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## Polarization of the excited states of twisted ethylene in a non-symmetrical environment

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### Abstract

The polarization behavior of the low lying excited states in the vicinity of the perpendicularly twisted ( $D_{2d}$ ) ethylene has been investigated in a quantum mechanical CISD approach, in which the quantum system was embedded in a polarized dielectric continuum modeling a non-symmetrical distribution of the solvent around the solute. The results show a strong polarization in the two lowest lying excited states in the region where the two vacuum energy surfaces of those states intersect, which strongly suggests that the lowering of the symmetry of the solvent shell can provide the adiabatic coupling for the avoided crossing between both potential energy surfaces. All examined values of  $\epsilon$ , with the exception of the smallest investigated value ( $\epsilon = 2.0$ ), showed the polarization to keep intact on progressive twisting towards the perpendicular geometry.

### 1. Introduction

For various reasons, the dynamic behavior of the photo-induced excited states of ethylenic systems has been the subject of numerous theoretical and experimental studies. For instance, interest in understanding cis–trans isomerization processes of ethylenic compounds in which the cis–trans isomerization of retinal, the key molecule in the mechanism of vision is probably the most exciting example [1], has contributed to the large number of studies performed on this class of compounds.

One of the most intriguing aspects of the behavior of the excited states of (symmetrical) alkenes is the existence of a polarized (charge separated) state, in

which two electrons – unpaired and distributed in the initial biradical excited state – are localized at one side of the molecule, thus leading to the formation of a considerable dipole moment.

Both direct and indirect experimental evidence of the existence of such a suddenly polarized [2] “phantom” state has been obtained from time resolved photo-induced excitation experiments on tetraphenylethylene (TPE) [3–9] and several other alkenes [10–12], in which a polarized state could be detected in several solvents.

A very remarkable observation in the experiments concerning TPE is the dependence of the lifetime of the polarized state on solvent polarity [5,6], in which a decreasing lifetime with increasing solvent polarity was observed. In these studies, increased coupling due to an decreased energy gap between the twisted ( $D_{2d}$ ) ground state and the more stabilized polarized

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excited state was suggested as a possible explanation for this observation. The occurrence of the polarization of TPE, in twisted geometries only, was deduced from the observation of a strong reduction of the quantum yield for formation of polarized excited TPE with increasing solvent viscosity [8] and by resonance Raman spectroscopy [13]. The twisting around the central bond will be increasingly hindered and fluorescence from the – nearly planar – relaxed vertically excited state, will become the dominant relaxation pathway.

On the origin of the localized states we note that after the vertical excitation of an electron from the  $D_{2h}$  ground state of ethylene, and other symmetrical alkenes, the C–C bond length will increase and a twist around the central C–C bond will be initiated. On progressive twisting, three low lying singlet states arise, which at the perpendicular  $D_{2d}$  geometry ( $\theta = 90^\circ$ ) are denoted as  $N(^1B_1;ab)$ ,  $V(^1B_2;a^2 - b^2)$  and  $Z(^1A_1;a^2 + b^2)$  and are very sensitive to rotation around the C–C bond. The N state is destabilized going from the  $D_{2h}$  to the  $D_{2d}$  geometry, while the V and Z states are stabilized, coming close together at near perpendicular geometries and—in the Born–Oppenheimer approximation—cross for  $\theta \approx 80^\circ$ . At and around the crossing V and Z are (nearly) degenerate and therefore wave functions of type  $V \pm Z$  are equally acceptable, resulting in localized  $a^2$  or  $b^2$  states which will have considerable dipole moments. A theoretical description of the vacuum situation should be based on the appropriate (open shell, many determinant) wave functions and symmetry, i.e.  $V \pm Z$  should have equal weights as long as the  $D_{2d}$  symmetry remains, and no dipole should exist.

Previous theoretical studies provided valuable insight into the possible polarization of the (near) perpendicularly twisted ( $D_{2d}$ ) excited states of ethylene. CISD studies by Brooks and Schaefer III [14] showed that lowering the nuclear symmetry to  $C_s$  by pyramidalization of one of the two carbon centers leads to the build up of large dipole moments due to considerable mixing between the – originally ( $D_{2d}$ ) V and Z – states. MRCI studies of Buenker et al. [15,16] have shown that combined pyramidalization and twisting of the central double bond leads to the formation of highly polarized states in the vicinity of the crossing of the Z and V state energy surfaces.

