

Effective Polarity of Frozen Solvent Glasses in the Vicinity of Dipolar Solutes

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Abstract: The polarity of frozen organic solvent glasses is found to be substantially larger than that of liquid solvents at room temperature. The extent of this increase depends on the dipolar character of both the solvent and solute as observed in differences in the shifts of the absorption spectra of two different classes of solvent polarity indicator dyes in a number of different frozen solvents. These findings cannot be explained solely by contributions from the contraction of the solvent at lower temperatures. Instead, the data are consistent with a model in which the local solvent organization around the solute increases as the temperature is lowered and depends on the dipolar properties of the solvent and solute. This ordering is preserved when the solvent freezes and leads to a much larger *effective* polarity in the vicinity of the solute that is not reflected in measurements of bulk solvent properties. Because this *effective* solvent polarity can affect electronic properties as well as reactivity of the solute, these results may have significant implications for the design of complex molecular systems in solid solution and models for protein function.

Introduction

Although solvent polarity is among the most widely used and useful concepts in chemistry (see refs 1–7 for reviews), there has been surprisingly little consideration of the changes in polarity associated with lowering the temperature and the formation of optical quality frozen glasses. Frozen solvent glasses are of widespread use in spectroscopy to give enhanced spectral resolution or to perform hole burning, and solid polymeric matrixes are often used as host materials in, for example, optical devices. Ordered solvent matrixes are an essential feature of biological systems, e.g. the constellation of amino acids and ordered water molecules in the vicinity of an enzyme active site. It is well established that the solvent polarity in the liquid state increases with decreasing temperature;^{4,6,8–15} however, nearly all studies of polarity have been limited to liquids far above their glass transition temperature.¹⁶ In the course of studies of the electronic structure of donor–acceptor polyenes with Stark spectroscopy,^{17,18} performed with the solute

dissolved in a variety of frozen glass matrixes, we noticed striking changes in the absorption spectra when the solvent was frozen compared with liquid solutions at room temperature. To make a quantitative connection between the electrooptic properties deduced from Stark spectroscopy in the solid state and those derived from nonlinear optical measurements in the liquid state, a meaningful solvent polarity scale for frozen solvents is required. In the following we demonstrate that the *effective* solvent polarity around a dipolar solute can increase tremendously as the temperature is lowered and a glass forms.

To date, no generally agreed upon definition of the term solvent polarity has emerged. In the broadest and most general sense the solvent polarity can be viewed as the sum of all interaction forces between a solute and the surrounding solvent molecules.⁶ These interactions can be described by two parameters characterizing the electronic structure of the solvent and solute, the dipole moment μ , and polarizability α , leading to four interaction categories:⁴

Solute	Solvent	dipole moment μ	polarizability α
dipole moment μ		dipole – dipole interactions	dipole – induced dipole interactions
polarizability α		solvent Stark effect	dispersion forces

Theoretical expressions for these four interaction categories

(16) The only other investigation (ref 13) of solvent polarity in rigid solvent matrixes we are aware of did not address this question. In fact, the authors of this study assumed a priori that a liquid solvent and a frozen glass will have an identical distribution of solvent molecules around the solute and thus attributed the observed increase in polarity exclusively to variations in the solvent dielectric constant.

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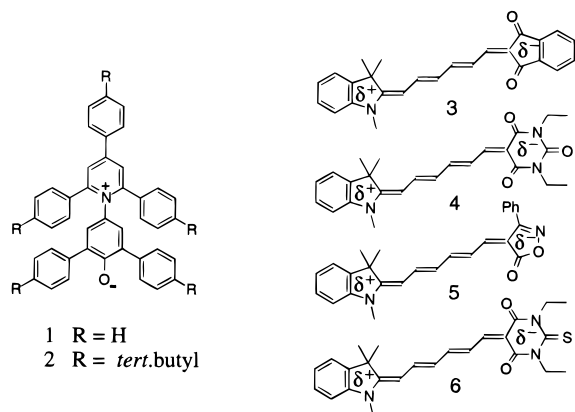


Figure 1. Chemical structures of the compounds used in this study.

usually employ a model that describes the interaction of an individual solute molecule with the reaction field created by the surrounding solvent, i.e., a microscopic model of the solute is combined with a macroscopic model of the solvent. It is difficult to separate the contributions based on experimental results as all are expected to have a similar dependence on the strength of the reaction field.

