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Solvent Induced Charge Separation in the Excited States of Symmetrical Ethylene: A Direct Reaction Field Study

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The polarization of the excited states of near-perpendicularly twisted ethylene in the condensed phase has been investigated by means of direct reaction field (DRF) calculations. In these calculations, five organic solvents with variable polarity and polarizability were simulated by 50 discrete, classically described solvent molecules. The excited states of near-perpendicular ethylene were described by ab initio methods at the CISD level of theory using a DZV basis set. It is demonstrated that there is a distinct correlation between the polarity of the solvent and the occurrence and stabilization of charge separated excited states of ethylene. Large dipole moments were observed for ethylene excited states in polar solvents, indicating that an asymmetric distribution of polar solvent molecules around the ethylene can introduce enough symmetry breaking to cause charge separation. This behavior was not observed for (models of) nonpolar solvents. This charge separation process can be designated as unbiased "sudden polarization" since the solvent shells used were in equilibrium with the nonpolarized ethylene solute.

Introduction

One of the most fundamental processes in chemistry is the photoinduced cis−trans isomerization of an olefinic double bond.[1] The importance of this process is illustrated by its presence in a large number of biological systems, for instance the ultrafast cis−trans isomerization in the retinal chromophore of rhodopsin which triggers a series of events ultimately leading to vision in mammals.[2] An overwhelming number of both theoretical[3−25] and experimental[26−56] studies focusing on the dynamics, lifetimes, and electronic features of these isomerizations in a wide variety of olefins has been performed in order to gain deeper insight in this process.

The first study of the electronic features of cis−trans isomerizations dates back to 1932 when Mulliken[1] predicted that the $(\pi,\pi{\to}\pi,\pi^*)$ excited state should undergo a large intramolecular rearrangement due to rotation around the ground-state double bond from a planar ground-state geometry to a (near) perpendicular excited-state geometry, the so-called phantom state.[57] By now it is well accepted that the driving force behind this relaxation is the reduction of the bond order in this bond accompanied by the repulsion of the two "non-bonding" -electrons and the opposite substituents on either side of the double bond. An interesting feature of this rearrangement is the possible occurrence of an avoided crossing between the S_1 (π,π^*) and S_2 (π^*,π^*) surfaces in the vicinity of the phantom-state geometry.[3]

On the basis of a simple two electrons in two orbitals (e.g., a and b) description, it was suggested that the electron configurations, a^2 and b^2, that give rise to these singlet excited states should be of ionic character.[1,57] As a consequence, the avoided crossing can lead to the occurrence of large dipole moments in situations where, due to symmetry breaking by for instance asymmetric substitution, the equivalence in the weight of both determinants is no longer present. Therefore even D_2 symmetrical alkenes, which lack a permanent dipole moment in their ground-state configuration, can exhibit large dipole moments in their relaxed excited-state geometries.

The nomenclature of the possible states is as follows. Around the 90° twisted configuration, one deals with a two-electron, open-shell problem. In minimal basis language, indicating the p-orbitals on the two carbon atoms that form the double bond in the ground state as a and b, the states $^1(ab)$, $^3(ab)$, and $^1(a^2 \pm b^2)$ arise. $^1(ab)$ is the ground (N) state at this geometry. States with a dipole moment, in which the electron density on one carbon atom differs from that of the other, are associated only with the states $^1(a^2 \pm b^2)$. At the twist angle where the $^1(a^2 \pm b^2)$ Born−Oppenheimer surfaces cross, these states are degenerate and any appropriate lowering of symmetry will induce localization of the charge distribution on one side of the molecule, leading to an avoided crossing and to a lower *charge-transfer* (CT) state like $^1(c_1a^2 + c_2b^2)$, where $c_1 \neq c_2$. This is known as the zwitterionic (Z) state. In contrast, the associated higher (V) state, $^1(c_3a^2 - c_4b^2)$ with $c_3 \neq c_4$, is destabilized by the same effect. Hence, there is a tendency to reduce the dipole moment when the molecule is on this potential surface.

The $^1(a^2 - b^2)$ state itself carries no dipole moment and is often classified as "biradical". In ESR spectroscopy it is common to use this expression for systems where two unpaired electrons are localized on relatively distant parts of a molecule and consequently show small singlet/triplet splitting. For ethylene and the like, the CT states are essentially singlets and cannot be "biradical" at all. The only states possibly leading to singlet/

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triplet splitting are the $^{1,3}(ab)$ states, and in earlier work[23] these states, which have symmetric electron distributions, were called "charge resonant" (CR). Although in this work we go beyond the minimal basis set and SCF level of theory, we use the "N, Z, V" nomenclature throughout.

A large number of both experimental[27,28,34,38,42,43,48,51,52,56] and theoretical[3,9,12,15,23,58−60] studies have been performed in an attempt to gain both experimental evidence and additional information about the driving forces governing this symmetry breaking, which is often referred to as sudden polarization,[4] especially in the condensed phase.

The most direct evidence for the charge transfer (CT) character of the tetraphenylethylene (TPE) relaxed excited state has been reported by Schuddeboom et al., who performed flash-photolysis time-resolved microconductivity (FP-TRMC) experiments.[43] A considerable increase in microwave absorption was observed upon excitation of the TPE with a laser pulse, which is indicative of a highly dipolar excited state.