Since experimental results always are related to

the condensed phase, we considered it worthwhile to investigate whether solvent polarization on its own could be responsible for the lowering of the symmetry required for localization of these states. If the system is embedded in some polarizable medium, the transient  $a^2$  or  $b^2$  states can generate reaction potentials which may live sufficiently long to lift the degeneracy and stabilize one with respect to the other, without lowering the symmetry of the nuclear arrangement.

To that end we applied our direct reaction field approach [17–19], which allows various ways of modeling solvent effects, e.g. representing the “solvent” by (sets of) discrete semi-classical solvent molecules (distributed multipoles + polarizabilities) or by a dielectric continuum, or both. We can treat *ab initio* RHF, ROHF, GVB, MCSCF and CI wave functions for ground and excited states in equilibrium and non-equilibrium situations, while the solute/solvent interactions may be accounted for fully self-consistent or as first order perturbations. For solvent effects from the discrete model at finite temperatures Monte Carlo sampling of the solvent’s degrees of freedom is provided. All this was implemented in the *ab initio* package HONDO 8.1 [20].

In this preliminary study we decided to use the dielectric model only [21], although we pointed out recently that this is not without problems [22]. Moreover, since *ab initio* calculations on TPE are not feasible on the level required, we used ethylene as model compound. Explicit studies on TPE are postponed until our solvent model is incorporated in a semi-empirical package.

## 2. Computational details

In this study, only the dielectric model has been used to simulate the effect of a non-symmetrical solvent shell around the ethylene molecule. The adopted geometry of ethylene is shown in Fig. 1.

Calculations in vacuum should yield symmetric wave functions with zero dipole moments for both

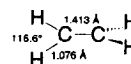


Fig. 1. Geometry of twisted ethylene.

ground and excited states at any point of the twisting energy surface. In our calculations we used the Dunning–Huzinaga double valence (DZV) basis. The singlet ROHF vectors for the N state were used to define the reference configuration in an all valence CISD ( $\sim 60\,000$  determinants involved). For all rotation angles, the CI wave functions yielded perfectly zero dipole moments for both the ground and the investigated excited states.

A non-symmetrical reaction potential was obtained from the dielectric continuum with various dielectric constants, generated by a localized charge density for the near  $90^\circ$  twist angles, which was obtained from a closed shell RHF procedure, in which an  $a^2$  solution was obtained with a considerable dipole moment ( $\mu_z \approx 4.0$  debye). Although physically incorrect in vacuo, this localized wave function yields a reasonable electron density distribution for a polarized excited state.

For the necessary boundary between discrete and continuum parts we took a Connolly surface [23] defined at twice the van der Waals radii of the ethylene atoms around the geometry of the solute at hand. This distance was considered large enough to avoid unphysical polarizations [22]. The point density was chosen such that about 600 surface elements resulted. Reaction potentials are obtained by solving numerically appropriate Poisson equations. At the selected geometries, self-consistent reaction potentials from the “closed shell” RHF ( $a^2$ ) wave functions were obtained and added to the one-electron Hamiltonian in the CISD calculations.

This procedure was performed for  $\epsilon = 2.0, 4.0, 6.0$  and  $10.0$ , which are typical values for a range of organic solvents with increasing polar behavior.

### 3. Results and discussion

From the first series of calculations we obtained the vacuum energies of the states of interest of ethylene. Since Buenker et al. showed the crossing surface between the Z and V states of ethylene, at a twist angle of approximately  $80^\circ$  for the central bond [16], to be the twist region highly sensitive to polarization, we have restricted our investigation to the  $70$ – $90^\circ$  twist area.

In the CISD calculations, all 12 valence electrons were included from the reference singlet ROHF wave function and were allowed to excite into the complete virtual space (17 virtuals) thus leading to a CI space of 60 480 determinants. Results are given in Table 1.

These CI expansions lead to perfectly zero dipole moments for all states at all investigated geometries, which shows that these CI expansions can reproduce the wanted symmetrical wave functions in vacuo. At this point, our findings differ from those by Schaefer III and Brooks [14], who found non-zero dipole moments for the  $D_{2d}$  Z and V states in similar expansions.

