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Solvent Effects on trans/gauche Conformational Equilibria of Substituted Chloroethanes: a Polarizable Continuum Model Study

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Conformational equilibria of 1,2-dichloroethane, 1-chloro-2-fluoroethane, and β-chloropropionitrile have been investigated in various solvents by using the polarizable continuum model (PCM). Two approaches for the evaluation of trans/gauche free energy differences have been compared: (a) the use, together with experimental intensities, of calculated infrared absorption coefficients and Raman scattering cross sections proper for each solvent; (b) the use of ab initio B3LYP/6-311+G** energy calculations in solution. The agreement between the two approaches is good. The importance of using absorption coefficients and Raman scattering factors proper for each solvent is discussed.

1. Introduction

The energy difference between rotational isomers is usually small (less than 3 kcal/mol), and the solvation energy of polar solutes in polar solvents being of the same order, the change in the medium may considerably affect the rotational equilibrium. Some examples are known in which the most stable rotamer in the gas phase is not the most stable conformer in solution and the equilibrium between conformations strongly changes in passing from nonpolar to polar solvents.[1,2]

Experimental estimates of conformational equilibria can be obtained with a variety of procedures, among which those based on spectroscopic measurements play an important role. Often, and we shall consider in this paper a specific case, experimental data must be elaborated, with the introduction of some approximations and of elements drawn from the theory, to get information about the equilibrium. Theoretical estimates can be derived directly from the calculation of energetic properties of the pertinent conformers computed at the proper geometry. Theory also plays an ancillary role in justifying approximations used in the elaboration of experimental data and in providing the necessary supplementary elements.

The interplay between experiments and theory has been recognized for a long time with regard to equilibria in the gas phase but also holds for equilibria in solution. In this case, however, things are more complex, and the potentialities of the theoretical approach have not been fully exploited yet. Here, we will use the same theoretical solvation model both to elaborate spectroscopic experimental data and to directly obtain information about the energetics of the equilibrium. In addition, by relying on such calculations, we can critically evaluate the extent of approximations widely used in the elaboration of experimental data. In particular, in this paper, we will study solvent effects on trans (T)/gauche (G) conformational equilibria of 1,2-dichloroethane (DCE), 1-chloro-2-fluoroethane (CFE) and β-chloropropionitrile (CPN) (see Figure 1) by collecting infrared (IR) and Raman experimental data from the literature and by exploiting the recently developed methodologies to treat infrared[3−5] and Raman[6,7] spectra in solution within the polarizable continuum model (PCM).[8,9] We will show calculated data, and we will compare our results with previous studies on the same topic; in addition, we will compare findings about conformational equilibria obtained by means of spectroscopic measurements with what can be found by simply calculating free energy differences through ab initio calculations in solution.

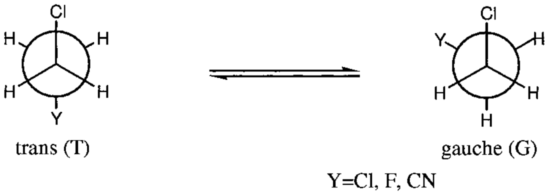

Figure 1. The trans/gauche equilibria studied in this work.

Various techniques have been used to get information about rotational equilibria under study and in particular on solvent effects on them: NMR,[10] IR,[11−20] Raman[21,22] and photoelectron[23] spectroscopies, and electron diffraction.[24] Computational methods, such as ab initio calculations[17,25−27] and numerical simulations,[28] have also been used.

Among the molecules here studied, the one used in the largest number of studies is DCE. The experimental and theoretical literature on DCE has been reviewed in a recent paper by Wiberg et al.[17] Experimental gas-phase studies on DCE agree in finding the trans rotamer to be more stable than the gauche one: the value found for $\Delta H°$ is around 1.1 kcal/mol. Photoelectron spectroscopy led to 1.0 ± 0.2 kcal/mol,[23] while electron diffraction to 1.05 ± 0.10 kcal/mol.[24a] Studies on the temperature dependence of IR band intensities led to the following estimates of $\Delta H°$ in the gas phase: 1.10 ± 0.05,[11] 1.03 ± 0.10,[12] 1.14,[13] 1.15 ± 0.15,[14] 1.09 ± 0.06,[15] and 1.17 ± 0.04 kcal/mol.[19] The same technique has been applied by Stolov and Ramizov to evaluate $\Delta H°$ of the T/G equilibrium of DCE in 19 solvents by considering the $\Delta H°$ itself to depend on the temperature.[18]

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Solvent effects on the conformational equilibrium of DCE have been also investigated by combining IR intensity measures and theoretical in vacuo energy calculations by Wiberg et al.[17] Raman spectroscopy has been used to elucidate solvent effects on the equilibrium. By assuming that the ratio between scattering cross sections of the trans and gauche conformers is independent of the solvent and the temperature, Kato et al.[21] reported $\Delta G°$ and $\Delta H°$ in various solvents. Meléndez-Pagán et al.[22] studied the effects of pressure and temperature on the T/G equilibrium of DCE in diethyl ether by using Raman spectroscopy.

Several ab initio studies on the conformational equilibrium of DCE in the gas phase are present in the literature.[17,25−30] Tanaka et al.[25] investigated the T/G equilibrium of DCE in the gas phase by using configuration interaction methods: the energy of the T conformer was found to be 1.48 kcal/mol lower than the energy of the G one. Conformational equilibria of several 1,2-dihaloethanes have been studied by Dixon et al.[30] by exploiting semiempirical, ab initio (SCF and MP2), and local density functional methods. The ab initio and density functional methods are in agreement with each other and with experimental data in finding the trans conformer to be the more stable conformer in the gas phase for DCE. Semiempirical results are qualitatively wrong.

SCF and correlated MP3 and MP4 methodologies have been used by Wiberg and Murcko to study rotational barriers of dihaloethanes.[29] The trans/gauche energy difference for DCE in the gas phase was predicted to be 1.39 kcal/mol (with the inclusion of zero-point and thermal corrections), in good agreement with experiments. A more recent study of the same group gave 1.20 kcal/mol for the rotational barrier at the G2/MP2 level.[17] The same paper also concerned the calculation of free energy differences in solution by exploiting the self-consistent isodensity polarizable continuum model (SCIPCM)[31] at the B3LYP/6-311+G** level.

The generalized Born (GB) solvation model has been recently applied to the study of the T/G equilibrium of DCE by Scarsi et al.[32] A trans/gauche $\Delta\Delta G° = 1.08$ kcal/mol in going from gas to pure liquid phase was predicted. Christiansen and Mikkelsen have reported theoretical calculations on the conformational equilibrium of DCE by using coupled-cluster solvent reaction field (CCSCRF) in various solvents at the CCSD/cc-pVTZ level.[27] Simulations have also been used to study the conformational equilibrium of DCE. A Monte Carlo study of dichloroethane in carbon tetrachloride, performed by Vilaseca,[28] put in evidence the importance of considering solute−solvent polarization effects to correctly predict conformational changes.