Other studies on TPE have revealed a strong correlation between the lifetime of this polarized excited state and solvent polarity. A spectacular drop in lifetime is observed when the solvent becomes more polar. Schilling and Hilinsky observed a dramatic drop in TPE excited-state lifetime from several nanoseconds in nonpolar solvents to only a few hundreds of picoseconds in (di)polar solvents.[34] Picosecond optical calorimetry studies by Ma et al.[38,52] showed a decrease of the energy gap between the ground and excited states of several (para-substituted) TPEs with increasing solvent polarity, which has led to the suggestion that the energy difference between ground and excited state is a measure of the coupling between the two states, thus explaining the decrease in lifetime of CT states in polar solvents.

The avoided crossing has also been suggested to play an important role in the isomerization of retinal, which indicates the generality of its occurrence in cis−trans isomerizations.[47]

From a theoretical point of view, various attempts have been made to describe the process of sudden polarization in symmetrical alkenes. Several configuration interaction (CI) studies on ethylene have shown that at (near) perpendicular geometries three important singlet states arise: the N state, which is the (CR) ground state at this geometry, and the ionic Z and V states, which become degenerate at a central bond twist angle of about 80°.[9,12] In the vicinity of this degeneracy, lowering of the nuclear symmetry by pyramidalizing one of the carbon centers leads to the formation of considerable dipole moments in the Z and V states of ethylene.

These calculations in a vacuum clearly point out the necessity of symmetry breaking to allow polarization to occur, in this case achieved by lowering the nuclear symmetry of ethylene. It was concluded from these studies that at (near) perpendicular geometries, the lowest energy conformation of the ethylene excited state must be of a zwitterionic nature and only exhibits C_s symmetry. The outcome of these studies has led to the general belief that intramolecular symmetry breaking (e.g., the pyramidalization of one of the two carbon centers forming the central olefinic bond) is an exothermic process, and, for that reason, the twisted excited state of these olefins is of an *intrinsically* zwitterionic nature,[43] where the solvent-dependent lifetimes are caused by the more effective stabilization of the zwitterion by more polar solvents.[38] This would lead to shorter lifetimes due to the narrowing of the gap between the photoexcited and ground-state potential energy surfaces and hence to an enhanced radiationless transition rate.

However, numerous photoinduced experiments on, for instance, *cis*-stilbene[39] and TPE[27,28,42,51] indicate that the observed solvatochromic dependence of the excited-state behavior cannot be explained by pure charge-transfer character in all cases. In fact, the CT state in such systems is only effectively populated in polar solvents, as we have recently demonstrated by means of femtosecond pump−probe experiments on TPE.[51] These studies revealed that for nonpolar solvents an equilibrium exists between a nonpolarized, charge resonant (CR) state and the CT state of TPE, which is in good agreement with earlier suggestions of a similar nature.[28,56]

On the basis of the observed solvatochromic excited-state CT behavior of (for instance) TPE in the experiments mentioned above, we have decided that it would be interesting to investigate the solvent-induced charge separation in the (in vacuo) charge symmetrical excited states of the parent alkene ethylene. In the condensed phase the necessary lowering of symmetry is automatically provided by the finite number of solvent molecules surrounding the solute, leading to a low-symmetry environment of the ethylene. It is therefore worthwhile to investigate the ability of various solvents to provide enough symmetry breaking to generate the charge separated states.

In an earlier study we have shown, by enveloping ethylene with a Connolly surface[61] carrying a nonsymmetrical distribution of dipole densities (i.e., a model for a solvent in equilibrium with a polarized solute), that an increase of the dielectric constant of the continuum leads to more pronounced polarization as well as stabilization for the ethylene excited states.[23]

In this paper we present the results of our study of the ability of several organic solvents with varying polarity as well as polarizability to "suddenly" polarize the ethylene excited states at near perpendicular geometries.

To achieve this we have employed the direct reaction field (DRF) method, which is a hybrid quantum mechanical/classical (QM/MM) method for including the effect of surroundings, e.g., a solvent shell in quantum chemical calculations.[62] In this method the system of interest (in this case ethylene) is described quantum mechanically by using an ab initio or semiempirical wave function whereas the surroundings are described classically by means of point charges and explicit polarizabilities. The DRF method is briefly discussed below.

We will show that increasing solvent polarity not only increases the expectation value of the ethylene dipole moment but that even for nonequilibrium solvent surroundings (i.e., a solvent in equilibrium with a nonpolarized charge distribution of the ethylenic excited state) a distinct stabilization of the charge separated excited state can occur.

Description of the Calculations

Direct Reaction Field Calculations.

The DRF method combines a quantum mechanical description of a solute with a classical description of its surroundings and is schematically shown in Figure 1. The quantum system is surrounded by classically described groups (molecules) A, B, ... These molecules are described by polarizabilities α_i^A and point charges q_i^A. The entire system may optionally be surrounded by a dielectric continuum described by total and optical dielectric constants ϵ and ϵ_∞, respectively, and a finite ion strength leading to a Debye screening radius of κ^{-1}. This method has been extensively described previously;[62−66] therefore, we will only discuss some specific issues that are relevant to the present work.

