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# Electrons in Molecular Clusters: Microscopic Probes of Fluids

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The world is full of clusters: from clusters of quarks to metal and molecular clusters on surfaces and in molecular beams, from ion clusters in the atmosphere to stellar clusters in the galaxy. Perhaps it is in the natural order of things that electrons can be trapped in clusters too, to form an intriguing and novel class of charged species with well-defined physical and chemical properties and a kinetic lifetime that spans the period from a molecular rotation to diffusion-controlled reactions. In fact, the electron can be trapped in a wide range of media,[1] from crystals[2] and glasses[3] to fluids[4] and supercritical vapors,[5] and in each case the dynamics, energetics, and lifetime of the final species are rather different.

It is the purpose of this Account to focus on electrons in fluids, in particular polar fluids, where the formation and energetics of the localized electron are largely determined by the dynamical molecular structure and local dielectric properties of the host fluid.[6] Electrons trapped in rigid matrices are not subject to an environment of continually fluctuating potentials, which, from our perspective, shape much of the behavior of electrons in fluids.

Electrons residing in clusters can be viewed as microscopic probes of both the local liquid structure and the molecular dynamics of liquids.[7,8] We will develop this theme by first describing the physical properties of a system which appear following the trapping of a low energy electron and then by examining current theories of these excess electron quantum states. In a future paper we will discuss the dynamics of electrons in fluids as revealed through picosecond spectroscopy[6-10] and the time-dependent models, which describe the mechanisms of electron localization and solvation in clusters.[5,6-8,11]

The study of electrons in fluids has become an important area for the theoretical and experimental work on the electronic states of disordered systems.[5,12-14] We can study the evolution of a system from a single particle to a collective state. At what stage does a group of metal atoms conduct like a metal and when does a cluster of water molecules begin to behave like a liquid? The role of disorder in terms of density, energy, and configurational fluctuations permeates the study of electrons in fluids. There is a symbiotic relationship between the excess electron and its supporting fluid, one which demands an understanding of the local structure of the fluid prior to the addition of the electron. Not unexpectedly, such molecular details are seldom anticipated through a knowledge of only the bulk properties of a liquid.

Trapped electrons are ubiquitous in chemistry and now may be discovered in many fields. Their generation and remarkable chemical reactivity have been well documented[15-18] and will not be reviewed here. Of the numerous techniques available for injecting electrons into fluids, laser-induced photoionization of molecules[19] (see Figure 3) and photodetachment of negative ions have the virtue of being selective and imparting to the ejected electron a known kinetic energy, whereas the relativistic electron beams in pulse radiolysis[20,21] lead

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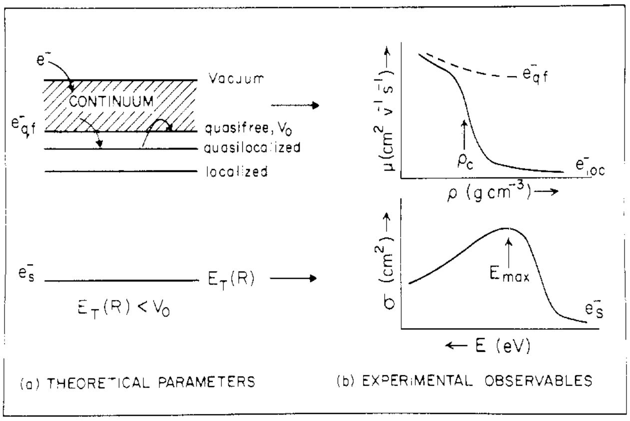

**Figure 1.** Relationship between theoretical parameters and experimental observations for the quasifree–bound transition of electrons in fluids. See text for discussion.

to extensive excitation and ionization of the molecular system under study. There are different advantages and unexpected complexities in both laser and pulse radiolysis techniques that deem them complementary, rather than mutually exclusive, approaches for the study of these short-lived species.