Results of the reaction field calculations with the closed and open shell RHF wave functions in the (non-)equilibrium reaction potentials of the former are shown in Table 2.

It should be noted that only geometries near  $90^\circ$  are able to yield such a polarized RHF wave function, since increasing overlap between the “ $p_z$ ” orbitals on the carbon centers on decreasing twist angles will lead to a delocalized RHF solution. A remarkable observation is that the energy gap between the closed shell and the open shell wave

Table 1  
CISD vacuum energies (au) of the N, Z and V states of ethylene in the  $70$ – $90^\circ$  twist range

Twist angle ( $^\circ$ )	70	75	80	85	90
N	–78.12256	–78.11431	–78.10736	–78.10260	–78.10088
Z <sup>a</sup>	–77.96553	–77.96810	–77.96996	–77.97108	–77.97145
V <sup>a</sup>	–77.94613	–77.95858	–77.96858	–77.97519	–77.97753

<sup>a</sup> See Fig. 4 for graphical representation of the potential energy surface of the Z and V states.

Table 2

SCF energies (au) and dipole moments (debye) of the  $\Psi_{\text{RHF}}$  and  $\Psi_{\text{ROHF}}$  singlet wave functions at different values of  $\epsilon$

$\epsilon$	$\Psi_{\text{RHF}}$ (au)	$\mu_z$ (debye)	$\Psi_{\text{ROHF}}$ (au)	$\mu_z$ (debye)
vacuo	-77.80991	+3.760	-77.93843	0.000
2.0	-77.81122	+3.887	-77.93715	+0.095
4.0	-77.81212	+3.972	-77.93625	+0.161
6.0	-77.81247	+4.006	-77.93590	+0.186
10.0	-77.81278	+4.034	-77.93563	+0.208

functions at the HF level yields a reasonable estimate of the energy gap between the ground state and the “polarized excited state” (0.128 au at the HF level in vacuo against 0.129 au at the CISD level with singlet open shell orbitals as reference, see Table 1 and Table 2 for actual values). Furthermore, when using the polarized closed shell orbitals in an all

valence CISD expansion at the  $D_{2d}$  geometry in vacuo, an energy similar to those of the symmetrical first excited state is obtained ( $E_{\text{CI}} = -77.97897$  au,  $\mu_z = 3.232$  debye for this polarized state).

The total energies ( $E_{\text{CI}} + E_{\text{DRF}}$ ) of the CISD expansion in the singlet ROHF orbitals of the three lowest lying states in the non-equilibrium reaction potentials, as well as the CI coefficients for the  $a^2$  and  $b^2$  contributions of the first two excited states are reported in Table 3.

As can be seen from the CI coefficients, strong polarization occurs in the vicinity of the crossing of the “pure” Z and V states in vacuo. This is emphasized in Fig. 2, which shows the dipole moments of the first two excited states in the 70–90° twist angle region.

Most remarkable feature from the observed dipole moments is the inability of the weak dielectric to maintain the large dipole moment on progressive

Table 3

CISD total energies (au), dipole moments (debye) and CI coefficients of both examined (polarized) excited states of twisted ethylene