Most solvent polarity scales are empirical and are based on kinetic, thermodynamic, or spectroscopic observables of certain reference reactions.⁶ Significantly, different empirical solvent polarity scales have been shown to be well correlated with each other,^{3,5-7,14} pointing to the existence of an underlying common feature. Empirical solvent polarity scales based on spectroscopic measurements usually employ changes in the absorption maximum of an indicator dye in different solvents (solvatochromism). This effect originates from the higher degree of orientation of polar vs nonpolar solvent molecules around the dipolar solute ground state and the change in dipole moment, $\Delta\mu$, during transition to the Franck–Condon excited state. Such spectroscopic methods have been used to demonstrate that the solvent polarity of a liquid increases upon lowering the temperature. This has been attributed to an increase of dipolar interactions between solvent and solute^{8,10} and has also been shown to be correlated with the temperature dependence of the solvent dielectric constant, ϵ_r .^{4,9,11,12,15} Steck and Richert investigated the polarity of 2-MeTHF between room temperature and temperatures just above the glass transition using the well-characterized solvent polarity indicator dyes **1** and **2** (cf. Figure 1).¹⁵ The authors focused their analysis on the upper temperature range where they were able to fit the observed increase in polarity as the temperature decreased using the mean spherical approximation model, an extended continuum model. In this temperature range the authors linked the increase in polarity to the properties of the bulk solvent as described by the solvent dielectric constant. Interestingly, below about 180 K, they observed a marked increase in solvent polarity that deviated dramatically from this model. They attributed this deviation to some factor that reflects the greatly increased solvent viscosity in this temperature region. In the current work we extend these observations for the same system through the glass transition temperature and examine several other solvents and solvent polarity indicators to determine whether this deviation is general. This comparison leads to a qualitative interpretation of the origin of the large effective polarity increase.

Two main differences between an organic liquid solvent and a low-temperature viscous solvent or frozen solvent glass are immediately obvious: the solvent contracts upon lowering the temperature and thermal motions of the solvent molecules are greatly reduced. Contraction affects the solvent–solute interac-

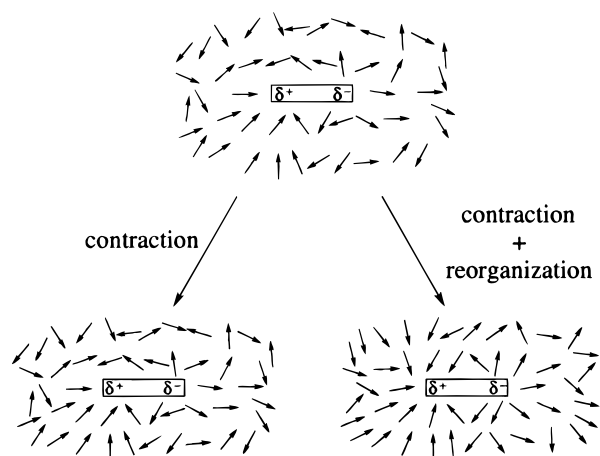


Figure 2. Two limiting models for the behavior of the solvent molecules immediately surrounding the solute as the temperature is lowered. Left: The solvent contracts but the orientations of the solvent molecules around the solute remain unchanged. Right: The solvent contracts and the solvent molecules reorient in the electric field created by the charges and partial charges of the solute. When the solvent freezes, this solvent organization is frozen in.

tions because all four interaction types fall off with the sixth power of distance. In a polar solvent the interaction forces are quite large leading to partial ordering of the solvent around a solute molecule, depending on the polarity of both solute and solvent. At low temperatures the viscosity of the solvent increases drastically and thermal motions are reduced, thus the relative weights of the interaction forces between solvent and solute increase. Two limiting models can be visualized (cf. Figure 2):

(1) The distribution of solvent molecules around a solute at room temperature is frozen in as the temperature is lowered and the glass forms. Any increase in solvent polarity is only due to the solvent contraction, and the relative contributions from each interaction type should remain the same as in a low-viscosity solvent. The observed temperature dependence is predicted to correlate with the temperature dependence of the solvent's bulk properties, e.g. its dielectric constant, as has been shown for liquid solvents far above their glass transition temperature.^{4,9,11-13,15}

(2) As the temperature is lowered, the solvent molecules in close proximity to the solute become more oriented to increase their interactions with the solute (i.e. they adopt a lower energy configuration), and this enhanced local organization is then frozen in. This would cause a pronounced increase in polarity in the region immediately surrounding the solute molecule. This increase in solvent polarity would not correlate with the bulk properties of the solvent because it only occurs locally. We denote this local orientational polarization effect the *effective* polarity of the frozen solvent in the vicinity of the solute.