When a low energy electron is injected adiabatically[22] into a fluid, the electron rapidly becomes thermalized and remains delocalized to a degree determined by the features of the electron–molecule scattering potential in the fluid. The excess electron may then undergo one of several competing events, which ultimately lead to either the formation of a stable quantum state of the electron trapped in fluid, $e^-_s$, or to the appearance of a transient negative ion, $S^-$.

What simple, physical picture of $e^-_s$ is consistent with the now abundant data for electrons in polar fluids? The evidence collectively points toward a molecular model in which a delocalized electron is initially trapped within small molecular clusters, whose configuration relaxes under the influence of the electronic charge while the molecular structure grows.[23] We are not dealing with a solvated molecular ion but a cluster of anywhere between 4 to 12 molecules over which the excess charge is distributed. The inner molecules are locked into this configuration during the kinetic lifetime of $e^-_s$, which at 295 K ranges from $10^{-9}$ to $10^{-4}$ s for most liquids. We presume that the electron resides in a floppy cluster. There will be characteristic vibrations associated with the cluster as a whole, and molecules more loosely bound at the edge of the cluster will be in dynamic equilibrium with the molecules in the surrounding fluid.

To the initiated electron observer, the descriptions of excess electrons that have appeared in the literature of the past decade offer strong visual imagery and some intuitive feeling for the state of the electron, but other readers may be somewhat bemused by such terms as free, quasifree,[5,22] dry,[24] damp,[25] quasilocalized,[26] trapped,[3] and solvated[15] electrons. We will define and use the terms *quasifree*, *trapped*, and *solvated*, since in this sequence each term describes a relatively well-understood period in the development of the final quantum state, $e^-_s$.

Figure 1 illustrates the electron energy scheme. By a *quasifree* electron, we mean an electron moving as a plane wave in a continuum of states or the conduction band of the fluid (similar to electron conduction in nonpolar crystals) whose minimum energy is defined as $V_0$.[5,22] This energy is also the work function for electron injection into the fluid. In helium there is a barrier to injection and $V_0 = 1.3$ eV; for most other fluids $V_0 < 0$. All electrons pass through this high mobility conduction state prior to trapping in the fluid.

The *trapped* electron is localized, bound in a weak potential and considerably less mobile. A sudden drop in electron mobility is characteristic of a quasifree–bound transition. Trapped electrons in liquids exhibit far-IR absorptions, and these states are sometimes referred to as quasilocalized because, as the arrows in Figure 1 imply, thermal fluctuations in the fluid can promote the electron back into the continuum. Localized electrons of unexpectedly high mobilities fall into this group. In fact, as a general feature, disordered systems reveal a tail of localized states on the conduction band.[14]

In the absence of a competing chemical channel, the trapped electron ultimately becomes a *solvated* electron ($e^-_s$) of total energy $E_T(R)$ via induced molecular relaxation in the surrounding medium. The binding and transition energies of $e^-_s$ are usually higher, but not necessarily so, than those of the trapped electron. It is a sequence in *time* rather than binding energy which we have described, since the term *trapped* is frequently employed to described the final quantum state of $e^-_s$ in nonpolar fluids and low temperature matrices, where induced orientational relaxations clearly play a restricted role.

## Electronic Properties

**Mobility.** The transport properties of excess electrons in fluids, from helium and the rare gases to hydrocarbons and polar liquids, have stimulated extensive interest.[11-13,26-29] The electron mobility $\mu_e$ varies enormously depending on the density, molecular structure, and composition of the supporting fluid. In $^4$He $\mu_e$ is $2 \times 10^{-2}$ cm$^2$ V$^{-1}$ s$^{-1}$ at 4.2 K, in *n*-hexane $\mu_e = 0.09$ cm$^2$ V$^{-1}$ s$^{-1}$ at 295 K, in tributylamine $\mu_e = 2 \times 10^{-3}$ cm$^{2-}$ V$^{-1}$ s$^{-1}$ at 293 K, and in the normal alcohols $\mu_e$ drops to $10^{-3}$ to $10^{-4}$ cm$^2$ V$^{-1}$ s$^{-1}$ at 293 K. Normal ions have mobilities in the $10^{-4}$ range, with the exception of the proton and hydroxyl ion which give $\mu = 3.6 \times 10^{-3}$ and $2 \times 10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$, respectively.