	“ $\mu^+$ ”				“ $\mu^-$ ”			
	$E_{\text{tot}}$ (au)	$\mu_z$ (debye)	“ $a^2$ ”	“ $b^2$ ”	$E_{\text{tot}}$ (au)	$\mu_z$ (debye)	“ $a^2$ ”	“ $b^2$ ”
twist angle = 70°								
$\epsilon = 2.0$	-77.96463	+0.657	0.669	-0.566	-77.94481	-0.349	0.507	0.618
$\epsilon = 4.0$	-77.96435	+1.073	-0.700	0.526	-77.94377	-0.592	0.467	0.649
$\epsilon = 6.0$	-77.96431	+1.226	-0.710	0.512	-77.94355	-0.669	-0.452	-0.660
$\epsilon = 10.0$	-77.96431	+1.353	0.718	-0.499	-77.94297	-0.731	0.439	0.669
twist angle = 75°								
$\epsilon = 2.0$	-77.96751	+1.183	0.720	-0.502	-77.95716	-0.894	-0.459	-0.687
$\epsilon = 4.0$	-77.96744	+1.802	-0.764	0.428	-77.95601	-1.317	0.383	0.734
$\epsilon = 6.0$	-77.96795	+1.997	0.777	-0.403	-77.95553	-1.437	0.357	0.747
$\epsilon = 10.0$	-77.96818	+2.148	0.787	-0.382	-77.95510	-1.522	0.337	0.757
twist angle = 80°								
$\epsilon = 2.0$	-77.97099	+2.885	-0.856	0.165	-77.96672	-2.592	-0.137	-0.848
$\epsilon = 4.0$	-77.97211	+3.090	0.865	-0.108	-77.96513	-2.599	0	-0.855
$\epsilon = 6.0$	-77.97270	+3.143	-0.866	0.097	-77.96448	-2.575	0	0.856
$\epsilon = 10.0$	-77.97314	+3.185	-0.867	0.088	-77.96392	-2.551	0	0.857
twist angle = 85°								
$\epsilon = 2.0$	-77.97534	+2.191	-0.805	-0.340	-77.96954	-1.896	0.352	-0.805
$\epsilon = 4.0$	-77.97638	+2.762	0.843	0.235	-77.96823	-2.266	-0.248	0.840
$\epsilon = 6.0$	-77.97686	+2.895	0.851	0.208	-77.96766	-2.322	-0.846	0.221
$\epsilon = 10.0$	-77.97731	+2.991	-0.857	-0.188	-77.96714	-2.349	-0.201	0.851
twist angle = 90°								
$\epsilon = 2.0$	-77.97719	+1.781	0.774	0.417	-77.96811	-1.474	0.772	-0.423
$\epsilon = 4.0$	-77.97999	+2.465	-0.824	-0.313	-77.96858	-1.941	-0.319	0.817
$\epsilon = 6.0$	-77.97823	+2.647	-0.835	-0.285	-77.96802	-2.047	-0.291	0.828
$\epsilon = 10.0$	-77.97858	+2.778	-0.843	-0.263	-77.96751	-2.107	-0.269	0.835

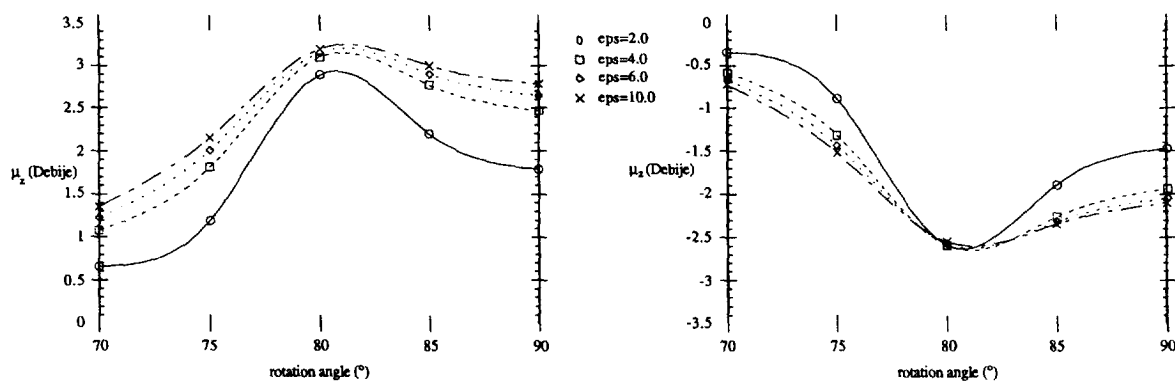


Fig. 2. Dipole moments of first (left plot) and second (right plot) excited state of ethylene.

twisting beyond the  $80^\circ$  point. From these findings, the conclusion can be made that for non-polar solvents the very weak electrostatic interactions with the solute are too small to sufficiently stabilize the polar state after formation. This can also be related to the total energies ( $E_{CI} + E_{DRF}$ ) of the investigated excited states. In comparison with the vacuum CI energies of the non-localized Z and V states, all lowest lying polarized states except for  $\epsilon = 2.0$  are stabilized relative to the vacuum lowest lying state (Fig. 3).