The computational level that is used to describe the quantum system in the DRF method can be of arbitrary complexity. The

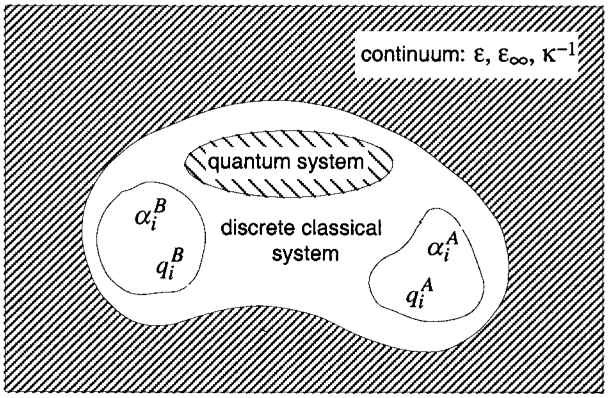

Figure 1. Schematic representation of the DRF model. The quantum system is surrounded by classical molecules A, B, ... described by point charges q_i^A and polarizabilities α_i^A. The entire system may optionally be surrounded by a dielectric continuum.

DRF method has been implemented for a number of single determinant ab initio methods, e.g., restricted Hartee−Fock (RHF) and restricted open shell Hartree−Fock (ROHF), as well as for multideterminant methods such as configuration interaction (CI). The latter type of wave function is of obvious importance for the description of excited states and will be used in the present study.

The point charges for the classical system used in this study were obtained by fitting to electrostatic potentials obtained from Hartee−Fock calculations in points selected according to the CHelpG scheme using Dunnings cc-pVDZ basis set. The atomic polarizabilities used here were taken from an extensive study by Van Duijnen and Swart,[67] who optimized the values used in the DRF method by fitting them to a set of experimental polarizabilities according to a method developed by Thole.[68] The actual values of all parameters used are listed in Table 1.

For the present study the ethylene (quantum system) was surrounded by 50 classical solvent molecules modeling approximately the first three solvent shells. A set of more or less random solvent shells was generated by performing fully classical Monte Carlo (MC) calculations using the DRF force field. After equilibration, a simulation of 200 000 MC steps was performed from which 20 randomly chosen solvent conformations were saved for the actual QM/MM analysis. The whole system was constrained to a spherical cavity with a radius chosen to obtain the experimental density.

In these conformation generating MC simulations, the ethylene solute was also treated classically in the same way as the solvent. It was represented by polarizabilities and point charges calculated for its vacuum (i.e., nonpolarized) N-state. In this way we can ensure that any polarization arising in the ethylene excited states can be truly regarded as "sudden" since the solvent shells represent the equilibrium surrounding of the nonpolarized ethylene.

The above-described procedure was performed using ethane, tetrachloromethane, chloroform, acetone, and carbon dioxide as solvents. All of these solvents have very little internal degrees of freedom, which makes them attractive solvents for the MC sampling, since the internal degrees of freedom can be omitted in these simulations. The choice of ethane and carbon dioxide as solvents deserves some further explanation since both of them are gases at ambient conditions. Ethane can be considered as a model system for nonpolar hydrocarbons such as *n*-hexane but has the advantage of little internal degrees of freedom. Additionally, supercritical ethane has been used in experimental studies by Sun et al.[56] on the charge separation behavior of TPE and it was found that its effect on the CT character and excited-state lifetime was comparable to that of *n*-hexane. Supercritical carbon dioxide was also used in the same study, and despite its lack of a permanent dipole moment, it was shown to exhibit behavior that is typical for polar solvents.

The influence of the different solvent configurations on the polarization and stabilization of the excited states of ethylene was investigated by performing mixed QM/MM calculations on the 20 solvent conformation obtained from the classical MC simulations. The ethylene was described by using a CI wave function including all single and double excitations from the valence orbitals using the vacuum orbitals of the N-state as the reference determinant (CISD). These reference orbitals were obtained from a singlet ROHF calculation using Dunning's DZV basis set. Such a procedure is known to produce perfectly zero dipole moments[23] in a vacuum for all states of interest, which is an obvious requirement for the present study.

The use of a multideterminant wave function in the DRF method introduces a complication for the evaluation of the dispersion contribution to the interaction energy between the quantum system and the classical solvent. This becomes evident when we consider the DRF definition of the interaction energy between a classical system described by polarizabilities and point charges and single determinant wave function:

$$\begin{aligned}\Delta U_{\text{int}}^{\text{QM/MM}} = {} & \sum_{A,i,j} q_i^A V_{ij}^{\,i} Z_j + e \sum_{A,i} q_i^A \langle V \rangle_i + \\ & + \sum_{A,i,j,r,s} q_i^A f_{ir} A_{rs} \boldsymbol{f}_{sj} Z_j + e \sum_{A,k,j,r,s} \mathrm{q}_{\mathrm{j}}^{\mathrm{A}} \boldsymbol{f}_{\mathrm{jr}} \mathrm{A}_{\mathrm{rs}} \langle \boldsymbol{f}(s;k) \rangle + \\ & + \frac{1}{2} \sum_{i,j,r,s} Z_i f_{ir} A_{rs} \boldsymbol{f}_{sj} Z_j + e \sum_{i,k,r,s} Z_i \boldsymbol{f}_{ir} A_{rs} \langle \boldsymbol{f}(s;k) \rangle + \\ & + \frac{\gamma}{2} e^2 \sum_{k,r,s} \langle \boldsymbol{f}(k;r) \mathrm{A}_{\mathrm{rs}}\, f(s;k) \rangle + \\ & \frac{1}{2} e^2 \sum_{k,l,r,s} \langle \_\boldsymbol{f}(k;r) \rangle_r A_{rs} \left(1 - \frac{\gamma}{2} P_{12} \right) \langle \boldsymbol{f}(s;l) \rangle + \Delta U_{\text{rep}}{}^{\text{QM/MM}} \end{aligned} \quad (1)$$