The theory of electron mobility exists at various levels. Electron conduction in nonpolar crystals formed the original conceptual basis for theories of *quasifree* electron transport in liquids such as the rare gases. The low-field-mobility $\mu_e$ was predicted to be:[28]

$$\mu_e = \tfrac{2}{3}(2/\pi mkT)^{1/2} e_0 \Lambda \qquad (1)$$

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$$\Lambda^{-1} = 4\pi\bar{a}^2 nS(0)$$

where $\Lambda$, the mean free path for momentum transfer, is related to $S(0)$, the low momentum limit of the liquid structure factor, the scattering length $a$, and the number density $n$ of the liquid. Clearly the de Broglie wavelength of the electron must be less than $\Lambda$ for this approach to be valid, which may not always be the case, for example, in some hydrocarbons.

Most quantitative studies to data have been on helium, hydrogen, and the rare gases, where the details of the intermolecular potentials are better constructed. However, a wealth of experimental mobility data now exists for electrons localized in hydrocarbons, and more qualitative models have been proposed to account for the wide range of temperature-dependent $\mu_e$ and $V_0$ values. Electron migration is presently discussed in terms of a two-state (quasilocalized) model, a trap-hopping model and a trap-tunnelling model, in which the experimental $\mu_e$ reflects the residence time in either different states or different traps. Scattering, localization, and diffusion of electrons in various electronic states are treated in terms of the effective scattering potential $V(r)$ and its local fluctuations through density, configurational, and energy fluctuations in the fluid medium. Since the electron mobility $\mu_e$ varies as $a^{-2}$, and $a$ is a function of $V(r)$, in principle $\mu_e$ may reveal important information on scattering cross sections in the density regime where collective effects are a distinctive feature of the system.

Mobilities also naturally impinge on the interpretations of the very fast reaction rates of localized electrons with other molecules, including those instances in which there may be resonant negative ion states, while simultaneous mobility and absorption data provide invaluable clues as to co-existence of electrons in different molecular trapping sites in the fluid. Furthermore, by sampling a different range of energy and momentum transfer, the electron affords us a view of the dynamic structure of the liquid that is complementary to the range of $S(K)$ values set by depolarized light scattering and coherent neutron scattering.[30]

**Spectroscopy.** The optical absorption of electrons in fluids has long been their simplest signature. Whether in polar or nonpolar fluids, in low-temperature glasses or as F centers in alkali halide crystals, localized electrons all display broad and structureless bands, skewed to the high-energy side. Figure 2 illustrates such an ensemble. Whereas the host site of the excess electron in a crystal is an anionic defect in a well-ordered lattice, electrons in molecular fluids are typical of the electronic states of disordered systems. Nevertheless, the similarity in their absorption spectra motivated much of the early theoretical work on $e^-_s$ through polaron models.[31] With the wisdom of hindsight, the similarity reveals only the possibility of strong electron–phonon coupling in both cases.

The absorption maxima $E_{max}$ of electrons in polar fluids span the region from 0.5 to 2.6 eV. The position of the band can be predicted[32-34] from (i) the identity of the dipole comprising the inside boundary layer of the molecular trap and (ii) the steric facility with which the optimum number of molecules can cluster about the electron to form a compact structure. Studies of $e^-_s$ in binary systems[34] indicate that the spectra exhibit diverse dependences on the mole fraction of the components, $\chi_i$, but any theoretical interpretation is complicated by the need to first understand the solute–solute and solute–solvent interactions prior to the addition of the electron. The spectra and dynamics of $e^-_s$ in ROH/alkane systems apparently remain unperturbed until dilutions $\chi_{ROH} \leq 0.15$, indicating that the structural integrity of the cluster has been maintained.[8]

