

Figure 3. Time-of-flight photoelectron spectrum of the HCCCD₂ radical following 10.49-eV photoionization, with the application of a 0.4-V dc retarding voltage (see Experimental Section). The electron energies for peaks a-h are listed in Table I.

TABLE I: Photoelectron Peak Energies (KE) and Spacings for HCCCD₂.

peak	KE, ^a eV	rel intensity	ΔE , ^b cm ⁻¹
a	1.81	1.0	
b	1.56	0.9	2020
c	1.33	0.7	1850
d	1.15	0.5	1450
e	1.00	0.4	1210
f	0.90	0.4	810
g	0.81	0.3	730
h	0.73	0.2	650

^a ± 0.02 eV. ^b ± 150 cm⁻¹.

energy photoionization are under way to further characterize this excited state.

A higher resolution PES of HCCCD₂ is shown in Figure 3. This spectrum was obtained with the use of a dc retarding potential to increase resolution, as described above. Peak positions, differences, and relative intensities are listed in Table I. The peaks appear to be due to a single vibrational progression in the cation, showing a smooth Franck-Condon envelope with peaks decreasing in intensity and frequency. The frequencies and relative integrated

peak intensities were obtained by least-squares deconvolution of the observed photoelectron spectrum using an instrument function fitted to a quadratic. Inclusion of additional peaks to simulate unresolved, lower frequency vibrations improved the fit, but did not significantly alter the positions or relative intensities of the main peaks. The most striking feature in the observed vibrational progression is the large anharmonicity. The spacing between the first and second bands is 2020 cm⁻¹, which decreases to 650 cm⁻¹ for the seventh and eighth bands. A fit of the vibrational progression to a Morse potential gives $\omega_e \approx 2270$ cm⁻¹ and $x_e\omega_e \approx 130$ cm⁻¹.

We tentatively assign the active vibration to a symmetric CC acetylenic stretch in propargyl cation. The harmonic frequency agrees well with the ab initio value¹² of 2194.6 cm⁻¹. The alternate assignment to a C-D stretch can be discounted because the dissociation limit for such an anharmonic C-D bond, estimated from $x_e\omega_e$, would be ≈ 1 eV. This would give a $\Delta H_f(\text{HCCCD}^{++})$ 3 eV below the accepted value²¹ and would suggest that we should observe the HCCCD⁺⁺ daughter ion in the 10.49-eV photoionization mass spectrum. Inspection of Figure 1 shows no such ion dissociation.

The large anharmonicity of a CC acetylenic stretch may be due to strong configuration mixing induced by changes in bond length. The harmonic frequency in the cation suggests a predominant acetylenic, rather than allenic, character for propargyl cation, and, by the Franck-Condon factors, propargyl radical as well, at their equilibrium geometries. Increased contribution by an allenic structure as the C≡C bond is stretched could result in a reduced force constant and the large anharmonicity.

Vibrational structure was not clearly discernible in the PES of HCCCH₂ and DCCCH₂, presumably because of spectral congestion by unresolved CH₂ modes. The improved resolution in HCCCD₂ is likely due to the reduction of these frequencies by deuteration.

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Field Strength Dependence of Dielectric Saturation in Liquid Water

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Molecular dynamics simulations have been used to study the field strength dependence of dielectric saturation in liquid water. The equilibrium polarization response in a box containing 216 water molecules is followed as a function of the magnitude of an applied electric field in a series of simulations. The polarization is approximately linearly proportional to the applied field strength up to fields $\sim 4 \times 10^8$ V/m. Large nonlinear effects associated with dielectric saturation are observed between 1×10^9 and 2×10^{10} V/m, at which point the dielectric response is fully saturated. Additional simulations of solvated ions and dipoles show that the hydration layer waters are orientationally saturated even though the hydration free energies of these solutes are closely approximated by continuum solvent formulas. While hydration free energies are relatively insensitive to dielectric saturation, many other solute-solvent properties will be sensitive to such effects.

The study of the dielectric properties of aqueous solutions has a long and venerable history.¹ Yet there remains considerable uncertainty regarding the relative importance of dielectric satu-

ration effects on either solvation energies or dielectric screening of electrostatic interactions. On the one hand, the electric field strengths at the surface of ions are very large, exceeding 10^{10} V/m. This leads to the expectation that dielectric saturation will occur in solvent regions close to the ion.²⁻⁷ It has been argued, however,

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that the high fields will cause electrostriction which will diminish the effects of saturation.^{8,9} Within the continuum picture, many models have been proposed to account for dielectric saturation by the introduction of a spatially varying dielectric constant.^{4,6,10} Modern analysis is concerned with the molecular origins of dielectric screening. In this context, it is necessary to consider the interplay between electrostatic and nonelectrostatic forces and also to consider the effects of the magnitudes and geometries of the electrostatic fields on dielectric properties. Statistical mechanics methods based on computer simulations provide potentially powerful tools for quantitating dielectric saturation effects in aqueous solutions.¹¹ In this Letter we report the results of computer experiments in which molecular dynamics simulations are used to study the field strength dependence of dielectric saturation in liquid water. The equilibrium polarization response in a box of water molecules is followed as a function of the magnitude of an applied electric field in a series of simulations.