In this equation q_i^A is the *i*-th point charge of group (molecule) A used to describe the electrostatic potential of the classical system. The Z_j are the nuclei in the quantum system. The A_{rs}s are elements of a supermatrix **A** which describes the response of the total classical polarizable system to the field caused by the quantum system. **A** can thus be considered as an effective polarizability of the entire classical system. $V_{sp} = (1/|\boldsymbol{r}_p - \boldsymbol{r}_s|)$ is the coulomb potential in **p**, brought about by a source in **s** and $\boldsymbol{f}_{sp} = -\nabla_p V_{sp}$ is the corresponding electric field. The scaling factor, γ, is for the dispersion which is discussed below, and P_{12} is the permutation operator. To distinguish between source and recipient in the expectation values of the field—e.g., $\langle \boldsymbol{f}(k;s) \rangle$, i.e., the electric field at *s* due to electron *k*—the electron labels (*k*,*l*) and the electronic charge (*e*) have been made explicit so as to avoid ambiguity in the signs of the various terms.

In eq 1 the first two terms describe the electrostatic interaction of the nuclei and electrons with the point charges of the solvent. The next two terms describe the interactions between the point charges and the dipoles induced by the nuclei and electrons and vice versa. The fifth and sixth term represent the screening of the nuclear repulsion and attraction, respectively. The seventh and eighth term describe the interaction of an electron with its own and the other electrons' induced dipole moments; the latter term is therefore a two-electron term which contains the induction and part of the dispersion interaction. The scaling factor γ is used for the dispersion and was shown to be roughly equal to the following expression including the second-order

TABLE 1: Parameters Used in the DRF Calculations

	general DRF parameters		formal atomic charges in the various molecules					
atom	**α^a/Bohr^3**	r^b/Bohr	$(CH_3)_2CO$	$CHCl_3$	CCl_4	CO_2	C_2H_6	C_2H_4
H		1.512	+0.086	+0.230			−0.005	+0.048
C	8.696	3.402	−0.328^c +0.715^d	−0.125	−0.244	+0.910	+0.015	−0.096
O	5.749	3.024	−0.575			−0.455		
Cl	16.20	4.234		−0.035	+0.061			

[a] Polarizability. [b] VanderWaals radii. [c] Methyl carbon. [d] Carboxyl carbon.

perturbation theory expression (SOP) for the dispersion:[64]

$$\Delta U_{\mathrm{disp}}^{\mathrm{SOP}} \approx \left\{\frac{E_{\mathrm{solvent}}^{\;i}}{E_{\mathrm{solute}}^{\;i} + E_{\mathrm{solvent}}^{\;i}}\right\}\Delta U_{\mathrm{disp}}^{\mathrm{DRF}} = \gamma \Delta U_{\mathrm{disp}}^{\mathrm{DRF}} \quad (2)$$

In eq 2 the E^i are the ionization potentials of the solute and solvent molecules.

The scaling factor γ can be used to redefine the reaction field operator by scaling the integrals for the screening of the one-electron self-energy as well as the two-electron exchange contributions. The latter rescaling is only then possible when the exchange interaction is explicitly defined, i.e., when dealing with a single determinant wave function. The present calculations were therefore performed using $\gamma = 0$.

An estimate of the dispersion interaction was added afterward by performing a series of separate DRF calculations on the R(O)HF wave functions corresponding to the three dominating (a^2, b^2, and ab; the two zwitterionic and the CR) configurations of the CI wave function. These wave functions were constructed from the vectors used in the CI calculations in the corresponding solvent configurations without allowing orbital relaxations, ensuring the use of the same MO space in the estimation of the dispersion contributions. The thus obtained dispersion contributions were weighted by the normalized CI coefficients of the corresponding determinant.

For the ionization potentials of the solvent molecules used in eq 2, experimental values were taken.[69] The ionization potentials of the various states of ethylene in its twisted geometry had to be determined theoretically, since for obvious reasons experimental data are lacking. The ionization potential of the $^1(ab)$ state was extracted from two successive ROHF calculations, the first one describing the full electron configuration at this geometry and the second one in which one electron was removed from the system without allowing orbital relaxations. The difference between these two energies can be used as an estimate of the vertical ionization potential of the N state of ethylene. The ionization potential of both the Z and V state, which were taken to be degenerate, was obtained by taking the excitation energy (energy difference between the N state and the Z and V states) from the vacuum CISD calculations described above and subtracting it from the ionization potential of the N state. The ionization potentials obtained in this way can be considered reasonable estimates of the ionization potentials of twisted ethylene in the N, V, and Z states and are listed in Table 2 together with the values for the scaling factor γ calculated according to eq 2.

TABLE 2: Ionization Potentials and Resulting γ of Applied Solvents and Perpendicular Ethylene

solvent	ionization potential, eV	γ (with ethylenic N/Z,V state)
ethane	11.5	0.540/0.647
tetrachloromethane	11.47	0.539/0.646
chloroform	11.42	0.538/0.645
carbon dioxide	13.77	0.584/0.687
acetone	9.69	0.497/0.609
ethylene (N state/Z,V state)	9.80/6.28	

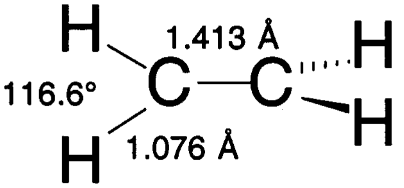

Figure 2. Ethylene geometry.