To the best of our knowledge, less studied are conformational equilibria of CFE and CPN. Two studies based on the vibrational spectrum of CFE in the gas phase found the trans conformer to be the more stable and the energy difference ($\Delta H°$) to be 0.82 ± 0.08[16] and 0.36 ± 0.02[19] kcal/mol. Ab initio calculations at the G2/MP2 level by Wiberg et al.[17] agreed with this description and found $\Delta G° = 0.55$ kcal/mol in the gas phase. The application of the SCIPCM method at the B3LYP/6-311+G** showed an increase in the weight of the gauche conformation in going from nonpolar to polar solvents.

2. Methodology

IR and Raman spectroscopies are used to study rotational equilibria of substituted ethanes both in vacuo and in solution; the usefulness of such techniques is due to the fact that the spectra of such compounds are the superposition of the corresponding distinct spectra of the rotational isomers.[1,17,21,22,33] IR intensities and Raman activities are functions of the number of molecules in the cell and, respectively, the absorption coefficient, ϵ, or the scattering cross section, σ, which are molecular properties.

The use of IR and Raman spectroscopies to evaluate the T/G free energy difference for the equilibria under study relies on the following relation:

$$\Delta G^{\circ}_{\mathrm{T}\to\mathrm{G}} = RT \ln \frac{2C_{\mathrm{T}}}{C_{\mathrm{G}}} = RT \ln \frac{2\tau_{\mathrm{G}}A_{\mathrm{T}}}{\tau_{\mathrm{T}}A_{\mathrm{G}}} \qquad (1)$$

where C is the molar concentration, A is the IR absorbance or the Raman activity, and τ is the absorption coefficient, ϵ, in the case of IR spectroscopy or the scattering cross section, σ, in the case of Raman spectroscopy. The factor 2 accounts for the statistical weight of the G conformer.

From the experimental point of view, it is relatively easy to obtain the ratio $A_{\mathrm{T}}/A_{\mathrm{G}}$, but it is in principle impossible to experimentally determine $\Delta G^{\circ}_{\mathrm{T}\to\mathrm{G}}$ from eq 1 because the $\tau_{\mathrm{G}}/\tau_{\mathrm{T}}$ ratio is unknown. However, another thermodynamic quantity related to the conformational equilibrium, $\Delta H^{\circ}_{\mathrm{T}\to\mathrm{G}}$, can be experimentally determined without estimating the $\tau_{\mathrm{G}}/\tau_{\mathrm{T}}$ ratio but with simply assuming that $\tau_{\mathrm{G}}/\tau_{\mathrm{T}}$ is temperature-independent.[1,18,21]

The most common procedure to evaluate the $\tau_{\mathrm{G}}/\tau_{\mathrm{T}}$ ratio relies on theoretical calculations. Such a strategy has been applied by Wiberg et al.[17] to the evaluation of solvent effects on rotational equilibria of DCE and CFE, by Kato et al.[21] to the study by means of Raman spectroscopy of the solvent dependence of the DCE conformational equilibrium, and by Goutev et al.[33] to the investigation of the conformational equilibria of 1,2-dimethoxyethane in the liquid phase and aqueous solution.

In particular, Wiberg et al.[17] evaluated a theoretical $\Delta G^{\circ}_{\mathrm{T}\to\mathrm{G}}$ in vacuo for DCE and CFE at the G2/MP2 level and used an experimental value of the IR absorbance ratio, $A_{\mathrm{T}}/A_{\mathrm{G}}$, in the gas phase to obtain, through eq 1, the $\epsilon_{\mathrm{G}}/\epsilon_{\mathrm{T}}$ ratio. Kato et al.[21] used the gas-phase $\Delta G^{\circ}_{\mathrm{T}\to\mathrm{G}}$ obtained by Wiberg et al.[17] to estimate the Raman scattering cross section ratio, $\sigma_{\mathrm{G}}/\sigma_{\mathrm{T}}$, from the gas-phase Raman spectrum at 24 °C.[34] Goutev et al.[33] directly calculated the ratio $\sigma_{\mathrm{G}}/\sigma_{\mathrm{T}}$ in vacuo for 1,2-dimethoxyethane at the MPW1PW91/6-311+G** level of density functional theory.

All of these studies assume that the $\tau_{\mathrm{G}}/\tau_{\mathrm{T}}$ ratio remains constant in going from the gas phase to solution and is independent of the choice of the solvent. The limitations of this procedure are evident because in principle the $\tau_{\mathrm{G}}/\tau_{\mathrm{T}}$ ratio varies in going from the gas phase to the solution and in changing the nature of the solvent. In this paper, these limitations will be examined and we will theoretically evaluate the proper ratio for each solvent. In the next sections, we will combine theoretically calculated $\tau_{\mathrm{G}}/\tau_{\mathrm{T}}$ ratios and experimental absorbance or Raman activity data to obtain $\Delta G^{\circ}_{\mathrm{T}\to\mathrm{G}}$ values (eq 1) in vacuo and in various solvents.

To calculate the $\tau_{\mathrm{G}}/\tau_{\mathrm{T}}$ ratio for systems in solution, we will exploit the PCM method in its recently revised version known as integral equation formalism (IEF−PCM).[35] In PCM, the solvated system is partitioned into a target molecule (the solute) and the surrounding solvent, which is modeled as a continuum, infinite, homogeneous, and generally isotropic medium, characterized by its dielectric properties. The solute is assumed to be inside a molecular-shaped cavity, and the electrostatic solute−solvent interactions are calculated by introducing an apparent charge distribution spread on the cavity surface. In computational practice, this charge distribution is made discreet

TABLE 1: Calculated C−Cl Stretching Frequencies (cm^{-1}) of 1,2-Dichloroethane in Vacuo and in Various Solvents and Solvent Static (ϵ_{stat}) and Optical (ϵ_{opt}) Dielectric Constants[a]

			trans		gauche			
			calc	exp[b]	calc		exp[b]	
	ϵ_{stat}	ϵ_{opt}	asym	asym	sym	asym	sym	asym
vacuum	1	1	703.62	727	650.28	674.63	669	694
n-hexane	1.88	1.88	695.44		642.82	665.78	662.5	686.5
cyclohexane	2.023	2.028	694.21	716	642.32	665.06	662	686
pentene	2.1	1.881	691.95	715	641.69	664.48	661	685.5
1,4-dioxane	2.2	2.006	691.53	707	641.50	664.21	653.5	673.5
carbon tetrachloride	2.228	2.129	691.40		641.40	664.01	660.5	685
tetrachloroethylene	2.3	2.226	691.06	714	641.03	663.71	660.5	685
p-xylene	2.3	2.237	691.06	710.5	641.06	663.74	657	680
carbon disulfide	2.64	2.64	689.52	714	640.92	661.21	659	683.5
di-*n*-butyl ether	3.08	1.951	687.84		639.21	659.25		
diisopropyl ether	4.1	1.871	687.79		635.13	656.33		
diethyl ether	4.335	1.829	687.65	711	635.10	656.19	657.5	680
ethyl acetate	6.0	1.883	686.04	709	633.03	653.79	654.5	673.5
THF	7.58	1.971	684.90		631.86	652.29		
mesityl oxide	15.0	2.085	683.12		629.79	649.93		
acetone	20.7	1.841	683.44	708	629.10	648.95	653	672
acetonitrile	36.64	1.806	683.01	708	628.59	648.35	653	672

[a] Asym = antisymmetric C−Cl stretch; sym = symmetric C−Cl stretch. [b] Reference 40.

by point charges each associated with a small portion (tessera) of the cavity surface and defined through a set of linear equations.