Molecular dynamics simulations have been carried out using the SPC water model, consisting of a Lennard-Jones potential between oxygens and a Coulomb potential between all pairs of charged sites.¹² All simulations of the pure liquid were performed in a cubic box containing 216 water molecules with dimensions 18.6 Å on a side, corresponding to a density of $\rho = 1.0 \text{ g/cm}^3$. A spherical cutoff was applied to the interactions between water molecules further than 8 Å apart; to account for the interactions of a water molecule with solvent beyond the cutoff, a reaction field correction term was included in the potential.¹³ An electric field along the z direction was modeled by adding a term to the potential of the form $\sum(\mathbf{E}\mu)$, where μ is the dipole moment of a water molecule and the sum is over all waters in the box. The simulations were carried out at a temperature $T = 298 \text{ K}$. Additional simulations of model ions and dipoles in water were performed. In these simulations, the solute was modeled as a spherical cavity with fixed Lennard-Jones parameters ($\epsilon = 0.118 \text{ kcal/mol}$, $\sigma = 4.417 \text{ Å}$) corresponding to a chloride ion.¹⁴ The ion (dipole) was modeled by placing a charge (point dipole) at the center of the cavity. The charge (dipole moment) was varied in different simulations. The solvation free energies of these solutes were calculated by the free energy perturbation simulation method.¹¹

Simulations of the neat liquid have been completed over a range of applied electric fields between 0.5×10^8 and $2.2 \times 10^{10} \text{ V/m}$. The polarization response of the water to the applied field is plotted in Figure 1. The polarization is calculated by dividing the net dipole moment in the box at each configuration by the volume and averaging. The polarization increases linearly with the electric field up to applied fields of $\sim 4 \times 10^8 \text{ V/m}$; the nonlinear response at higher fields can be clearly seen in the plot. By $E = 5 \times 10^9 \text{ V/m}$, the dielectric response is almost completely saturated. In the linear regime, the slope of the curve can be used to calculate the dielectric constant.¹⁵ The dielectric constant for the SPC

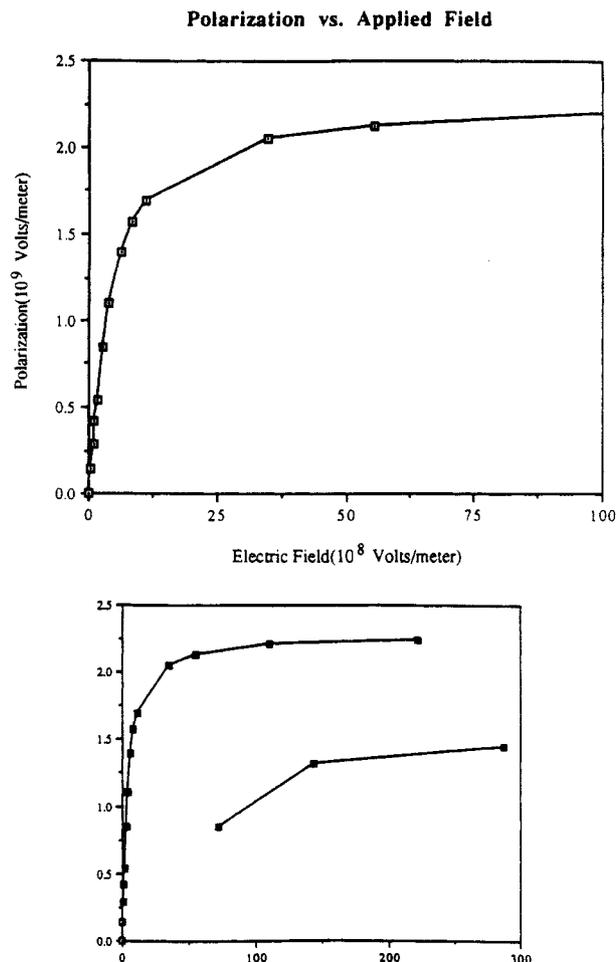


Figure 1. The polarization P of water in the presence of an external field vs the electric field strength (white box symbols). The polarization is in units of 10^9 V/m on the left vertical axis. (Note: the ordinate in figs. 11 and 13 of ref 16a is incorrectly labeled; $(4\pi/3)P$ is plotted instead of P in these figures.) The electric field strength is in units of 10^8 V/m . Inset: the average cosine made by the water dipoles in the first hydration shell around a (chloride) anion with the radial vector from the ion (black diamond symbols). The points correspond to three separate simulations with ion charge $-1/2$, -1 , and -2 . The electric field strength is ensemble-averaged over the first hydration shell. The polarization vs electric field strength (white box symbols) may also be read off the vertical axis in the inset using the relation $\langle \cos \theta \rangle = P(E)/P_{\text{tot}}$ where $P(E)$ is the average polarization in the presence of an external electric field \mathbf{E} and $P_{\text{tot}} = N^* \mu / V$, where N is the number of water molecules and μ is the dipole moment of a water molecule.