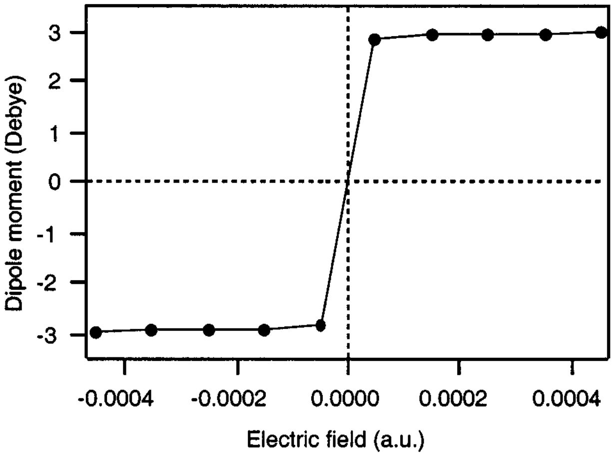

Figure 3. Induced dipole moment of the first excited state of 81° twisted ethylene as a function of applied electric field.

Ethylene Geometry.

The geometry of ethylene used in this study is shown in Figure 2. Bond lengths and angles were taken from a RHF geometry optimization using a basis set of double-ζ quality including polarization functions. In the present work all calculations were performed at a twist angle (i.e., the H−C−C−H dihedral angle) of 81°, which was found to be the angle where the maximum excited-state polarizability occurs (vide infra) and therefore the maximum polarization effect can be expected at this angle. This angle of "maximum effect" appears to be independent of the level of theory.[23]

Results and Discussion

Polarizability of Ethylene Excited States at Different Twist Angles.

The finite field method was used to calculate the polarizability of the first excited state of ethylene in the 70−90° twist area. Initial calculations using field strengths of ~ 10-4 au revealed a strongly nonlinear behavior of the polarizability component along the C−C bond as evident from Figure 3. An induced dipole moment of 2.8 D is obtained at a field strength of 5 x 10^{-5} au, further increase of the electric field increases the dipole moment only slightly. Thus the electric field of 5 x 10^{-5} au is sufficient to cause an energy difference between the two carbon atoms that is large enough for a full charge separation to occur.

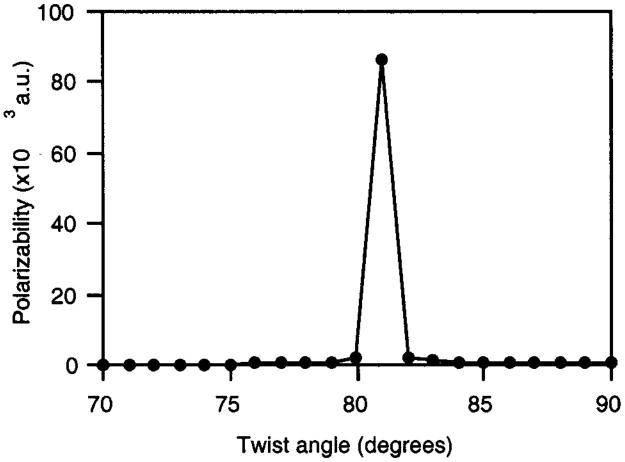

Figure 4. Polarizability component along C−C axis of the first excited state of 81° twisted ethylene.

TABLE 3: Average Solvent Induced Dipole Moments (μ_z, Absolute Values) of the Three States of Interest for 81° Twisted Ethylene

	$\lvert\mu z\rvert$, D		
	N state	Z state	V state
ethane	0.00 (±0.00)	0.09 (±0.06)	0.08 (±0.06)
tetrachloromethane	0.01 (±0.01)	0.72 (±0.46)	0.70 (±0.44)
chloroform	0.05 (±0.05)	2.07 (±0.92)	1.93 (±0.82)
carbon dioxide	0.09 (±0.06)	2.62 (±0.75)	2.37 (±0.59)
acetone	0.10 (±0.05)	2.61 (±0.66)	2.38 (±0.53)

Further calculations were performed with electric fields strengths of the order of 10^{-6} au; at these values the induced dipole moment was found to depend linearly on the electric field. The excited-state polarizability along C−C axis attains an enormous value around the 81° twist region (Figure 4; note the polarizability scale!). The largest polarizability was found for near-perpendicular ethylene with a twist angle of 81°. However, the dramatic increase shown in Figure 4 should be interpreted with some caution, since the (near-)degeneracy of the Z and V surfaces in the vicinity this geometry leads to a heavy mixing of both states resulting in an avoided crossing area for which the Born−Oppenheimer approximation no longer holds. Inclusion of the coupling between electronic and nuclear motion in the wave function (as for instance in a quantum dynamical treatment) would lead to a better description of the phenomenon but is beyond the scope of this work.

These finite field calculations clearly point out that, within the theoretical framework of choice in this study, the degeneracy of the Z and V surfaces leading to the enhanced excited-state polarizability occurs around the 81° twist angle. Therefore, the twist angle was set equal to this value in the remainder of the work presented here.

Solvent Induced Charge Separation in Twisted Ethylene. The solvent induced dipole moments along the central C−C bond obtained from the DRF calculations described above are listed in Table 3 for the three states of interest. These values represent the absolute value for the dipole moment averaged over the 20 CI calculations with different solvent conformation. In reality, the calculated values exhibit both positive and negative values, dependent on the direction of the effective (static) field of the surrounding solvent. Averaging over the actual values would result in near-zero dipole moments, which is undesirable here since this provides no insight into the magnitude of the polarization of especially the Z and V excited states of the twisted ethylene.