Within the double harmonic approximation, the calculation of IR and Raman spectra (frequencies and intensities/activities) requires the evaluation of some molecular property derivatives. In particular, vibrational frequencies can be obtained from the diagonalization of the Hessian matrix (the matrix of the second derivatives of the energy with respect to the nuclear coordinates), IR intensities are related to solute dipole derivatives with respect to nuclear coordinates, and Raman activities can be obtained as derivatives of the dynamic molecular polarizability with respect to nuclear coordinates. Such derivatives have to be evaluated at stationary points of the potential energy surface and then a methodology to evaluate gradients is needed.

The formulation within PCM of analytic gradients and free energy second derivatives with respect to nuclear coordinates is reported in the literature.[3,36] The basic methodology assumes a complete solvent response to molecular vibrations, but this scheme has recently been generalized to treat nonequilibrium solvent response to molecular vibrations.[5] The evaluation of infrared intensities and Raman activities has already been treated within PCM, both in the equilibrium[4,6] and nonequilibrium[5,7] frameworks by including local field effects.

3. Results and Discussion

3.1. Computational Details. Infrared and Raman calculations were performed by using density functional theory (DFT) with the B3LYP hybrid functional and the 6-31+G** basis set. Such a combination of functional and basis set has already been used in the same context by Wiberg et al.[17] Extensive analyses of the effect of the choice of the functional and of the basis set for gas-phase IR and Raman calculations are available in the literature.[37] The calculation of infrared frequencies and intensities in solution was performed in the complete nonequilibrium framework.[5] Raman intensities were calculated both in vacuo and in solution by assuming the wavelength of the incident radiation to be 514.5 nm; solvent electronic nonequilibrium[7] is accounted for in the calculations in solution. Vibrational nonequilibrium effects on Raman intensities were proved to be small;[7] for this reason, they have not been considered.

Following Wiberg et al.,[17] the larger 6-311+G** set was used in the PCM energy calculations (geometries optimized at the same level). Zero-point and thermal corrections were obtained with standard methodologies[38] at the B3LYP/6-31+G** level.

A development version of the Gaussian program[39] was used for the calculations both in vacuo and in solution. The IEF version[3,35] of PCM was exploited for all of the calculations in solution. The geometries of all of the systems were optimized in each phase. The cavity used was of molecular shape and was built by interlocking spheres. The radii of the spheres were obtained by multiplying by the $\alpha = 1.2$ cavity size factor the following values: 1.7 Å for carbon, 1.2 Å for hydrogen, 1.7 Å for fluorine, 1.75 Å for chlorine, and 1.6 Å for nitrogen.

3.2. Solvent Effects on $\Delta G^\circ_{T \rightarrow G}$ from Infrared and Raman Spectra. *3.2.1. 1,2-Dichloroethane.* We report in Table 1 calculated harmonic frequencies for the C−Cl stretching mode of DCE both in vacuo and in selected solvents. Experimental values taken from Oi and Coetzee[40] are also reported. For the gauche conformer, both the symmetric and antisymmetric stretches are considered, while for the trans isomer, we focus on the antisymmetric mode only because the symmetric stretch is IR inactive. All of the calculated frequencies that we report are not scaled.

The agreement between calculated and experimental values is satisfactory; they differ from each other by an almost constant factor (around 20 cm^{-1}). As we have said above, all previous studies on conformational T/G equilibria assume the ϵ_T/ϵ_G ratio to be independent from the choice of the solvent and to remain constant in going from the gas phase to solution. In particular, Wiberg et al.[17] theoretically estimated the behavior of such a ratio in passing from vacuum to acetone solution within the SCIPCM: a small change (about 10%) in the values was found (3.4 in vacuo and 3.1 in acetone for the T(antisym)/G(sym) ratio).

In Table 2, we show calculated IR intensities for the C−Cl stretching mode and the ϵ_T/ϵ_G ratio in vacuo and in each solvent. The reported ϵ_T/ϵ_G values range from 5.10 to 3.68 for the symmetric stretch of the G conformer and from 3.40 to 2.98 for the antisymmetric one. Such changes correspond to a variation in the ΔG° values of 0.20 and 0.08 kcal/mol for the symmetric and antisymmetric stretches, respectively. As a

TABLE 2: Calculated Absorption Coefficients, ϵ (km/mol), for the C−Cl Stretching of 1,2-dichloroethane in Vacuo and in Various Solvents[a]

	trans	gauche		ϵ_T/ϵ_G	
	asym	sym	asym	asym/sym	asym/asym
vacuum	112.12	21.97	33.00	5.10	3.40
n-hexane	123.59	28.17	38.35	4.39	3.22
cyclohexane	123.76	28.51	38.69	4.34	3.20
pentene	127.69	29.40	39.79	4.34	3.21
1,4-dioxane	126.82	29.43	39.66	4.31	3.20
carbon tetrachloride	125.45	29.29	39.40	4.28	3.18
tetrachloroethylene	124.26	29.28	39.01	4.24	3.18
p-xylene	124.73	29.35	39.15	4.25	3.19
carbon disulfide	122.77	30.09	37.79	4.08	3.25
di-*n*-butyl ether	128.91	31.97	40.65	4.03	3.17
diisopropyl ether	130.81	32.66	42.21	4.00	3.10
diethyl ether	131.15	33.06	41.82	3.97	3.14
ethyl acetate	132.66	34.13	43.06	3.89	3.08
THF	133.42	34.91	43.65	3.82	3.06
mesityl oxide	134.78	36.60	44.25	3.68	3.05
acetone	135.87	36.31	45.48	3.74	2.99
acetonitrile	136.59	36.71	45.80	3.72	2.98

[a] Asym = antisymmetric C−Cl stretch; sym = symmetric C−Cl stretch.