These models lead to testable predictions that can be compared with experimental data. Contrary to the first model, the second model predicts that the magnitude of the increase in polarity should depend explicitly on the particular solvent/solute combination. For example, a very polar solvent is already highly oriented around a dipolar solute in the liquid state, and this orientation cannot increase as much upon lowering the temperature as for a less polar solvent. A solvent of intermediate polarity, which in the liquid phase exhibits less orientation around the solute, should exhibit a larger increase in polarity as the temperature is lowered. A nonpolar solvent should again display less of an increase in polarity if the solute–solvent

Table 1: Absorption Peak Location of **1** and **2** in Four Different Glass Forming Solvents of Different Polarity at Room Temperature (298 K, liquid solution) and 77 K (frozen glass)

compd no.	solvent	$\bar{\nu}_{\max}(298\text{K})^a$ [cm^{-1}] (liquid solution)	$\bar{\nu}_{\max}(77\text{K})^b$ [cm^{-1}] (frozen glass)	$\Delta\bar{\nu}_{\max}$ [cm^{-1}]
1	EtOH	18100	21000	2900
1	2-MeTHF	13000	17500	4500
2	EtOH	17900	20500	2600
2	2-MeTHF	12900	17100	4200
2	toluene	12000	15700 ^c	3700 ^c
2	MCH ^d	11000	15300	4300

^a Experimental error ± 100 cm^{-1} . ^b Experimental error ± 200 cm^{-1} .

^c For solutions of **2** in toluene shoulders were observed at 77 K at about 14500 and 16800 cm^{-1} . The spectral shift of these features with respect to the room-temperature absorption peak is 2500 and 4800 cm^{-1} , respectively. ^d For concentrated solutions of **2** in MCH additional features were observed around 13500 cm^{-1} both in the frozen glass and in liquid solution. These are likely due to the presence of aggregates.

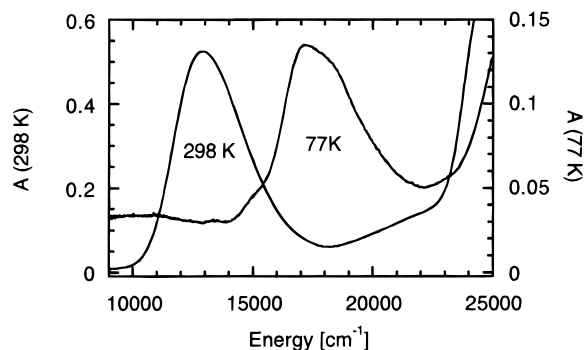
interactions are not strong enough to lead to a large degree of orientation. Similar effects would be expected for different solute molecules in the same solvent, e.g., a solute with large local charges should lead to a larger degree of reorientation of a moderately polar solvent than a solute where these charges are small. As will be outlined below, our results agree with the predictions derived from the second model and cannot be explained by the first model.

Experimental Section

Absorption spectra of two classes of solvent polarity indicator dyes (betaines **1** and **2**, and merocyanines **3–6**) were taken at room temperature (liquid solution) and at 77 K (frozen glass). The chemical structures of compounds **1–6** are shown in Figure 1. All spectra were taken on a Perkin-Elmer Lambda 12 UV-vis spectrophotometer. Dye **1** was purchased from TCI Chemicals and dye **2** was supplied by Prof. Reichardt (Marburg, Germany). Both compounds were used without further purification. All solvents (MCH, toluene, 2-MeTHF, EtOH)¹⁹ were dried over 3 Å molecular sieves. Spectra taken using solvents which had not been previously dried showed clear differences in the absorption peak location at 77 K (up to 600 cm^{-1}); however, these deviations are much smaller than the shifts observed upon freezing (vide infra). Compound **1** did not dissolve in MCH and solutions of **1** in toluene did not have a high enough optical density to obtain spectra with a sufficient signal-to-noise ratio at 77 K. For the low-temperature (77 K) absorption spectra, sample cuvettes with 25 to 100 μm path length were fabricated from microscope slides held apart by a thin Kapton spacer. For the low-temperature spectra of **2** dissolved in MCH cuvettes with 0.5 to 1 cm path length were used. The samples were frozen by immersing them in liquid nitrogen. The low-temperature absorption peak location was found to be independent of concentration within the experimental error, except where otherwise noted (MCH—cf. Table 1). Low-temperature absorption spectra of dyes **3–6** in 2-MeTHF were obtained under identical conditions as described above and have been reported previously.¹⁸ Room temperature absorption peak locations of these compounds in liquid dioxane, THF, CHCl_3 , CH_2Cl_2 , DMF, and DMSO²⁰ were taken from ref 17.

