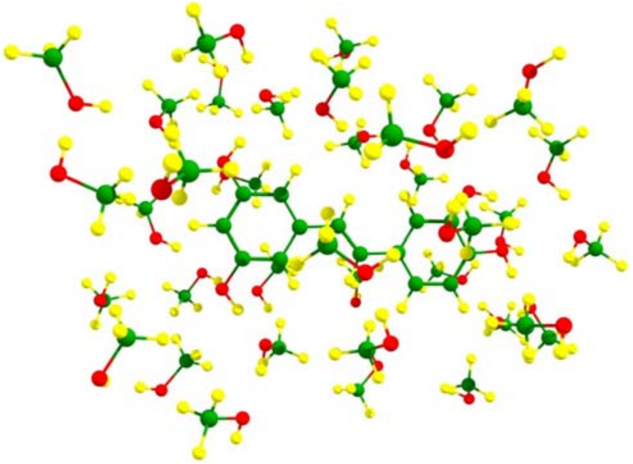

Fig. 6 Snapshot of one arbitrary configuration of the first solvation shell of PC molecule obtained from the MDDF

It is interesting to remark that the average value of the $\pi \rightarrow \pi^*$ transition energy of PC obtained in Fig. 7 incorporates into a single value, and a lot of information is not explicitly shown [56]. Therefore, in order to show the full information contained in the previously mentioned statistical average, we computed and plotted in Fig. 8 the distribution of the $\pi \rightarrow \pi^*$ transition energy calculated values of PC in methanol obtained for the first solvation shell [56].

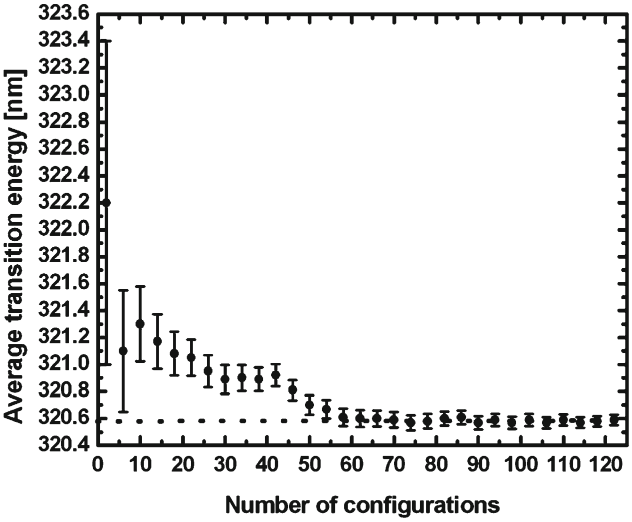

Fig. 7 Statistical convergence of the average value of the $\pi \rightarrow \pi^*$ transition energy of PC in methanol obtained for the first solvation shell

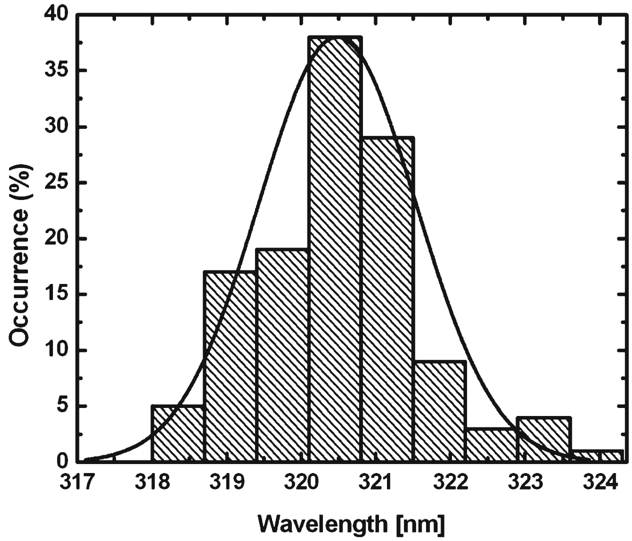

Fig. 8 Distribution of the $\pi \rightarrow \pi^*$ transition energy calculated values of PC in methanol obtained for the first solvation shell

In addition, for comparison purposes, a rough inclusion of the bulk solvent effects on the $\pi \rightarrow \pi^*$ transition energy of PC was calculated by means of the polarizable continuum model (PCM) solvation method [57–60]. By way of this method, PC molecule is immersed in a spherical cavity characterized by the dielectric constant of methanol ($\varepsilon = 32.63$) and some other features [61]. The PCM calculations were initiated using the optimized gas phase geometry of PC molecule [61].

Therefore, using the PCM–B3LYP/6-31+G(d,p) approximation, a value of 321.3 nm (with oscillator strength = 0.90) was calculated for the $\pi \rightarrow \pi^*$ transition energy of PC. This value matches very well with the $\pi \rightarrow \pi^*$ average transition energy of PC calculated above using the molecular liquid structures of the first solvation shell as well as with the experimental result [7].