water model is calculated from the initial slope in Figure 1 to be $\epsilon = 70$, which is in agreement with the value calculated by an entirely different simulation method¹⁶ and close to the experimental value for water.²

The fields at the surface of ionic and dipolar solutes can easily exceed 10^{10} V/m . For example, the electric field at the surface of a chloride ion is $\sim 3 \times 10^{10} \text{ V/m}$, while at the surface of a small dipolar solute like formaldehyde ($\mu = 2.4 \text{ D}$) it is $\sim 3 \times 10^9 \text{ V/m}$. From the field strength dependence of the polarization response of water (Figure 1), it would appear that the hydration sphere around ionic and dipolar solutes would exhibit dielectric saturation. Computer simulations can be used to study this effect. The dielectric response corresponds to the tendency of waters to align their dipoles along the electric field direction. Defining θ to be the angle formed between a water dipole moment vector and the direction of the electric field generated by the solute, the dielectric response of waters in the first hydration shell of an ion or dipole can be obtained by computing the average value of θ in the first

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TABLE I: Comparison of Hydration Free Energies^a of a Model Dipolar Solute Obtained from Continuum and Molecular Methods

dipole moment ^b	continuum ^c	molecular ^c	dipole field ^d
2.2	-9.5	-7.8	2.4×10^9
4.4	-38.1	-37.2	4.8×10^9
8.8	-152.5	-158.4	9.6×10^9

^aEnergies in kcal/mol. ^bDipole parameters: μ is measured in debyes. ^cSolvation free energies calculated from continuum solvent model using the Onsager formula;^{1c} calculated from molecular solvent model using free energy perturbation simulations.¹¹ ^dElectric field in units of volts/meter calculated at a distance of 2.3 Å from the dipole origin.

shell. The orientational dielectric saturation of waters in the first hydration shell of a spherical ion ($R = 2.2$ Å) is plotted in Figure 1 as a function of the field strength, as the charge on the ion is varied between $-1/2$ and -2 in a series of simulations. Similar results are obtained for the dielectric saturation in the first hydration shell of a model dipolar solute as the dipole moment is varied between 2.2 and 8.8 D. The small rate of change of the orientational polarization with increasing charge is indicative of strong dielectric saturation effects at the ion surface. That the maximum value of the polarization is ~ 0.6 instead of 1.0 reflects the competition between the orienting electric field of the ion and the specific anisotropic interactions between the first-shell waters and its nearest neighbors. A recent analysis of the orientational response at the surface of a small cation ($R = 0.95$ Å) to increasing charge reported by Jayram et al.^{9a} is qualitatively consistent with the present results, although the maximum polarization of the hydration layer is greater for the smaller cation.

The results presented in Figure 1 imply that continuum treatments of solute-solvent interactions that use a bulk water dielectric constant to characterize the dielectric response will fail for solutes that generate electric fields in the solvent region which exceed $\sim 10^9$ V/m. Recent studies have shown, however, that calculations of molecular solvation free energies based on con-

tinuum and microscopic treatments of water are in close agreement for many solutes.^{9,17} Indeed, we have now verified this result for neutral dipolar solutes with very large dipole moments (up to 8.8 D); the solvation free energies are listed in Table I. The apparent contradiction is resolved by noting that the continuum formulas for solvation free energies in high dielectric solvents are quite insensitive to dielectric saturation.^{1c} For spherical solutes the dielectric constant enters in the expression $(1/\epsilon - 1)$, so that a 10-fold decrease in the dielectric constant of water would only change the hydration free energy by 12%. Other dynamic and thermodynamic properties will be more sensitive to the dielectric saturation of water by solute electric fields.^{7,10,18} The existence of dielectrically saturated hydration shells around ions can significantly decrease the extent of the screening of the ionic interactions between ions in water. Limited information concerning these effects is available from recent computer simulations of the potentials of mean force (pmfs) between ions in water at relatively small ($R < \sim 6$ Å) ion separations.¹⁹ At these separations, the pmfs are highly structured and the minima and maxima are associated with specific solute-solvent configurations. Further work is required to clarify the spatial extent of dielectric saturation in the vicinity of solvated ion pairs.

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Supercritical Solubility of Solids from Near-Critical Dilute-Mixture Theory

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A recently derived asymptotic theory for Henry's constant near the critical point of a solvent is adapted to the description of the solubility of solids in supercritical fluids. When solubility data for several systems are examined in the manner suggested by the theory, all the experimental isotherms for a given system (with the exception of a few near-critical points where the deviations are attributed to finite-concentration effects) collapse onto a single curve that is linear over a substantial range of solvent densities. This work provides a theoretical justification for some often-noted empirical relationships between solubilities and enhancement factors and the density of the supercritical solvent.

Introduction

The use of supercritical fluids as solvents for extraction and other processes continues to attract interest.¹⁻³ Design and evaluation of supercritical fluid technology is often hampered by the difficulty of predicting and modeling the phase equilibria in these highly asymmetric systems. A variety of semitheoretical

approaches have been used (with mixed success) to model supercritical mixtures; a review is given by Johnston et al.⁴

For systems where the supercritical fluid is equilibrated with a solid, many workers⁵⁻¹⁰ have noticed a striking regularity in the

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