Another interesting observation when examining the CI coefficients of the excited states along the twisting coordinate is the switch of the dipole mo-

ment with positive sign from a "V state symmetry" ( $c_1 a^2 - c_2 b^2$ ) for twist angles  $\alpha \leq 80^\circ$  to a "Z state symmetry" ( $c'_1 a^2 + c'_2 b^2$ ), the state with the positive dipole moment always being the lowest in energy since they couple favorably with the external potential.

Fig. 4 shows that this can be seen in terms of an avoided crossing between these states, in which the solvent asymmetry provides the required coupling for the occurrence of the avoided crossing of the Z and V state. This coupling of the dipole moment with the state lowest in energy has, to the best of our knowledge, not been reported in earlier studies.

Finally, investigation of the energy gap between

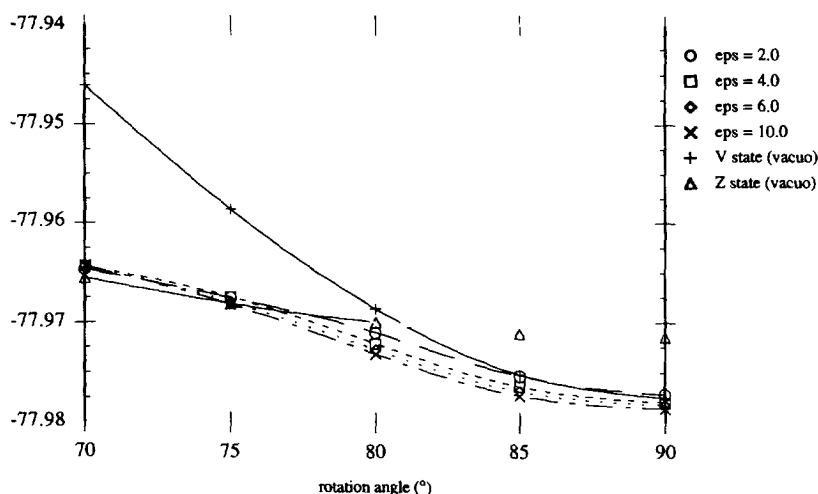


Fig. 3. Total energies of the lowest embedded states (dashed lines) and vacuum energies (solid lines).

the polarized excited states and the twisted ground state in the  $D_{2d}$  symmetry shows a significant lowering in energy of these states in comparison with the vacuum energies, which is in agreement with earlier made assumptions.

It should be reminded that the solvent model applied here is a simulation of an equilibrium situation, which especially for short living polarized states (lifetime within the limit of the relaxation time of the solvent) in fact leads probably to an overestimation