Through these results, it can be noted that the shifts due to solvent effects are very small. Compared to the gas phase case, the presence of methanol molecules in the $\pi \rightarrow \pi^*$ electronic transition calculations induced average values red-shifted by only 1.8 ± 0.58 and 5.2 ± 0.41 nm due to the hydrogen bond and first solvation shells, respectively. Although the $\pi \rightarrow \pi^*$ transition energy of PC was weakly changed by the methanol molecules within the hydrogen bond and first solvation shells, the addition of this solvent in the semiempirical INDO/S–CI calculations satisfactorily reproduced the available experimental result [7].

4 Summary and conclusions

In the current work we investigated how the methanol molecules of solvation affect the $\pi \rightarrow \pi^*$ transition energy of PC through the sequential Monte Carlo/quantum mechanical approach. PC was treated by B3LYP/6–31+G(d,p) level of theory and methanol was described by OPLS force field.

The gas phase $\pi \rightarrow \pi^*$ transition energy of PC was calculated as 315.3 nm. The suitable identification of hydrogen bond structures was performed through the geometric and energetic analysis of the molecular liquid under study. The number of hydrogen bonds that the PC molecule can form with the methanol ranges from two to six. The hydrogen bond shell $\pi \rightarrow \pi^*$ average transition energy was calculated as 317.1 ± 0.58 nm, this energy being in good concordance with the results of the solution experiment.

The first solvation shell $\pi \rightarrow \pi^*$ average transition energy was calculated as 320.5 ± 0.41 nm which is almost exactly the experimental value of 320.0 nm. According to this result, we concluded that the arrangement of 36 methanol molecules around the PC molecule was sufficient to reproduce experimental absorption spectrum of PC in methanol. Indeed, this modeling succeeds in reproducing the available experimental result.

Acknowledgments We are deeply grateful to Prof. S. Canuto and Prof. K. Coutinho for providing their high level Monte Carlo simulation program DICE. This work was supported by the Brazilian agency CAPES.

References

1. Roupe KA, Remsberg CM, Yáñez JA, Davies NM (2006) Curr Clin Pharmacol 1:81–101
2. Howitz KT, Bitterman KJ, Cohen HY, Lamming DW, Lavu S, Wood JG, Zipkin RE, Chung P, Kisielewski A, Zhang LL, Scherer B, Sinclair DA (2003) Nature 425:191–196
3. Jin CY, Moon DO, Lee KJ, Kim MO, Lee JD, Choi YH, Park YM, Kim GY (2006) Pharmacol Res 54:461–467