In all CI calculations the dipole moments along the *z*-axis of the two excited states within a single calculation were of opposing signs, a direct result of the orthogonality (a^2 vs b^2) of the two (heavily mixed) states.

The most interesting feature that can be observed from the results in Table 3 is the distinct difference in expectation values of the dipole moments of the, in a vacuum near-degenerate, Z and V states in nonpolar and polar solvents. In the nonpolar solvents ethane and tetrachloromethane the induced dipole moments of these states are relatively small, especially in ethane (∼0.1 D). In tetrachloromethane, slightly larger dipole moments (∼0.7 D) are induced, although the spread (standard deviation) in the values is rather large (∼0.45 D). In fact, dipoles ranging from approximately 0.2 to 1.6 D were obtained from the various calculations using tetra as a solvent. This indicates that an asymmetric distribution of polarizabilities around the ethylene can sometimes introduce enough symmetry breaking to induce charge separation, even if no permanent electric field is present.

The excited states of the twisted ethylene exhibit larger dipole moments in the more polar solvents. In chloroform, which exhibits moderate polarity, the average dipole moments are already 2.0 D, although the spread is still large (±0.9 D). Calculated dipoles ranged from 0.1 to 3.2 D, indicating that large polarization can take place in certain but not all solvent geometries.

When looking at CO_2 and acetone, induced dipole moments in the excited states are very large (∼2.6 D) with a small spread compared to that of the less polar solvents (±0.6 D; under 25% of the average induced dipole moment), indicating that in (nearly) every solvent configuration large excited-state polarization is achieved. For instance, in acetone the excited-state dipole moments mainly range between 1.8 and 3.3 D.

Observations for the "ground" (N-)state are less dramatic; moderately small polarizations up to 0.1 D in acetone are found and show the expected correlation with increasing solvent polarity (or polarizability) and will not be discussed any further.

The results presented above clearly demonstrate that there is a relation between the nature of the solvent and the amount of symmetry breaking in the ethylenic excited states. To gain deeper insight into the origin of this relation, a more detailed look into the interactions between the various electronic states of the twisted alkene and its solvent surroundings is necessary.

Tables 4−8 specify the total interaction energy as well as the various components of that energy of the three states of interest for the 81° twisted ethylene with ethane, tetrachloromethane, chloroform, carbon dioxide, and acetone, respectively.

Five components contributing to that energy are specified:

− The repulsion energy (ΔE_{rep}) between the quantum and classical parts. This is a "classical" (pairwise atomic) interaction energy, defined in terms of formal atomic radii. Hence this contribution is the same in all states. This contribution is not "felt" by the electrons in the quantum system and is only included to get an estimate of the total interaction energy.

− The polarization energy (ΔE_{pol}), which consists of three contributions; the interaction between the quantum system and the moments induced by the classical charge distribution in the classical system (1), the interaction between the classical charge distribution and the moments that the quantum system induces in the classical system (2), and the cost of inducing all the dipoles in the classical system.

− The induction interaction (ΔE_{ind}), which is the interaction between the permanent charge distribution of the quantum

TABLE 4: Various Averaged Contributions to the Average Total Interaction Energy of the Three States of Interest for 81° Twisted Ethylene in Ethane (kcal·mol^{-1})

	N state	Z state	V state
ΔE_{tot}	−3.25	−4.77	−4.71
ΔE_{rep}	4.23	4.23	4.23
ΔE_{pol}	0.02	0.03	0.03
ΔE_{ind}	−0.04	−0.06	−0.07
ΔE_{elec}	0.00	0.00	0.00
ΔE_{disp}	−7.46	−8.97	−8.90

TABLE 5: Various Averaged Contributions to the Average Total Interaction Energy of the Three States of Interest for 81° Twisted Ethylene in Tetrachloromethane (kcal·mol^{-1})

	N state	Z state	V state
E_{tot}	−0.99	−1.69	−1.69
ΔE_{rep}	2.44	2.44	2.44
ΔE_{pol}	0.01	0.03	0.03
ΔE_{ind}	−0.01	−0.05	−0.06
ΔE_{elec}	−0.03	−0.06	0.00
ΔE_{disp}	−3.40	−4.05	−4.10

TABLE 6: Various Averaged Contributions to the Average Total Interaction Energy of the Three States of Interest of 81° Twisted Ethylene in Chloroform (kcal·mol^{-1})

	N state	Z state	V state
E_{tot}	−1.93	−3.31	−2.33
ΔE_{rep}	2.62	2.62	2.62
ΔE_{pol}	0.02	0.25	0.11
ΔE_{ind}	−0.02	−0.37	−0.32
ΔE_{elec}	−0.13	−0.75	0.38
ΔE_{disp}	−4.42	−5.06	−5.12

TABLE 7: Various Averaged Contributions to the Average Total Interaction Energy of the Three States of Interest in the 81° Twisted Ethylene with Carbon Dioxide (kcal·mol^{-1})

	N state	Z state	V state
E_{tot}	−4.09	−7.22	−4.77
DE_{rep}	3.57	3.57	3.57
ΔE_{pol}	0.07	0.59	0.26
ΔE_{ind}	−0.05	−0.82	−0.67
ΔE_{elec}	−0.64	−2.26	0.33
ΔE_{disp}	−7.04	−8.30	−8.26

TABLE 8: Various Averaged Contributions to the Average Total Interaction Energy of the Three States of Interest for 81° Twisted Ethylene with Acetone (kcal·mol^{-1})

	N state	Z state	V state
Etot	−3.81	−9.13	−6.38
ΔErep	8.06	8.06	8.06
ΔEpol	0.09	0.85	0.46
ΔEind	−0.07	−1.44	−1.15
ΔEelec	−0.41	−2.49	0.27
ΔEdisp	−11.48	−14.11	−14.02

system with the dipole moments it induces in the classical system.