TABLE 3: Calculated Frequencies (cm^{-1}) of Additional Modes of Dichloroethane in Vacuo and in Various Solvents of Interest in This Study

	trans	gauche
vacuum	1268.20	1327.46
n-hexane	1275.92	1319.47
carbon tetrachloride	1276.41	1318.11
	1495.79	1468.27
carbon disulfide	1275.72	1318.14
acetonitrile	1266.91	1313.76

TABLE 4: Calculated Absorption Coefficients, ϵ (km/mol), of Additional Modes of 1,2-Dichloroethane in Vacuo and in Various Solvents of Interest in This Study

	trans	gauche	ϵ_T/ϵ_G
vacuum	44.01	50.05	0.879
n-hexane	37.35	41.92	0.891
carbon tetrachloride	36.24	40.64	0.892
	5.88	16.01	0.367
carbon disulfide	33.63	36.81	0.914
acetonitrile	36.16	42.82	0.844

TABLE 5: $\Delta G°$ and $\Delta\Delta G° = \Delta G°_{vac} - \Delta G°_{sol}$ Values (kcal/mol) for the trans/gauche Equilibrium of 1,2-Dichloroethane from Experimental IR Intensity Ratios

	$\Delta G°$		$\Delta\Delta G°$	
	this work	others	this work	others
vacuum	1.27 ± 0.04[a]	1.20[g]		
	1.26 ± 0.09[b]			
n-hexane	1.07 ± 0.08[b]		0.20 ± 0.12	
cyclohexane	0.87 ± 0.03[a]	0.70[h]	0.40 ± 0.07	0.50[h]
	1.08−0.97[c]	0.91[g]	0.19−0.30	0.29[g]
pentene	1.03−1.00[c]		0.24−0.27	
1,4-dioxane	0.41−0.54[c]		0.86−0.73	
carbon tetrachloride	0.99 ± 0.04[b]		0.28 ± 0.08	
	1.00 ± 0.03[d]		0.27 ± 0.07	
p-xylene	0.55−0.77[c]	0.70[g]	0.72−0.50	0.50[g]
tetrachloroethylene	0.91−0.95[c]	0.89[g]	0.36−0.32	0.31[g]
carbon disulfide	0.78 ± 0.06[b]	0.83[g]	0.49 ± 0.10	0.37[g]
	0.92−0.88[c]		0.35−0.39	
	0.87 ± 0.05[e]		0.40 ± 0.09	
di-*n*-butyl ether	0.73 ± 0.02[a]	0.51[h]	0.54 ± 0.06	0.69[h]
diisopropyl ether	0.75[f]		0.52	
diethyl ether	0.59−0.77[c]	0.69[g]	0.68−0.50	0.51[g]
ethyl acetate	0.37−0.50[c]	0.42[g]	0.90−0.77	0.78[g]
THF	0.36 ± 0.04[a]	0.11[h]	0.91 ± 0.08	1.09[h]
mesityl oxide	0.56[f]	0.47[g]	0.71	0.73[g]
acetone	0.12 ± 0.03[a]	−0.14[h]	1.15 ± 0.07	1.34[h]
	0.10−0.28[c]	0.18[g]	1.17−0.99	1.02[g]
	0.08 ± 0.05[e]		1.19 ± 0.09	
acetonitrile	0.04 ± 0.03[a]	−0.22[h]	1.23 ± 0.07	1.42[h]
	0.07 ± 0.08[b]	0.15[h]	1.20 ± 0.12	1.05[h]
	0.13−0.26[c]		1.14−1.01	
	0.05 ± 0.09[e]		1.22 ± 0.13	

[a] Experimental data for the C−Cl stretching band were taken from ref 17. [b] Experimental data at 296 K for the band around 1200 cm^{-1} were taken from ref 18. [c] Experimental data for the C−Cl stretching band were taken from ref 40. [d] Experimental data at 296 K for the band around 1400 cm^{-1} were taken from ref 18. [e] Experimental data at 296 K for the C−Cl stretching band were taken from ref 18. [f] Experimental data for the C−Cl stretching band were taken from ref 41. [g] Experimental values were taken from ref 1, chapter 13. [h] Experimental values were taken from ref 17.

consequence, while in the case of the T(antisym)/G(antisym) ratio the use of the value calculated in vacuo leads to errors within the experimental uncertainty, larger discrepancies are obtained for the T(antisym)/G(sym). In particular, 0.20 kcal/mol is comparable to the $\Delta G°$ values obtained in polar solvents (see below). In our opinion, a possible reason of the smaller dependence of ϵ_T/ϵ_G on the medium in the case of T(antisym)/G(antisym) is the similarity in the nature of the two modes.

For the sake of completeness, we report in Tables 3 and 4 calculated frequencies and intensities (as well as ϵ_T/ϵ_G ratios) of some other modes that have been used in the literature to obtain experimental energy differences in vacuo and in various solvents. The range of variation of the reported ϵ_T/ϵ_G is small (0.914−0.844) and corresponds to a change in $\Delta G°$ of 0.05 kcal/mol.

In Table 5, the values of $\Delta G°$ obtained through eq 1 from the experimental A_T/A_G[17,18,40,41] and the calculated ϵ_T/ϵ_G (Tables 2 and 4) are collected. As it can be seen, all of the $\Delta G°$ values are positive; this means that T is the most stable conformer for the solvents here considered. This picture agrees with the findings of Abraham and Bretschneider (Chapter 13 in ref 1), whereas the results of Wiberg et al.[17] show a preference of G in acetone and acetonitrile (see Table 5). It is worthwhile to note that the values of $\Delta G°$ obtained from different bands (in a given medium) differ from the mean value by ±0.1 kcal/mol, which can be assumed as the experimental uncertainty.

To focus our attention on the effects of the medium on the T/G equilibria, we report in Table 5 the differences in $\Delta G°$ between in vacuo and in solution, $\Delta\Delta G° = \Delta G°_{vac} - \Delta G°_{sol}$. Such quantities are less sensitive to the level of calculation than the absolute $\Delta G°$. The analysis of the obtained values shows the dependence of the conformational equilibrium on the solvent. In particular, polar solvents affect $\Delta G°$ by as much as 1.0−1.2 kcal/mol. Our results are generally between the ones of ref 1 and ref 17.

As we have already said, eq 1 can be used to obtain $\Delta G°_{T\rightarrow G}$ values from Raman activity data. In ref 21, the gas-phase $\Delta G°_{T\rightarrow G}$ obtained by Wiberg et al.[17] has been used to estimate the Raman scattering cross section ratio, σ_T/σ_G, from the gas-phase Raman spectrum at 24 °C.[34] Because neither the σ_T/σ_G nor the A_G/A_T ratio can easily be extracted from data reported in ref 21, we will limit ourselves to estimate $(\Delta\Delta G°)_{Raman} = (\Delta G°_{vac})_{Raman} - (\Delta G°_{sol})_{Raman}$, which can be obtained as the following:

$$(\Delta\Delta G°)_{Raman} = \Delta\Delta G°_{cnst} - RT\ln\left(\frac{\sigma_{T,vac}}{\sigma_{G,vac}}\frac{\sigma_{G,sol}}{\sigma_{T,sol}}\right) \qquad (2)$$

TABLE 6: Calculated Raman Scattering Cross Sections, σ (Å^4/amu), for the C−Cl Stretching Band of 1,2-Dichloroethane[a]

	trans	gauche		σ_T/σ_G	
	sym	sym	asym	sym/sym	sym/asym
vacuum	82.15	20.22	12.19	4.06	6.74
n-hexane	165.88	45.78	26.77	3.62	6.20
cyclohexane	177.57	48.09	35.75	3.69	4.97
THF	190.99	67.64	44.94	2.82	4.25
acetonitrile	180.13	47.18	26.95	3.82	6.68
water	177.65	46.85	26.63	3.79	6.67

[a] Asym = antisymmetric C−Cl stretch; sym = symmetric C−Cl stretch.