4. Potter GA, Patterson LH, Wanogho E, Perry PJ, Butler PC, Ijaz T, Ruparelia KC, Lamb JH, Farmer PB, Stanley LA, Burke MD (2002) Br J Canc 86:774–778
5. Djoko B, Chiou RYY, Shee JJ, Liu YW (2007) J Agric Food Chem 55:2376–2383
6. Heynekamp JJ, Weber WM, Hunsaker LA, Gonzales AM, Orlando RA, Deck LM, Jagt DLV (2006) J Med Chem 49:7182–7189
7. Lin LL, Lien CY, Cheng YC, Ku KL (2007) J Chromatogr B 853:175–182
8. Ham CL, Jurs PC (1985) Chem Sens 10:491–505
9. Gasparrini F, D'Acquarica I, Pierini M, Villani C (2001) J Separ Sci 24:941–946
10. Canuto S, Coutinho K (1997) Adv Quantum Chem 28:90–107
11. Demetrius FJ (1990) Brazil's national alcohol program: technology and development in an authoritarian regime. Praeger, New York
12. Roehr M (2001) The biotechnology of ethanol: classical and future applications. Weinheim, Wiley-VCH
13. Mendelson JH, Mello NK (1973) Science 29:1372–1374
14. Gavish M, Popovitz-Biro R, Lahav M, Leiserowitz L (1990) Science 250:973–975
15. Atsumi S, Hanai T, Liao JC (2008) Nature 451:86–89
16. Reichardt C (1979) Solvents effects in organic chemistry. Verlag Chemie/Weinheim, New York
17. Sivagurunathan P, Dharmalingam K, Ramachandran K (2006) Spectrochim Acta A 64:127–129
18. Ghanadzadeh A, Zeini A, Kashef A (2007) J Mol Liq 133:61–67
19. Suresh SJ, Prabhu AL, Arora A (2007) J Chem Phys 126:134502–134506
20. Sakota K, Komoto Y, Nakagaki M, Ishikawa W, Sekiya H (2007) Chem Phys Lett 435:1–4
21. Jorgensen P, Forster JS, Hvelplund P, Nielsen SB, Tomita S (2001) J Chem Phys 115:5101–5106
22. Garberoglio G, Vallauri R (2001) J Chem Phys 115:395–401
23. Castellari M, Sartini E, Fabiani A, Arfelli G, Amati (2002) J Chromatogr A 973:221-227
24. Paul B, Chereyathmanjiyil A, Masih I, Chapuis L, Benoît A (1998) FEMS Microbiol Lett 165:65–70
25. Montsko G, Nikfardjam MSP, Szabo Z, Boddi K, Lorand T, Ohmacht R, Marka L (2007) J Photochem Photobiol A Chem doi:10.1016/j.jphotochem.2007.11.011
26. Canuto S, Coutinho K (2000) Int J Quantum Chem 77:192–198
27. Rocha WR, Martins VM, Coutinho K, Canuto S (2002) Theor Chem Acc 108:31–37
28. Coutinho K, Canuto S (2003) J Mol Struc (Theochem) 632:235–246
29. Georg HC, Coutinho K, Canuto S (2005) J Chem Phys 123: 124307–124308
30. Allen MP, Tildesley DJ (1987) Computer simulation of liquids. Clarendon Press, Oxford
31. Wilhoit RC, Zwolinski BJ (1973) J Phys Chem Ref Data (Suppl) 2:427–438
32. Jorgensen WL (1986) J Phys Chem 90:1276–1284
33. Jorgensen WL, Madura JD, Swenson CJ (1986) J Phys Chem 90:1276–1284
34. Jorgensen WL, Maxwell DS, Tirado-Rives J (1996) J Am Chem Soc Ref Data (Suppl) 118:11225–11236
35. Breneman CM, Wiberg KB (1990) J Comput Chem 1:361–373
36. Coutinho K, Saavedra N, Serrano A, Canuto S (2001) J Mol Struc (Theochem) 539:171–179
37. Ridley J, Zerner MC (1973) Theor Chim Acta 32:111–134
38. Zerner MC (1999) ZINDO: a semi-empirical program package, University of Florida, Gainesville 32611
39. Canuto S, Coutinho K, Trzesniak D (2002) Adv Quantum Chem 41:161–183
40. Broo A, Pearl G, Zerner MC (1997) J Phys Chem A 101:2478–2488
41. Malaspina T, Fileti EE, Rivelino R (2007) J Phys Chem B 41: 11935–11939
42. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Gonzalez C, Challacombe M, Gill PMW, Johnson BG, Chen W, Wong MW, Andres JL, Head-Gordon M, Replogle ES, Pople JA (1998) Gaussian 98, revision A.11.2 Gaussian, Pittsburgh
43. Coutinho K, Canuto S (1997) DICE: a Monte Carlo program for molecular liquid simulation. University of São Paulo, São Paulo
44. Jeffrey GA, Saenger W (1991) Hydrogen bonding in biological structures. Springer, Berlin
45. Leopoldini M, Marino T, Russo N, Toscano M (2004) J Phys Chem A 108:4916–4922
46. Vishnyakov A, Laaksonen A, Widmalm G (2001) J Mol Graph Modell 19:338–342
47. Dixit S, Crain J, Poon WCK, Finney JL, Soper AK (2002) Nature 416:829–832
48. Tuckerman ME, Marx D, Parrinello M (2002) Nature 417:925–929
49. Lerbret A, Bordat P, Affouard F, Descamps M, Migliardo F (2005) J Phys Chem B 109:11046–11057
50. Saiz L, Padró JA, Guàrdia E (1997) J Phys Chem B 101:78–86
51. Ramalho TC, Cunha EFF, Alencastro RB (2004) J Phys Condens Matter 16:6159–6170
52. Swiatla-Wojcik D (2007) Chem Phys 342:260–266
53. Georg HC, Coutinho K, Canuto S (2007) J Chem Phys 126: 034507–034508
54. Capote R, Mainegra E, Ventura A (1998) J Phys G Nucl Part Phys 24:1113–1123
55. Ludwig V, Coutinho K, Canuto S (2004) Phys Rev B 70:214110–214114
56. Cramer CJ (2004) Essentials of computational chemistry: theories and models. Wiley, New York
57. Miertus S, Tomasi J (1982) Chem Phys 65:239–252
58. Miertus S, Scrocco E, Tomasi J (1981) Chem Phys 55:117–129
59. Cossi M, Barone V, Cammi R, Tomasi J (1996) Chem Phys Lett 255:327–335
60. Autschbach J, Le Guennic B (2003) J Am Chem Soc 125:13585–13593
61. Wang LY, Chen QW, Zhai GH, Wen ZY, Zhang ZX (2006) J Mol Struc (Theochem) 778:15–20