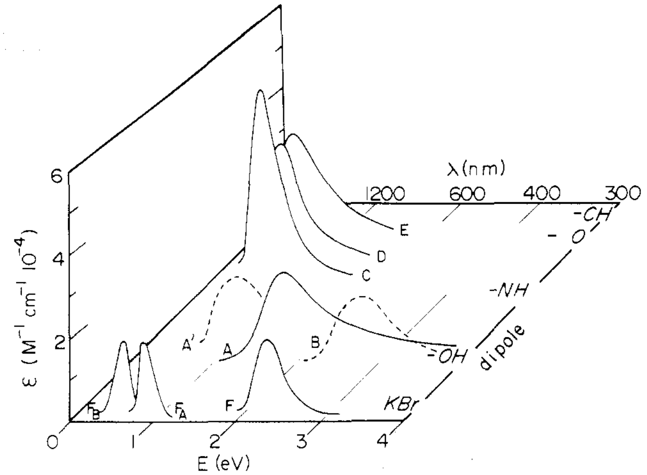

Figure 2. Optical spectra of localized electrons: intensity and energy of optical transition as a function of molecular dipole and liquid structure. (A) Normal alcohols, (A′) tertiary alcohols, (B) chelating alcohol, (C) ammonia, (D) ether, (E) alkane, (F) KBr F center. ($F_{A,B}$) absorption and stimulated emission from $F_A$(II) center in KBr.

All absorption bands undergo a gradual red shift with increasing temperature, consistent with the notion that the cluster molecules experience strong thermal fluctuations, weakening the electron–molecule interactions. Subjected to pressures of kilobars, $e^-_s$ exhibit a small blue shift, implying compression of the trap. We conclude from this and other evidence that variations in matrix, temperature, and pressure merely cause concomitant shifts in the whole band rather than revealing fine structure or specific changes in the line width and line shape.

The line widths ($\Delta$), historically the most awkward variable in the theory[1,22] of $e^-_s$ optical spectra, vary from 0.4 eV in ammonia to $\geq 1$ eV in alcohols, but the integrated absorption intensities or oscillator strengths are similar, $0.5 < f < 0.8$. Recent pulsed-laser studies of $e^-_s$ in alcohols provided the first direct measurements of the optical absorption coefficients ($\epsilon$) through a counterion technique.[35] These data are given in Table I, together with $\epsilon_{max}$ estimated from measurements of $G\epsilon$ in pulse radiolysis.[15,36] Typically, $\epsilon_{max} \sim 2 \times 10^4$ M$^{-1}$

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Table I
Selected Physical Properties of Localized Electrons in Polar Fluids

| | $e^-_{aq}$ [a] | $e^-_{ROH}$ [b] | $e^-_{amm}$ [c] | $e^-_{ether}$ [d] |
|---|---|---|---|---|
| $E_{max}$, eV | 1.73 | 1.80 ± 0.10 | 0.88 | 0.67 |
| $\epsilon_{max}$, $10^{-4}$ $M^{-1}$ $cm^{-1}$ | 1.85 | 1.1-2.0 | 50 | 2.9 |
| $\Delta$, eV | 0.93 | 1.1 ± 0.1 | 0.46 | 0.5 |
| $f$ | 0.66 | 0.5-0.8 | 0.75 | 0.71 |
| $\partial E/\partial T$, $10^3$ eV $K^{-1}$ | −2.9 | | −1.1 | −2 |
| $\partial E/\partial P$, $10^2$ eV $kbar^{-1}$ | −3.8 | −5 | −9 | |
| $\overline{V}$, mL $mol^{-1}$ | 7 | | 80 | |
| $\mu$, $10^3$ V $cm^{-2}$ $s^{-1}$ | 1.98 | 0.4-0.9 | 10 | |

[a] 298 K, ref 15, 36. [b] Methanol to undecanol, 298 K, ref 33, 34. [c] 225 K, ref 15, 36, 37. [d] Diethyl ether, 180 K, ref 36.

$cm^{-1}$ for most $e^-_s$, making this a strongly allowed electric-dipole transition.