− The electrostatic interaction (ΔE_{elec}), which is the interaction between the permanent charge distribution of the quantum system with the static charge distribution of the solvent.

− The dispersion interaction (ΔE_{disp}) between the quantum system and the solvent.

Note that this kind of decomposition is rather arbitrary since the "permanent" charge distribution of the quantum system depends very much on the solvent surrounding it as shown above; however, this polarized charge distribution is taken as the permanent charge distribution for the evaluation of ΔE_{elec}. The main advantage of being able to break the total interaction energy down to its separate physically relevant components is that the origin of possible state particulate interactions can be detected.

Table 4 shows the interaction energies of the three electronic states of interest of ethylene in ethane solution. It clearly shows that for all states the only significant stabilizing contribution to the interaction energy is the dispersion interaction, which is therefore solely responsible for the larger interaction of the excited states with the solvent. No significant charge separation takes place in this solvent and therefore the electrostatic contribution to the interaction energy is practically zero. The same applies of course to ΔE_{pol} and ΔE_{ind}. In the case of tetra, similar observations can be made (Table 5). Again, the dispersion term is the only significant contribution to the interaction energy of each state.

Only a very small increase is observed in the electrostatic interaction between the first excited (Z) state and tetrachloromethane when compared with ethane, this is the interaction of the charge separated ethylene with the point charges that model the tetrachloromethane. This small charge separation is caused by the asymmetric distribution of polarizabilities around the ethylene as argued above.

In the weakly polar chloroform, some significant differences with the earlier discussed solvents occur (Table 6). The dispersion interaction is the main contributor to the total interaction energy. No significant difference in dispersion interaction occurs between the two excited states, which was the same for the previous solvents.

However, here for the first time a significant difference in electrostatic interaction with the solvent occurs for these states. The first, lower lying excited state has an attractive interaction with the solvent, whereas the state with the roughly equal but opposing dipole moment has a repulsive electrostatic interaction with the field.

This can be rationalized by realizing that the solvent shell, especially in the case of a polar solvent, introduces an electric field with a more or less random direction at the position of the twisted ethylene solute. This field will in general have some component along the C−C bond of the ethylene which causes charge separation to occur if the field is large enough. This leads to two charge-separated states with opposing dipole moments. The lowest of these states will have an attractive electrostatic interaction with the solvent which lowers its energy, whereas the higher one has a repulsive interaction with the static field of the solvent, and hence its energy increases.

Thus the interaction with the solvent removes the degeneracy between the two excited states. The equilibrium electronic state of ethylene will therefore shift toward the polarized shape, unlike the case of ethane and tetra, where both excited states stay more or less degenerate. It can be seen in Table 6 that there is also a contribution from the induction interaction to the total interaction energy, the magnitude of this component is similar for both excited states, which indicates that the magnitude of the dipole moments is about the same (see also Table 3), but they have opposing directions.

For the polar solvents CO_2 and acetone (Tables 7 and 8) the results are quite similar and resemble those found for chloroform. The dispersion interaction dominates the interaction energy of all states. The main difference with chloroform is the magnitude of the electrostatic interaction. This contribution is much larger in CO_2 and acetone for the Z state (the first excited state) and is responsible for a more pronounced splitting between state Z and V. For CO_2 this may seem surprising because CO_2, unlike chloroform, does not exhibit a permanent dipole moment. However, CO_2 does have a large quadrupole moment, which

TABLE 9: Average Solvent Induced Gap Closure ($\Delta\Delta E_{int}$, kcal·mol^{-1}) for 81° Twisted Ethylene

	$\Delta\Delta E_{int}$, kcal·mol^{-1} (N state−Z state)	$\Delta\Delta E_{int}$, kcal·mol^{-1} (Z state−V state)
ethane	−1.52	0.00
tetrachloromethane	−0.70	0.00
chloroform	−1.78	+0.98
carbon dioxide	−3.13	+2.45
acetone	−5.32	+2.75

apparently is enough to provide substantial electrostatic interactions with the induced ethylenic dipole moments. For acetone the contribution of the induction and dispersion interactions is somewhat larger (for both excited states), probably because of the larger polarizability of acetone.

The marked difference in the polarization and stabilization of the ethylene excited state in ethane and CO_2 provides an explanation for the experimental shortening of the TPE excited-state lifetime in supercritical CO_2 compared to in supercritical ethane observed by Sun et al.[56] In CO_2, an additional stabilization of 1.5 kcal·mol^{-1} is observed for the Z state (the first excited state) compared to the ground state, which lowers the energy gap and therefore leads to an enhanced radiationless crossing rate between the two states, resulting in a shortening of the excited-state lifetime. It should be emphasized that the solvent shells used here are in equilibrium with the nonpolarized ethylene charge distribution (i.e., the ground state), which means that a considerable additional stabilization of the polarized excited state can be expected upon relaxation of the solvent on the polarized charge distribution of the ethylene. It has been shown experimentally[51] that for TPE the formation of the excited-state CT population in polar solvents takes place in 5−10 ps, whereas its lifetime is on the order of several tens or even hundreds of picoseconds, depending on the polarity of the solvent. This window gives the solvent ample opportunity to adjust to the altered charge distribution in the solute. This additional stabilization will further decrease the excited-state lifetime, also because the rearranged solvent shells will no longer be in equilibrium with the ground (N) state, thus destabilizing this state, which closes this gap even more. This effect is absent in ethane.