Results and Discussion

Figure 3 shows the dramatic effect of freezing the solvent on the absorption spectrum of **2** for the case of 2-MeTHF. Table 1 gives room temperature (liquid solution) and 77 K (frozen glass) absorption maxima for **1** and **2** in four glass-forming solvents of different room temperature polarity. The absorption peak locations of both **1** and **2** in 2-MeTHF at 77 K are

**Figure 3.** Absorption spectra of solutions of **2** in liquid 2-MeTHF at room temperature (298 K) and in a frozen 2-MeTHF glass at 77 K.

consistent with an extrapolation of the previously published temperature-dependent data just above the glass transition.¹⁵ The commonly used $E_T(30)$ solvent polarity scale^{6,7} is based on the extremely large solvatochromic shifts observed in the absorption spectra of **1** and its more hydrophobic derivative **2**. The room temperature absorption maximum of **1** can shift across the entire visible spectrum in different solvents leading to solution colors ranging from blue (H_2O , $\lambda_{\max} = 453$ nm) to red (CCl_4 , $\lambda_{\max} = 881.5$ nm). Dye **2** combines a similar solvatochromism with the advantage of increased solubility in nonpolar solvents.²¹ Because the dipole moment in these dyes decreases upon excitation ($\Delta\mu < 0$), negative solvatochromism is observed (a hypsochromic shift). The large hypsochromic shift in absorption upon freezing solutions of **1** and **2** in all solvents thus demonstrates a large increase in the effective polarity of the frozen solvents compared to their liquid state at room temperature.

The gas-phase absorption maximum of **2** has been estimated to be approximately 10 500 cm^{-1} .¹⁵ Since dispersion interactions will usually cause a bathochromic shift,²² at room temperature in the less polar solvents (especially MCH) the dipolar interactions cannot be much larger than the dispersion forces. The large hypsochromic shift observed upon freezing thus points to a dominating increase of the dipolar interactions rather than to a parallel increase of all interaction forces. The smallest spectral shift upon freezing was observed in EtOH, where the dipole-dipole interactions are already very strong at room temperature. If the origin of the observed spectral shifts upon freezing were solely the contraction of the solvent (first model), one expects the largest hypsochromic shift for EtOH, contrary to what is observed. Both observations, on the other hand, are in accord with the second model.

The structures of the merocyanine dyes **3–6** (cf. Figure 1) differ substantially from that of the betaine dyes **1** and **2**. In particular, the ground-state charge separation is smaller in these dyes than in **1** and **2**, i.e., the nitrogen and oxygen atoms in **1** and **2** carry a full positive and negative charge, respectively, while in **3–6** only partial charges, δ^+ and δ^- , are present at opposite ends of the polyene bridge as illustrated in Figure 1. The absorption maxima of **3–6** can also be used as a measure of solvent polarity, and Figure 4 shows the differences in the room temperature absorption maxima for **3–6** with respect to that observed in a frozen 2-MeTHF glass at 77 K [$\Delta\bar{\nu} = \bar{\nu}(\text{liquid solution}) - \bar{\nu}(\text{frozen 2-MeTHF})$]. The seven liquid solvents are displayed in order of increasing room temperature

(19) MCH = methylcyclohexane; 2-MeTHF = 2-methyltetrahydrofuran; EtOH = ethanol.

(20) THF = tetrahydrofuran; DMF = dimethylformamide; DMSO = dimethyl sulfoxide.