Electrons solvated by the –OH dipole group exhibit the highest transition and binding energies, as seen in Figure 2. Within a homologous series of liquids, such as methanol to undecanol, the stable $e^-_s$ spectra[32,33] (A) are remarkably similar, $E_{max} = 1.8 \pm 0.1$ eV, despite the wide variation in static dielectric constants, from $\epsilon_s = 34$ to $\epsilon_s = 5$. It is clearly the *local* dielectric properties that are important. When liquids of comparable $\epsilon_s$ but different structures are studied (for example, the isomeric butanols), the $e^-_s$ spectra (A′) dramatically shift to the red, indicating the sensitivity of the electron–molecule interaction to steric hindrance.[33] The high $E_{max}$ for ethylene glycol[34] (2.15 eV, B) can be attributed to the high number density of –OH groups, which favors the formation of a chelate structure about the electron.[33] These configurations are present in the neat fluid and require a minimal degree of medium reorganization in forming a cluster about the electron.

The claim that the electron is a microscopic probe of its local environment is further strengthened as we study the amines. Once again a spectral grouping[34] appears for those fluids containing NH dipoles; $e^-_{amm}$ at 243 K has a narrow (0.4 eV) absorption peaking at 0.8 eV while in liquid amines the band broadens to 0.7 eV and $E_{max}$ lies within 0.73 ± 0.04.[37] Graphic examples of how highly polar liquids do not necessarily imply strong electron binding are given by both dimethyl sulfoxide and hexamethylphosphoramide.[38] The localized electron sees a cluster of weak –CH "dipoles", each attached to a sterically awkward molecule. Thus the absorption bands here resemble those seen for electrons trapped in alkanes[39] where $E_{max} \geq 0.5$ eV. Electrons in ethers[34,35] also exhibit relatively strong absorptions in the 1800–2300-nm region of the infrared. The high mobility of electrons in alkanes and ethers suggests, however, that the clusters may have a fleeting existence as local coincidences of the rotational motion of fluctuating molecules. Table I summarizes some of the optical and kinetic properties of $e^-_s$ in the above polar fluids.

Intuitively we anticipate a minimum fluid density, $\rho$, below which electrons cannot be localized, as implied in the mobility plot of Figure 1, but optical studies of electrons in dense gases and supercritical vapors[5,15] revealed that electrons could be stabilized up to and above the critical temperature in $D_2O$. The $E_{max}$ red-shifted from 1.73 eV in liquid water to 0.95 eV at $\rho = 0.1$ g $cm^{-3}$ while exhibiting little further density dependence to the limit of the study where $E_{max}$ was 0.8 eV at $\rho = 0.02$ g $cm^{-3}$. Electron spectra could be detected in $ND_3$ at $\rho \sim 5 \times 10^{-3}$ g $cm^{-3}$, but above the coexistence curve the spectrum vanished. What is the state of the dense gas? Molecular dynamics studies have shown that a specific distribution of molecular cluster sizes describes the equilibrium properties of these density regimes. The role of density and configurational fluctuations in providing preexisting trapping sites for electrons is already a pivotal point in interpretations of picosecond electron solvation dynamics[6-8] and in spectroscopic and mobility studies in alcohol/alkane systems.[11] Similar arguments can reconcile the $E_{max}$ density dependence in these sub- and supercritical vapors where the dominant role of short-range electron–molecule interactions is clearly affirmed.

By synthesizing a molecular trap for the electron through the creation of clusters of specified sizes, in very dilute polar fluids,[8,40] in dense gases or molecular beams[41] and observing the optical spectrum, we may soon unravel the molecular structures of $e^-_s$. In fact, the cluster and cavity vibrations should be detected in Raman spectra. To date no evidence has been seen for low frequency modes in metal–ammonia solutions,[42] in contrast to the F-center case; a differential Raman technique may yet reveal the totally symmetric cavity vibrations calculated[22] to be about 174 $cm^{-1}$ in ammonia and 202 $cm^{-1}$ for $e^-_{aq}$.