TABLE 7: $(\Delta\Delta G°)_{\mathrm{Raman}}$ Values (kcal/mol) at 298 K for the trans/gauche Equilibrium of 1,2-Dichloroethane from Experimental Raman Activity Ratios

	$(\Delta\Delta G°)_{\mathrm{Raman}}$	
	this work	others[a]
n-hexane	0.24 ± 0.13	0.31 ± 0.13
cyclohexane	0.33 ± 0.13	0.38 ± 0.13
THF	0.81 ± 0.13	1.03 ± 0.13
acetonitrile	1.19 ± 0.13	1.23 ± 0.13
water	1.22 ± 0.13	1.26 ± 0.13

[a] Experimental values reported by Kato et al.[21]

where the quantity $\Delta\Delta G°_{\mathrm{cnst}}$

$$\Delta\Delta G°_{\mathrm{cnst}} = -RT\left(\ln \frac{I_{\mathrm{G,vac}}}{2I_{\mathrm{T,vac}}} - \ln \frac{I_{\mathrm{G,sol}}}{2I_{\mathrm{T,sol}}}\right) \qquad (3)$$

can be calculated from the $\Delta G°$ data reported by Kato et al.[21] The range of variation of the calculated σ_T/σ_G ratio (see Table 6) in passing from one medium to another is comparable to what we have found for ϵ_T/ϵ_G in the case of T(antisym)/G(sym) (compare Table 6 and Table 2).

In Table 7, we report $(\Delta\Delta G°)_{\mathrm{Raman}}$ values as obtained through eq 2 by using data of the T(sym)/G(sym) bands. In general, the overall differences between our results and data reported by Kato et al.[21] are similar to the ones found for IR calculations. The maximum difference is found for THF solution (around 0.2 kcal/mol); the agreement between $(\Delta\Delta G°)_{\mathrm{Raman}}$ and the corresponding IR data calculated with our method is good. Thus, the discrepancies between IR and Raman $\Delta\Delta G°$ values, which have been put in evidence by Kato et al.,[21] are reduced once the dependence of both ϵ_T/ϵ_G and σ_T/σ_G on the solvent is accounted for.

3.2.2. 1-Chloro-2-fluoroethane. In Table 8, calculated harmonic (nonscaled) frequencies for the C−Cl stretching mode of CFE both in vacuo and in selected solvents are shown, together with experimental values reported in the literature.[16,41] The agreement between calculated and experimental values is satisfactory, differing from each other by around 20 cm^{-1}, with the exception of values in dioxane.

The differences in the ϵ_T/ϵ_G ratio (Table 9) in passing from vacuum to solution and from one solvent to another are smaller than the ones previously noted for DCE but still noticeable. In this case, the assumption that ϵ_T/ϵ_G is independent of the medium is more justified than in the case of DCE and would lead to variations of about 0.08 kcal/mol in the $\Delta G°$ value.

The analysis of $\Delta G°$ data in Table 10 puts in evidence that, contrary to what was observed for DCE, the gauche conformer becomes the more stable species as the polarity of the medium increases. This different behavior does not depend on a greater stabilization of the CFE gauche conformer caused by the solvent but is mainly due to the smaller $\Delta G°$ value in vacuo. Such a consideration arises from the inspection of the $\Delta\Delta G°$ values reported in Table 10, which are similar to the ones found for DCE in the same solutions. Notice that our findings on $\Delta G°$ in vacuo are in agreement with previous studies on the same topic; in particular, it is known that the change in the nature of the halogen (from chlorine to fluorine) increases the relative stability of the gauche conformer.[42] The differences between our $\Delta G°$ results and data reported by other authors (see Table 10) are similar to what was obtained for DCE (see Table 5).

TABLE 8: Calculated C−Cl Stretching Frequencies (cm^{-1}) of 1-Chloro-2-fluoroethane and Solvent Static (ϵ_{stat}) and Optical (ϵ_{opt}) Dielectric Constants

			trans		gauche	
	ϵ_{stat}	ϵ_{opt}	calcd	exptl[a]	calcd	exptl[a]
vacuum	1	1	756.43	775/779[b]	665.64	685/688[b]
cyclohexane	2.023	2.028	748.48	766	655.33	677
dioxane	2.2	2.006	748.08	751	654.31	688
di-*n*-butyl ether	3.08	1.951	744.34		649.76	
diiodomethane	5.32	3.036	739.80		644.25	668
iodomethane	7.0	2.365	739.79	759	643.44	669
THF	7.58	1.971	740.36		643.69	
methyl isobutyl ketone	13.1	1.949	739.26		641.37	
methyl isopropyl ketone	15.0	1.927	739.09		640.98	
acetone	20.7	1.841	738.88	758	640.45	663

[a] Experimental values were taken from ref 41. [b] Experimental values were taken from ref 16.

TABLE 9: Calculated C−Cl Stretching Absorption Coefficients, ϵ (km/mol), of 1-Chloro-2-fluoroethane

	trans	gauche	ϵ_T/ϵ_G
vacuum	50.90	33.91	1.50
cyclohexane	56.80	40.46	1.40
dioxane	58.37	41.59	1.40
di-*n*-butyl ether	59.62	43.65	1.37
diiodomethane	58.87	44.56	1.32
iodomethane	61.20	46.21	1.32
THF	61.93	46.47	1.33
methyl isobutyl ketone	62.62	47.64	1.31
methyl isopropyl ketone	62.77	47.68	1.32
acetone	63.07	48.06	1.31

TABLE 10: $\Delta G°$ and $\Delta\Delta G° = \Delta G°_{\mathrm{vac}} - \Delta G°_{\mathrm{sol}}$ Values (kcal/mol) for the trans/gauche Equilibrium of 1-Chloro-2-fluoroethane from Experimental IR Intensity Ratios