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(22) This is clearly expected for molecules with a positive change in polarizability, $\Delta\alpha$, between ground state and excited state, but has also been proposed to be generally true. See ref 2.

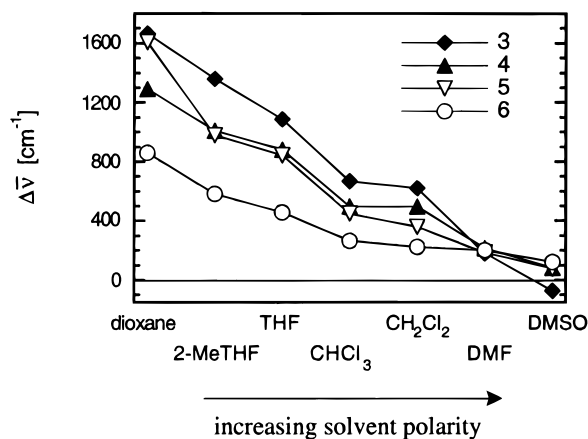


Figure 4. Difference in room temperature (liquid solution) absorption peak location with respect to that observed in frozen 2-MeTHF solutions for **3–6** in seven different liquid solvents: $\Delta\bar{\nu} = \bar{\nu}$ (liquid solution) $- \bar{\nu}$ (frozen 2-MeTHF solution). Room temperature absorption peak locations for **3–6** in solvents other than 2-MeTHF were taken from ref 17.

polarity. The slopes of these $\Delta\bar{\nu}$ vs polarity curves are different due to the different magnitudes of $\Delta\mu$ for the compounds [$\Delta\mu(\mathbf{3}) > \Delta\mu(\mathbf{4}) \approx \Delta\mu(\mathbf{5}) > \Delta\mu(\mathbf{6})$].¹⁸ It is observed that all four curves intersect at a polarity corresponding to that of liquid DMF at room temperature.

Depending on the polarity of the solvent, a merocyanine dye will adopt a more or less dipolar ground-state structure: a polar solvent shifts the ground state toward greater charge separation, while a nonpolar solvent shifts it toward a less polar structure.^{17,18,23–26} This is reflected in the solvent dependence of both β (the second-order nonlinear optical coefficient) and $\Delta\mu$ for these compounds. The two are connected through the two-level approximation which predicts that β is proportional to $\Delta\mu$. This approximation gives good estimates for β for this class of compounds,^{27,28} but we found that the measured values of β obtained in liquid solutions and $\Delta\mu$ determined in a frozen 2-MeTHF glass by Stark spectroscopy for **3–6** were in good agreement *only* if the effective polarity of the frozen 2-MeTHF was assumed to be approximately that of liquid DMF.¹⁷ It is significant that a similar result is obtained from the solvatochromic shifts of compounds **3–6** (cf. Figure 4).²⁹ Thus, if the solute molecule is one of the merocyanine dyes **3–6**, frozen 2-MeTHF has an *effective* polarity corresponding to liquid DMF, while for **1** or **2** the *effective* polarity of frozen 2-MeTHF is much larger and close to that of liquid EtOH. For comparison, the absorption maxima of **1** and **2** in liquid DMF are located at 15 100 and 14 935 cm^{-1} , respectively.^{7,21} The shift upon freezing of the absorption maxima of **1** and **2** in 2-MeTHF thus is more than 2000 cm^{-1} larger than would be expected if the

frozen 2-MeTHF surrounding them had an *effective* polarity corresponding to liquid DMF. This result, again, cannot be explained by the first model, but corresponds exactly to the predictions derived from the second model.

The large hypsochromic shifts upon freezing observed for solutions of **2** in the less polar solvents toluene and MCH are surprising. For weak solvent–solute interactions the second model predicts a small increase in *effective* solvent polarity upon freezing. While some uncertainty exists for the case of toluene due to the limited solubility of the dye, a strikingly large hypsochromic shift of 4300 cm^{-1} is observed for **2** in MCH upon freezing (cf. Table 1). In this case the formation of aggregates as the temperature is lowered and the glass forms may complicate the picture. We were able to observe aggregates both in liquid and frozen solution at high solute concentrations (cf. Table 1) at a position about 2500 cm^{-1} blue-shifted from the room temperature absorption peak location. If the 4300 cm^{-1} shift observed upon freezing of a more dilute solution were due to aggregate formation during the freezing process, this aggregate would have to be quite different from the aggregate that is present at higher concentrations of the dye. On the other hand, the large observed shift can also be seen to be in accord with the other observations, suggesting the presence of large dipolar solvent–solute interactions. The relevant interactions are local and even a solvent molecule that lacks an overall dipole moment has local bond dipole moments that can give rise to substantial dipole–dipole interactions as has been observed for octatetraene dissolved in *n*-hexane.³⁰ Another well-documented example is the interaction of a nonpolar solvent (polyethylene) with a nonpolar solute (terrylene) where a substantial induced dipole moment is caused by local bond dipole moments.³¹