**Photophysics.** The photophysical properties of $e^-_s$ are crucial in assigning the probable origins of the optical absorption and thus to choosing a model of $e^-_s$ for any quantum mechanical theory. The interpretation of the optical spectrum hinges on the answers to two questions. First, is the spectrum homogeneously broadened, that is, does the line width originate from absorption of a single species, or not? Second, is the principal electronic transition into a bound or continuum excited state?

If photoexcitation of $e^-_s$ promotes the electron into the continuum, then the band is homogeneously broadened and the line width and line shape are determined by the photodetachment cross section, posing far fewer problems for the theorists. The spectrum of

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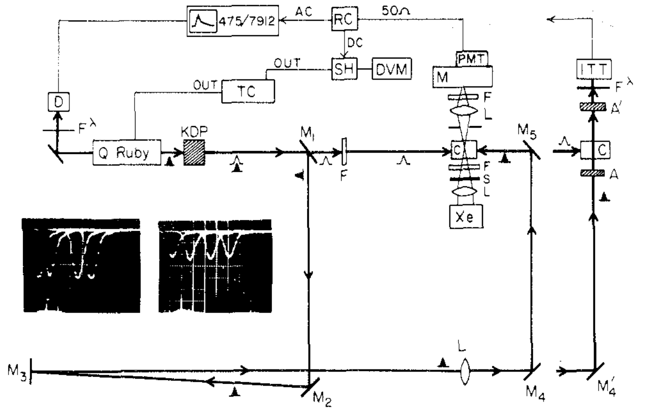

**Figure 3.** Generation of $e^-_s$ via laser-induced photoionization[35] at 347 nm and laser saturation experiments[44] at 694 nm. The 20-ns 347-nm (Λ) and 694 nm (▲) laser pulses are split at $M_1$, and the kinetics of $e^-_s$ in C are monitored with a pulsed Xe lamp before and after saturation; ▲ is delayed by 40 ns and propagates via $M_2 \rightarrow M_5$. Alternatively the transmission of ▲ itself can be examined in hole-burning, by using $M_2 \rightarrow M_4'$. Inset shows four transmitted high-flux and low-flux laser pulses in this configuration, demonstrating a high degree of saturation or hole burning in the first set, with attenuator (A) in position A′.

an F center has been assigned to a 2p ← 1s transition and the band shown to be homogeneously broadened.[2] Similar assumptions, derived from polaron theory, were imposed on electrons in fluids. Among alternative explanations for the much broader line width of $e^-_s$ in fluids have been a series of "Rydberg" states (although the potential is not strictly coulombic), strong phonon-broadening, a distribution of trapping sites in the fluid, and a convolution of bound–bound and bound–continuum transitions.

These basic questions have been posed over several years and in many ways by many authors, but only recently has the ephemeral nature of $e^-_s$ yielded any direct photophysical evidence pertinent to its electronic structure. Several picosecond and nanosecond laser saturation experiments have now been reported on $e^-_s$ in water,[43] alcohols,[44,45] and amines.[9] We will summarize these data here and defer any detailed discussion of the implications for electron dynamics to a future review.

No radiative processes have been detected in relaxation of electronically excited $e^-_s$; however any weak emission would probably be reabsorbed by the solvent. Predictions[22] for radiative configurational relaxation from 2p(1s) to 2p for $e^-_{amm}$ at 2000 nm remain as yet unsubstantiated. Infrared emission has been observed from $F_A$(II) centers in several alkali halide crystals following optical excitation, and the KBr data are shown ($F_A$,$F_B$) in Figure 2. The fluorescence quantum yield is sufficient to obtain high gain CW or pulsed lasing action on the transition from a configurationally relaxed (2p) bound state to the ground (1s) state, with wavelength tuning over typically 2000 cm$^{-1}$.[46] These new sources of coherent and tunable radiation span the 0.3- to 3-$\mu$ region and will have wide applications in kinetics and spectroscopy, including the IR photophysics of their less cooperative cousins, $e^-_s$ in fluids!