	$\Delta G°$		$\Delta\Delta G°$	
	this work	others	this work	others
vacuum	0.61 ± 0.03[a]	0.55[b]		
		0.90[c]		
cyclohexane	0.19 ± 0.02[a]	0.09[b]	0.42 ± 0.05	0.46[b]
	0.11[d]	0.30[c]	0.50	0.60[c]
dioxane	0.12[d]		0.50	
di-*n*-butyl ether	−0.07 ± 0.02[a]	−0.18[b]	0.68 ± 0.05	0.73[b]
diiodomethane	−0.47[d]	−0.31[c]	1.08	1.21[c]
iodomethane	−0.33[d]	−0.17[c]	0.94	1.07[c]
THF	−0.43 ± 0.02[a]	−0.56[b]	1.04 ± 0.05	1.11[b]
methyl isobutyl ketone	−0.67[d]	−0.53[c]	1.28	1.43[c]
methyl isopropyl ketone	−0.68[d]	−0.53[c]	1.29	1.43[c]
acetone	−0.73 ± 0.02[a]	−0.87[b]	1.34 ± 0.05	1.42[b]
	−0.80[d]	−0.65[c]	1.41	1.55[c]

[a] Experimental data for the C−Cl stretching band were taken from ref 17. [b] Experimental values obtained in ref 17 are reported. [c] Experimental values were taken from ref 1. [d] Experimental data for the C−Cl band were taken from ref 41.

TABLE 11: Calculated C−Cl Stretching Frequencies (cm^{-1}) of β-Chloropropionitrile and Solvent Static (ϵ_{stat}) and Optical (ϵ_{opt}) Dielectric Constants

			trans		gauche	
	ϵ_{stat}	ϵ_{opt}	calcd	exptl[a]	calcd	exptl[a]
vacuum	1	1	756.28	771.5	668.27	686
cyclohexane	2.023	2.028	749.45	767	659.90	680
dioxane	2.2	2.006	748.67	754	659.81	670
diiodomethane	5.32	3.036	741.67	762	648.90	673
iodomethane	7.0	2.365	741.89	758	647.85	671
methyl isobutyl ketone	13.1	1.949	741.39	758	645.54	669
methyl isopropyl ketone	15.0	1.927	741.25		645.65	
diethyl ketone	17.0	1.939	741.05		645.05	

[a] Experimental value was taken from ref 41.

TABLE 12: Calculated C−Cl Stretching Absorption Coefficients, ϵ (km/mol), of β-Chloropropionitrile

	trans	gauche	ϵ_T/ϵ_G
vacuum	54.36	25.93	2.10
cyclohexane	59.47	32.09	1.85
dioxane	60.90	32.13	1.89
diiodomethane	61.21	35.43	1.73
iodomethane	63.90	36.63	1.74
methyl isobutyl ketone	65.82	37.69	1.75
methyl isopropyl ketone	66.01	37.77	1.75
diethyl ketone	66.13	37.84	1.75

TABLE 13: ΔG° Values (kcal/mol) for the trans/gauche Equilibrium of β-Chloropropionitrile from Experimental IR Intensity Ratios Taken from Ref 41

	ΔG°
vacuum	
cyclohexane	0.28
dioxane	−0.20
diiodomethane	−0.31
iodomethane	−0.15
methyl isobutyl ketone	−0.54
methyl isopropyl ketone	−0.63
diethyl ketone	−0.63

TABLE 14: PCM-Calculated ΔE, ΔG°, and $\Delta\Delta G^\circ$ (kcal/mol) for the T/G Equilibrium of 1,2-Dichloroethane in Vacuo and in Various Solvents[a]

	PCM			others	
	ΔE	ΔG°	$\Delta\Delta G^\circ$	ΔE	$\Delta\Delta G^\circ$
vacuum	1.59	1.50		$1.56^b/1.35^c/1.45^d$	
n-hexane	1.18	0.95	0.55		
cyclohexane	1.14	0.91	0.59	$1.17^b/1.07^c/1.22^d$	$0.39^b/0.28^c$
pentene	1.10	0.82	0.68		
1,4-dioxane	1.08	0.82	0.68	1.19^d	
carbon tetrachloride	1.07	0.81	0.69		
tetrachloroethylene	1.05	0.79	0.71		
p-xylene	1.05	0.79	0.71		
carbon disulfide	0.97	1.03	0.47	1.15^d	
di-*n*-butyl ether	0.87	0.89	0.61	$0.97^b/0.92^c$	$0.59^b/0.43^c$
diisopropyl ether	0.72	0.83	0.67		
diethyl ether	0.70	0.61	0.89	1.03^d	
ethyl acetate	0.54	0.48	1.02	0.97^d	
THF	0.46	0.38	1.12		
mesityl oxide	0.27	0.19	1.31		
acetone	0.22	0.13	1.37	$0.47^b/0.58^c/0.85$	$1.09^b/0.77^c$
acetonitrile	0.15	0.06	1.44	0.83^d	
water	0.09	0.02	1.48	0.81^d	

[a] ΔG° and $\Delta\Delta G^\circ$ account for thermal and zero-point contributions ($T = 298$ K). Values were calculated at the B3LYP/6-311+G** level. [b] Values from ref 17 calculated with SCIPCM at the B3LYP/6-311+G** level (geometry optimized in vacuo) are reported. [c] Values from ref 17 calculated with SCIPCM at the MP2/6-311+G** level (geometry optimized in vacuo) are reported. [d] Values from ref 27 calculated with SCRF at the CCSD/cc-pVTZ level (geometry optimized MP2/cc-PVTZ in vacuo) are reported.

TABLE 15: PCM-Calculated ΔE, ΔG°, and $\Delta\Delta G^\circ$ (kcal/mol) for the T/G Equilibrium of 1-Chloro-2-fluoroethane in Vacuo and in Various Solvents[a]

	PCM			others	
	ΔE	ΔG°	$\Delta\Delta G^\circ$	ΔE	$\Delta\Delta G^\circ$
vacuum	0.45	0.38		$0.44^b/0.46^c$	
cyclohexane	−0.05	−0.12	0.50	$0.11^b/0.13^c$	$0.33^b/0.33^c$
dioxane	−0.11	−0.18	0.56		
di-*n*-butyl ether	−0.32	−0.38	0.76	$-0.21^b/-0.04^c$	$0.65^b/0.50^c$
diiodomethane	−0.61	−0.65	1.03		
iodomethane	−0.73	−0.76	1.14		
THF	−0.76	−0.79	1.17		
methyl isobutyl ketone	−0.91	−0.95	1.33		
methyl isopropyl ketone	−0.95	−0.98	1.36		
acetone	−1.01	−1.04	1.42	$-0.75^b/-0.46^c$	$1.19^b/0.92^c$

[a] ΔG° and $\Delta\Delta G^\circ$ account for thermal and zero-point contributions ($T = 298$ K). Values were calculated at the B3LYP/6-311+G** level. [b] Values from ref 17 calculated with SCIPCM at the B3LYP/6-311+G** (geometry optimized in vacuo) are reported. [c] Values from ref 17 calculated with SCIPCM at the MP2/6-311+G** (geometry optimized in vacuo) are reported.