In summary, as the temperature of a solvent approaches its glass transition temperature the increase in solvent polarity around a dipolar solute can no longer be explained exclusively by changes in the bulk properties (e.g. contraction) of the solvent. This deviation was already noted by Streck and Richert¹⁵ for **1** and **2** in 2-MeTHF above the glass transition temperature and the deviation increases still further when 2-MeTHF is frozen; large differences between room temperature and frozen solvent are observed for several other solvents as well. The observed additional increase in *effective* solvent polarity beyond that expected by contraction is large, and its dependence on the particular solvent/solute combination is consistent with what would be expected if the solvent molecules in close proximity to the solute become more organized as thermal motions decrease, leading to an increase in dipolar interactions between the solvent and solute. The increase in the viscosity of the solution also creates a significant barrier for any reorientation process and this is locked in as the solvent freezes. The extent of the local increase in polarity as described in this paper thus should also depend on the rate of cooling during glass formation, and it would be interesting to compare our results with those which one would obtain using ultrafast cooling methods.³²

These results have broader implications for Stark measurements of small molecules in frozen media, especially for ionic transition metal complexes^{33–38} and molecules whose ground-state electronic structure depends on the solvent polarity such

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(29) Interestingly, the four curves shown in Figure 3 intersect at $\Delta\bar{\nu} \approx 200 \text{ cm}^{-1}$ and not at zero, as would be expected if the frozen 2-MeTHF and liquid DMF had exactly the same effective polarity. As discussed earlier, one of the main differences between liquid and frozen solvents is the contraction upon freezing, and we can speculate that the 200 cm^{-1} difference might be caused by the increase of dispersion forces due to this contraction.

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as **3–6**.^{17,18} The difference between the externally applied electric field and the internal field present at the position of the studied molecule (the local field correction) is usually calculated by using the bulk dielectric constant of the frozen medium, i.e., a continuum model of the solvent is used.³⁹ Our results indicate that this approach is not sufficient. Locally, the structure of the solvent around the solute in the glassy state corresponds to a more ordered dielectric, and the magnitude of the local field correction thus might deviate substantially from estimates obtained from a simple continuum model, especially if based on values of the dielectric constant obtained from bulk capacitance measurements.^{36,37}

These results also have consequences for the design of molecular charge-transfer systems embedded in solid or ordered matrixes.^{40,41} If the local environment of an electron donor and acceptor pair were adapted to the charge-separated state, the efficiency of the charge-transfer process should increase compared to that in a disordered matrix (an ordered matrix will have little effect on the neutral state prior to charge separation). Therefore, it may be possible to increase the electron-transfer efficiency and to imprint this solvent organization by freezing

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in the charge-separated state. An interesting example of this is found in the long-distance electron-transfer reactions in photosynthetic reaction centers where freezing the sample in the charge-separated state freezes in structural changes in the protein “solvent”, which facilitates subsequent low-temperature charge separation reactions.⁴² These ideas are similar to the transition state analogue model in enzyme catalysis. A preexisting organization and constraint of the protein solvent may also play a significant role in determining the efficiency and directionality of the ultrafast initial electron-transfer steps in photosynthesis.⁴³ In proteins the solvent of an embedded chromophore or catalytic center consists primarily of constrained amino acid residues and, in some cases, relatively immobilized water, so the polarity is likely to change less as the temperature is lowered than for the same chromophore or a model system for the catalytic center in a simple unconstrained solvent. The absence of surrounding solvent organization similar to that found in proteins may well be why so many models of enzymatic catalysis that contain the essential chemical constituents nonetheless fail to achieve catalytic efficiencies comparable to those of real enzymes.

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