Table 9 summarizes the solvent effect on the energy difference between the three states studied in this work. Negative values indicate a decrease in the energy gap between the two states, whereas positive values represent an increase. The energy gap between the ground (N) state and the first excited (Z) state decreases in all solvents. This is mainly caused by dispersion interactions as argued above. This dispersion contribution is always larger in the excited states and hence lowers the energy gap. The decrease in the energy gap is more pronounced in polar solvents. This is a direct consequence of the charge separation in the excited state, which leads to enhanced electrostatic interactions between solvent and solute in this state. The energy gap between the two excited (nearly degenerate) states is not influenced by apolar solvents. In polar solvents, however, the charge separation that occurs causes a distinct energy splitting between these two states. This is of course mainly caused by the electrostatic interactions between the polarized ethylene and the solvent. This interaction is attractive for the lower state, while it is repulsive for the higher excited state.

One may wonder why the dispersion contribution to the total energies in tetrachloromethane, while having the largest polarizability, is smaller than in all other solvents. The dispersion between two molecules decreases roughly with the sixth power of the distance between them, and hence it depends on the number of solvent molecules in the first solvation shell and their distance to the solute. Since, e.g., ethane is much smaller than tetra, there are more solvent molecules in the first shell and they are closer. De Vries and Van Duijnen[70] addressed the same question. A more detailed account can be found there.

Summary and Conclusions

We have performed all valence CISD calculations at the 81° twist angle of ethylene using the Dunning−Huzinaga DZV basis, embedding the quantum system in a discrete classical surrounding using the direct reaction field model. The classical surrounding consisted of 50 discretely described solvent molecules, each fitted with a molecular polarizability. Twenty different solvent configurations were randomly selected from a fully classical Monte Carlo simulation. This procedure was performed with ethane, tetrachloromethane, carbon dioxide, chloroform, and acetone as solvents.

The 81° twist angle was chosen from a finite field study using the same wave function in vacuo. At this angle the excited-state polarizability of the twisted ethylene proved to be the largest in this basis set, making this geometry the most likely candidate for solvent-induced sudden polarization studies.

The DRF studies revealed that the expectation value of the ethylenic excited-state dipole moments remain small in the investigated nonpolar solvents, ∼±0.1 D in ethane and ∼±0.7 D in tetra. Furthermore, the degeneracy of the two excited states was not lifted in these solvents, which indicates that these solvents are not capable of breaking the symmetry of the excited-state wave functions to a large extent. It can therefore be concluded that nonpolar solvents are unlikely to induce the sudden polarization in the twisted excited states of ethylene and that some sort of intramolecular symmetry breaking is required to generate the zwitterionic states.

The solvent-induced stabilization of the degenerate excited states with respect to the ground (N) state is solely governed by the enhanced dispersion interaction with the solvent for these states. Even though this has to be treated with some caution, due to the approximate way this interaction is calculated, it is in agreement with intuitive concepts based on the assumed larger polarizabilities and smaller ionization potentials of excited states in general in comparison to their electronic ground-state configuration.

A marked difference from the behavior mentioned above was observed in the more polar solvents chloroform, CO_2, and acetone. In these solvents, significant dipole moments (>2 D) were generated in the ethylenic excited states. For the weakly polar chloroform there were still significant fluctuations between the values in various solvent configurations.

The more polar CO_2 and acetone showed a more pronounced polarization of the ethylene excited states, in (nearly) all investigated solvent configurations. In addition, a significant lift of the degeneracy of the two excited states was observed in these solvents (Table 9). This splitting between the two excited states is most pronounced in acetone (∼2 kcal·mol^{-1}). Analysis of the various contributions to the interaction energy shows that the difference in electrostatic interaction with the solvent is mainly responsible for this splitting. Interestingly, the induction interaction had no significant influence on this process, suggesting that the polarity rather than the polarizability of the solvent is responsible for the symmetry breaking.

It can therefore be concluded that polar solvents are capable of breaking the symmetry of the ethylene excited states even when the alkene exhibits a symmetrical (i.e., unpyramidalized) nuclear configuration. We emphasize that in all cases the surrounding solvent shells were in equilibrium with an unpolarized charge distribution. The inclusion of solvent relaxation will lead to more pronounced differences in excited-state energies in cases where large dipoles are being generated and stabilized. Although beyond the scope of this work, this is an interesting topic to be addressed in the future, since the solvent-dependent narrowing of the gap between ground and excited state has been used as an explanation for the shortened lifetimes of the excited states in, for instance, tetraphenylethylene (TPE) as a function of increasing solvent polarity.[42]

In experimental studies performed on the excited-state behavior of TPE and other symmetrical olefins, it is usually assumed that the electronic structure of the twisted excited states of these alkenes was zwitterionic in nature due to an intramolecular symmetry breaking. The results of this work show that the solvent plays a very important role in the symmetry breaking. This is especially relevant for substituted symmetrical ethylenes, since in these cases the steric repulsion between the substituents will make intramolecular symmetry breaking by pyramidalization rather unlikely.

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