The lifetime ($\tau^*$) of the electronically excited state(s) of $e^-_s$ and the spectral homogeneity of the band can be explored through laser optical saturation techniques, as shown in Figure 3. The intense and narrow line width of the saturation laser pulse (▲) selectively depopulates the ground state of absorbers, whose electronic transition occurs at the laser frequency $\nu_{ij}$. In the absence of competing radiative or chemical channels, the "hole" burnt in the absorption spectrum will fill in with a wavelength and time dependence which is determined both by the degree of spectral homogeneity (if any) of the band and the radiationless relaxation rate $k_{ji}$ of the excited state.

The first hole-burning experiments on $e^-_{aq}$ placed $\tau^*_{694}$ at ≤6 ps.[43] This very short excited-state lifetime would be typical of an efficient vibronic relaxation assisted by multiphonon processes within the cluster. Vibronic relaxation in several dye molecules can occur within 0.3 ps.[47] However, if $e^-_{aq}{}^*$ were promoted into the continuum with sufficient kinetic energy to escape the residual trap, then we could identify the photoexcited state as the quasifree state and $\tau^*$ should correlate with the quasifree–bound solvation times $\tau_s$ for $e^-_s$ in the same fluid.

This esthetically appealing picture does not describe the most recent saturation data on other $e^-_s$. In liquid alcohols, the $\tau^*$ values,[44] while still in the picosecond domain, are generally shorter than $\tau_s$, which systematically increase with increasing chain length in the alcohol up to 50 ps for decanol.[7] Interpretation of the saturation data is complicated by the existence of a highly reactive photochemical channel for $e^-_s{}^*$ in alcohols against which rapid vibronic relaxation must compete. Laser saturation studies[44] recently revealed a deuterium effect, which identifies the onset of this selective reactivity with the motion of the OH bond. The product of the laser-induced photochemistry appears to be RO$^-$, but subpicosecond laser studies[47] will be required to directly observe this mechanism. Nevertheless, the evidence indicates that $e^-_s{}^*$ is a bound state, a conclusion also reached in picosecond laser studies of $e^-_s$ in ammonia and amines. In both alcohols and amines, there is also good evidence for homogeneous spectral broadening.[9,44]

Thus the tacit assumptions of the early polaron theory are finally given experimental support. The results also confirm the expectations of current clusterlike models, in which the bound–continuum transitions appear far on the high-energy side of $E_{max}$. Yet if electrons were trapped in a distribution of molecular clusters in the fluid, it is clear that the consequences and interpretation of "inhomogeneous broadening" depend on the time scale of observation.[6,38,44] If the slowest cross-relaxation between different trapping sites is determined by the molecular dynamics of the liquid, then the hole in the spectrum can fill in by $10^{-12}$ s, by borrowing intensity from elsewhere in the band. This would lead always to the appearance of homogeneous broadening, except at low temperatures where site-to-site fluctuations in ground-state energy would be frozen-in. We are currently exploring this point, which may be the link between the observed homogeneous broadening in liquids and the inhomogeneous spectral

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Table II
Selected Results from Model Calculations[a] on Electrons in Fluids

| | Fluid | | | | |
|---|---|---|---|---|---|
| Variable | $^4$He | Ar | $H_2O$ | $C_2H_5OH$ | $NH_3$ |
| Temp, K | 4.2 | 87 | 298 | 298 | 203 |
| $V_0$, eV | 1.28 (1.05)[a] | −0.20 (−0.2)[b] | 0.19[d] | | −0.22[d] |
| photoconductivity threshold, eV[i] | (1.1) | | | | 1.94[e] (1.61) |
| $E_{\max}$, eV (2p←1s) | - | - | 2.7[d] (1.72)<br>2.0[e]<br>2.15[f]<br>1.2[g] | 1.79[f] (1.80)<br>1.80[h] | 0.94[d] (0.8)<br>0.89[e]<br>1.18[f]<br>0.80[g] |
| Δ, eV | - | - | 0.51[e] (0.92) | 1.3[h] (1.3) | 0.25[e] (0.46) |
| $\partial E/\partial T$, $10^3$ cm$^{-1}$ K$^{-1}$ | - | - | −0.3[c] (−0.1) | | −0.3[c] (−0.2) |
| $r_d$, Å | - | - | 1.15[d]<br>2.9[e]<br>1.93[f]<br>2.45[g] | 2.54[f] | 2.7[d]<br>2.87[e]<br>2.66[f]<br>2.75[g] |