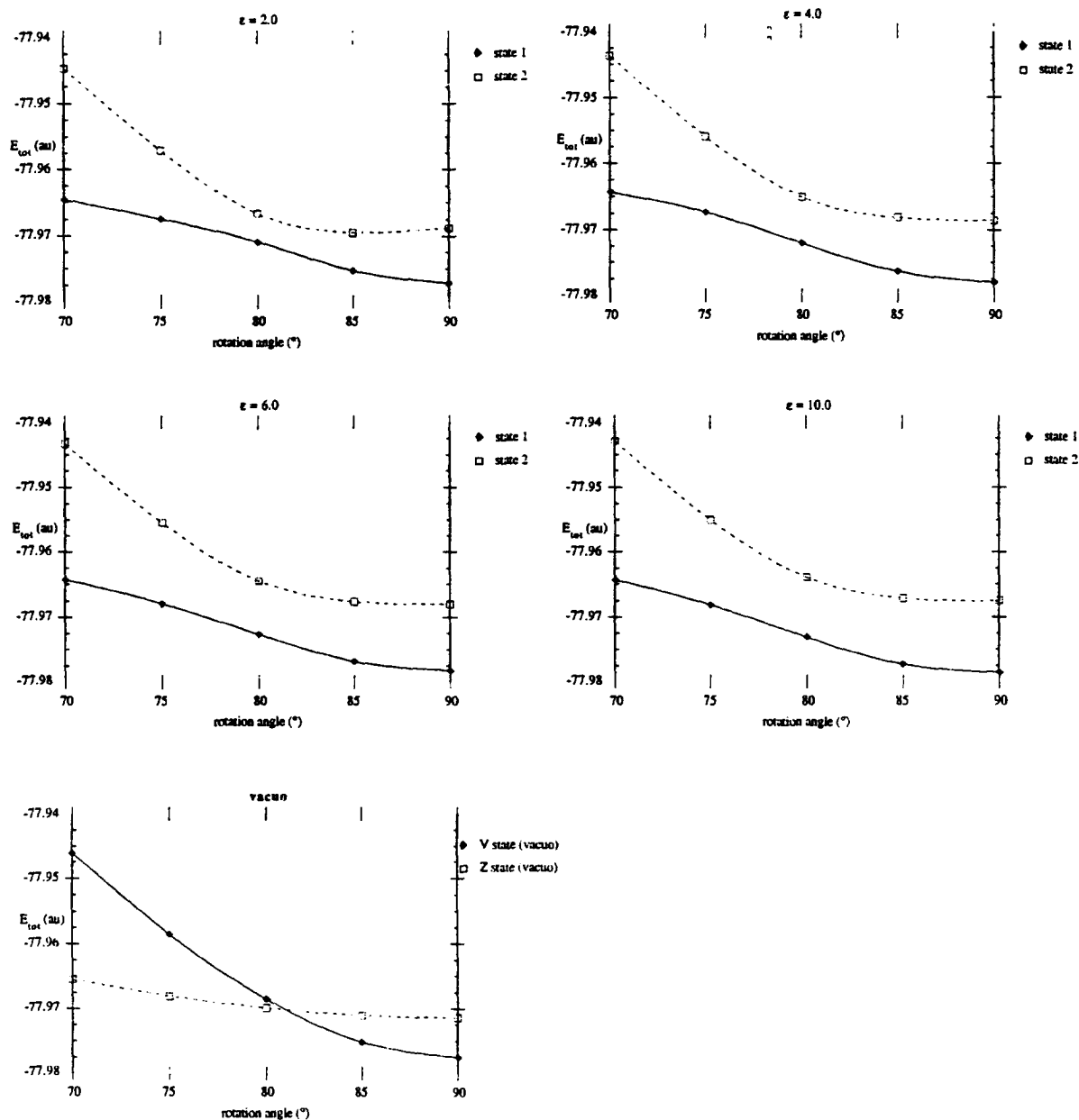


Fig. 4. Total energies of first two excited states of ethylene in various dielectrics.

of the stabilizing effect from the solvent. On the other hand, the distance between the ethylene charge distribution and the boundary is so large, that the reaction field will be too small to account for the total electrostatic part of the solvation energy [22].

DRF calculations in which discrete, classically described solvent layers with explicit molecular polarizabilities are used as a model for the first solvent shells have shown to give a quantitatively correct description of the various contributions in the solvent–solute interactions [24]. Such calculations are performed presently, and results will be presented in the near future.

Also it can be expected that symmetrical alkenes with stronger polarizable functional groups (like tetrachloro- or tetraphenylethylene) will show a more explicit behavior on the changes in solvent polarity. Our current investigations also focus on these possible effects.

#### 4. Conclusion

The presence of solvent layers with low symmetry around the twisted excited states of ethylene, here modeled by a dielectric in equilibrium with a prepared polarized state, effectively leads to large charge separations in the vicinity of the crossing intersection between these low lying excited (Z and V) states of ethylene. For dielectrics modeling (weakly) polar solvents, the energy of the lowest polarized excited state is stabilized relative to the pure Z and V states in vacuo. This is emphasized by the remaining dipole moments for those states on progressive twisting beyond the 80° point. The strong decrease in dipole moment on progressive twisting, together with the lack of stabilization of the polar state for a dielectric with  $\epsilon = 2.0$  suggests that a relatively strongly polar compound in the various contributions of the solvation stabilization is needed to trap the polarized states in the near perpendicular geometries of the ethylene. Better DRF calculations, i.e. involving discrete solvent models with explicit group polarizabilities will be performed to verify these suggestions.

The lowest lying polarized state switches from V to Z symmetry around the 80° twisting point of the central bond (the crossing region of the Z and V in

vacuo potentials), which is in nice agreement with earlier findings. The dipole moment of both states changes from sign when the avoided crossing has taken place. This change in electronic behavior for an excited state with given symmetry has not been observed before.

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