3.2.3. β-Chloropropionitrile. In Table 11, calculated and experimental[41] frequencies for the C−Cl stretching mode are reported. The agreement between calculated (nonscaled) and experimental values is similar to the one already noticed for the two other molecules under study.

The range of variation of the ϵ_T/ϵ_G ratio (Table 12), 2.10−1.73, is between those for DCE and CFE; 0.11 kcal/mol of difference in the ΔG° value in diiodomethane would arise if the actual ϵ_T/ϵ_G value was approximated with the in vacuo one. The gauche form is the most stable one for a larger range of solvent polarity compared to both DCE and CFE (see Table 13). The unavailability of an experimental absorption intensity ratio for CPN in the gas phase does not allow the calculation of the corresponding ΔG° value in vacuo and therefore does not permit the calculation of any of the $\Delta\Delta G^\circ$ values.

3.3. Solvent Effects on $\Delta G^\circ_{T\rightarrow G}$ from PCM Energy Calculations. In this section, we will present PCM calculated ΔG° and $\Delta\Delta G^\circ$ values. All of the values are obtained by including zero-point and thermal contributions (calculated following the same scheme as in vacuo but with quantities evaluated in solution) and by considering only the pure electrostatic solute−solvent interaction. Such a choice is in our opinion justified because the correlation between experimental and calculated frequencies, obtained by exploiting the pure electrostatic model, is good (see the previous section). Moreover, previous studies[17,41] on solvent effects on the T/G equilibrium of DCE have shown that observed stretching frequencies, absorbance ratios, and ΔG° correlate well with the simple Onsager function, $(\epsilon_{stat} - 1)/(2\epsilon_{stat} + 1)$. In addition, because we are considering differences between two conformers of the same compound, it is reasonable that the differential nonelectrostatic contributions (dispersion, repulsion, and cavitation)[9] to $\Delta G^\circ_{T\rightarrow G}$ are small (at least as small as the uncertainty given by the available methodologies used to estimate them). Numerical tests that we have performed on DCE in various solvents have shown that the amount of the cavitation[43] contribution to ΔG° is less than 0.05 kcal/mol and that of the dispersion + repulsion[44] is less than 0.15 kcal/mol.

In Tables 14, 15, and 16, we report calculated PCM ΔG° and $\Delta\Delta G^\circ$ values for the trans/gauche equilibria of the three

TABLE 16: PCM-Calculated ΔE, $\Delta G°$, and $\Delta\Delta G°$ (kcal/mol) for the T/G Equilibrium of β-Chloropropionitrile in Vacuo and in Various Solvents[a]

	PCM		
	ΔE	$\Delta G°$	$\Delta\Delta G°$
vacuum	0.95	0.94	
cyclohexane	0.55	0.49	0.45
dioxane	0.50	0.46	0.48
diiodomethane	0.07	0.30	0.64
iodomethane	−0.03	−0.06	1.00
methyl isobutyl ketone	−0.20	−0.33	1.27
methyl isopropyl ketone	−0.23	−0.23	1.17
diethyl ketone	−0.25	−0.45	1.39

[a] $\Delta G°$ and $\Delta\Delta G°$ account for thermal and zero-point contributions ($T = 298$ K). Values were calculated at the B3LYP/6-311+G** level.

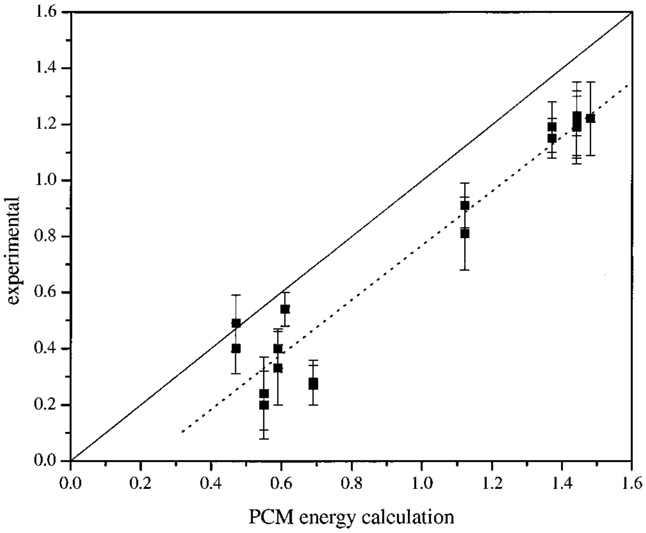

Figure 2. Comparison between $\Delta\Delta G°_{T\to G}$ values as obtained by PCM free energy calculations (PCM energy calculation) and by using experimental intensity ratios combined with PCM-calculated τ_G/τ_T values (experimental) for 1,2-dichloroethane. The dotted line is obtained through a linear fit: slope 0.97, linear regression coefficient $R = 0.9635$.

molecules under study. To evaluate the agreement between PCM calculated values and experimental data reported in the previous section, we show such data as plots in Figures 2, 3, and 4. We have not included all of the available experimental data in the plots because in our opinion, as already remarked by Wiberg et al.,[17] some of them (those extracted from the oldest works, refs 40 and 41) are less reliable. The use of the $\Delta\Delta G°$ values instead of $\Delta G°$ is, as previously stated, a direct measure of solvent effects.

In Figure 2, PCM calculated vs experimental $\Delta\Delta G°$ values for DCE are shown. Both IR and Raman $\Delta\Delta G°$ are used as experimental data. The linear fit of the data yields an almost unitary slope (0.97) but a y-intercept of −0.20 kcal/mol. Thus, the calculated PCM data give the correct trend but overestimate the experimental values by a constant value (0.20 kcal/mol). This shift is compatible with the combination of the experimental and theoretical uncertainties. The latter is due to the neglect in the calculations of nonelectrostatic interaction terms and to some arbitrariness in the choice of the molecular cavity. A numerical test performed by varying the cavity-size factor α in the range of 1.1−1.3 led to an uncertainty in PCM-calculated $\Delta\Delta G°$ of ±0.15 kcal/mol.

We note that the largest deviations from the fitting line are shown by the values in the less polar solvents; this is not surprising, because we are using a purely electrostatic model.

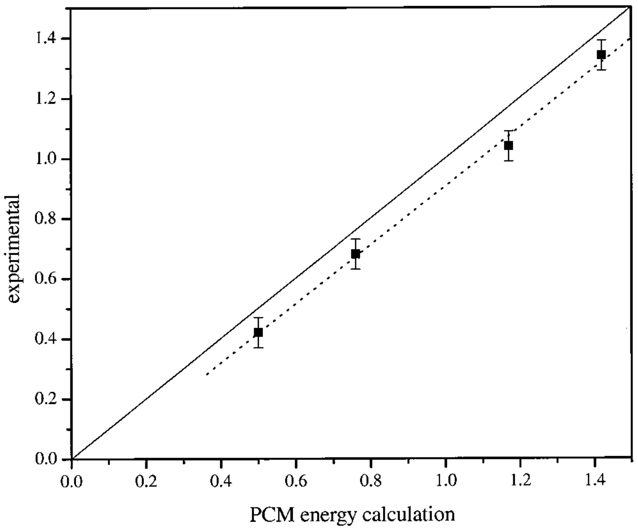

Figure 3. Comparison between $\Delta\Delta G°_{T\to G}$ values as obtained by PCM free energy calculations (PCM energy calculation) and by using experimental intensity ratios combined with PCM-calculated τ_G/τ_T values (experimental) for 1-chloro-2-fluoroethane. The dotted line is obtained through a linear fit: slope 0.98, linear regression coefficient $R = 0.9983$.

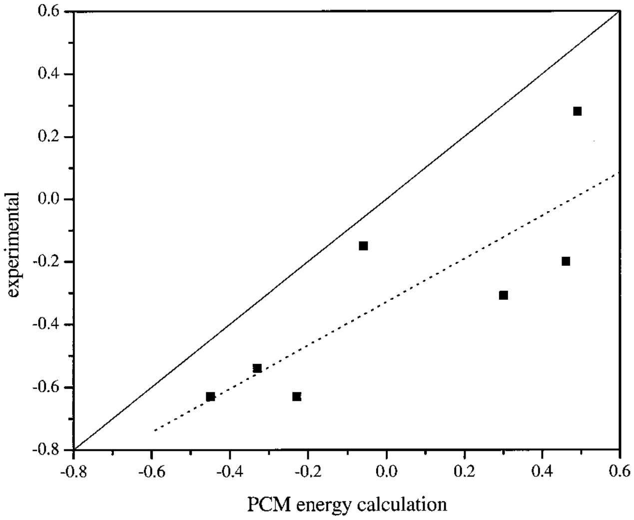

Figure 4. Comparison between $\Delta G°_{T\to G}$ values as obtained by PCM free energy calculations (PCM energy calculation) and by using experimental intensity ratios combined with PCM-calculated τ_G/τ_T values (experimental) for β-chloropropionitrile. The dotted line is obtained through a linear fit: slope 0.69, linear regression coefficient R = 0.8175.

In the case of CFE (see Figure 3), the PCM calculated $\Delta\Delta G°$ values show both a correct trend and a small deviation from the experimental values (0.07 kcal/mol). Such a deviation is smaller than what we have found for DCE; in the present case, nonelectrostatic terms should reasonably be less important because the substitution of a chlorine atom with a fluorine one decreases the polarizability of the system (dispersion term), the solute charge penetration into the solvent (repulsion term), and the molecular volume (cavitation term). For both DCE and CFE, the agreement between PCM-calculated and experimental data obtained from Oi and Coetzee[40] and El Bermani et al.[41] (not included in the plots) is worse.

As we have already pointed out, for CPN, the experimental $\Delta G°$ value in vacuo cannot be estimated. For this reason in Figure 4, we show PCM calculated vs experimental $\Delta G°$ values instead of $\Delta\Delta G°$. To the best of our knowledge, the only available experimental data are those of El Bermani et al.,[41] which, as stated above, are less reliable than the ones shown in the two previous cases. For CPN, the agreement between experimental data and PCM-calculated values is less satisfactory. In our opinion, because the quality of the calculation (quantum mechanical (QM) level and solvation model) is the same as for DCE and CFE, larger discrepancies between calculated and experimental values are mainly due to a large uncertainty in the experimental data.

As final remark, let us compare PCM-calculated data for DCE and CFE with theoretical values obtained by other authors by exploiting different QM levels and solvation models (Tables 14 and 15). The comparison with SCIPCM values by Wiberg et al.[17] (at the same QM level) shows increasing discrepancies in going from nonpolar to polar solvents for both DCE and CFE. Even larger differences are noted when comparing our data with SCIPCM ones at the MP2/6-311+G** level (see Tables 14 and 15).

For DCE calculations of $\Delta E_{T\rightarrow G}$ (internal energy difference) at the CCSD/cc-pVTZ level, both in vacuo and in solution (SCRF model) are reported in the literature.[27] The proposed in vacuo value (1.45 kcal/mol) is smaller than the DFT one (1.59 kcal/mol) and goes in the direction of the experimental result. Solvent effects are strongly underestimated with respect to our calculated and experimental data.

4. Summary and Conclusions

In this paper, we have used the PCM method to study conformational equilibria of three substituted chloroethanes in solution. Theoretical PCM calculations have been used with two aims: (a) to evaluate IR absorption coefficients, ϵ, and Raman scattering cross sections, σ, in each of the solvents considered, which are to be combined with experimental intensities found in the literature; (b) to directly obtain energy differences by means of ab initio energy calculations in solution. The results can be analyzed by considering both the absolute changes of $\Delta G^{\circ}_{T\rightarrow G}$ in passing from vacuum to solution (the $\Delta\Delta G^{\circ}_{T\rightarrow G}$ previously defined in the text) and the trend of such changes in passing from a given solvent to another. With regard to the trend, the results obtained by using method a or method b are in very good agreement. For $\Delta\Delta G^{\circ}_{T\rightarrow G}$ absolute values, the agreement is less satisfactory but still good; if reliable IR and Raman experimental data are used, final results obtained by means of method a or b differ from each other by about 0.2 kcal/mol for DCE and 0.07 kcal/mol for CFE. Notice that experimental uncertainties are on the order of ±0.1 kcal/mol for DCE and ±0.05 kcal/mol for CFE. In our opinion, these findings are proof of both the reliability of the results we have reported and the "robustness" of the method we have used to treat systems in solution.

The calculation of IR absorption coefficients, ϵ, and Raman scattering cross sections, σ, in each solvent has permitted evaluation of the differences in such parameters in passing from one medium to another. The approximation, widely used in the practice, that consists of neglecting such variations would make the agreement between the two mentioned approaches a and b get worse. In fact, such an approximation affects the results to a various extent depending on the medium considered (up to 0.2 kcal/mol for the most polar solvent).

Some approximations have been exploited in our model: nonelectrostatic solute–solvent interactions have been neglected, spectroscopic quantities are calculated within the double-harmonic approximation, and in the calculation of thermal contributions, terms explicitly dependent on the presence of a solvent medium (such as hindered rotations) have been neglected. While the first two approximations affect the calculation both of ab initio energies in solution and of ϵ and σ, the third one is invoked only when energy differences are directly obtained by means of ab initio energy calculations in solution. The use of such assumptions seems to be justified from the results we have presented; in particular, the combination of the harmonic picture with a pure electrostatic solvation model gives calculated frequencies in good agreement with experiments. Because thermal corrections on energy differences are small (less than 0.3 kcal/mol), reasonably the inclusion of solvent-dependent terms would not greatly affect the final result.

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