[a] Experimental data are in parentheses and are discussed in text; typical results from $N = 4$ calculations in ref 22 and 50–54, matching $V_0$ where possible. [b] Reference 5. [c] Reference 22. [d] Reference 50. [e] Reference 51. [f] Reference 52. [g] Reference 53. [h] Reference 48. [i] Reference 26 and 56.

broadening reported for $e^-_t$ in several glasses at 77 K.[3]

## Theory of Electrons in Polar Fluids

The calculation of the energy levels of a electron in a fluid poses a particular challenge to a quantum chemist who, skilled at experimenting with the choice of potentials, wave functions, and approximations to solve the Schroedinger equation, is now faced with a disordered fluid whose dynamical structure is an intimate part of the problem. Recently a new formalism[48] based on quantum and statistical mechanical principles successfully reproduced the $e^-_s$ optical spectra in ethanol and anthracene glasses. From our perspective this approach would appear to unify the electron and its host fluid in the most natural way, analogous to the quantum statistical calculation in $^4$He.[22]

Nevertheless, much insight into the microscopic domain has been gained from the semiempirical theories that have been developed for electrons in polar fluids. These models can be broadly classified into three groups, each emphasizing a difference role for the short- and long-range electron–fluid interactions.[49] Dielectric continuum models envisage the electron localized in a cavity by long-range polarization interactions in a structureless medium. Semicontinuum models explicity introduce short-range and long-range interactions, with varying boundary conditions, for an electron trapped in a discrete structure, which itself is embedded in a structureless fluid. Finally, the structural models consider the electron as localized in a molecular structure of specified symmetry and preclude long-range contributions to the local potential.

The history and evolution of these models have been reviewed in eloquent detail[31] and will not be covered here. Rather we will focus on the results of contemporary cluster and semicontinuum models[50-54] and the correlation function formalism[48] for the prediction of $E_{\max}$, line width, and line shape of the optical spectra of $e^-_s$ in fluids. Typical results are displayed in Table II. Since the stability criterion for electron localization is $E_T(\mathrm{R}) < V_0$ (Figure 1), we will first briefly outline the calculation of $V_0$.

As the *quasifree* electron scatters through the fluid the molecular structure remains unperturbed. The electron–medium interaction energy ($V_0$) is the sum of a kinetic term, due to the *multiple* scattering ($T$) and the long-range electronic polarization in the fluid ($U_p$).[22,28]

$$V_0 = \frac{\hbar^2 k^2_0}{2m} + U_p = T_0 + U_p \qquad (2)$$

The validity of assumptions used in calculating $V_0$ for atomic fluids[22] rests on the relative importance of short-range order (imposed by the steeply repulsive intermolecular potential) and the long-range order in the fluid, which is overemphasized in lattice models of liquids. The scattering in argon, for example, is determined primarily by the hard-core repulsive potential.[28]

For the liquid rare gases, the agreement between theory and experiment is good, as Table II implies. Discrepancy appears at the diatomic level, and it has been conjectured that the neglect of electron–quadrupole interactions might be at least partially responsible.[22] Extending such calculations (and the assumptions) to systems other than monatomic fluids is extremely difficult, but in polyatomic fluids an angle-averaged spherical potential and angle-averaged polarization can be used to estimate $V_0$.[26] Experimental $V_0$ data can generate the scattering length $a$ for $e^-_{qf}$ in hydrocarbons through this model. In trimethylsilane, $a$ = 2 Å from $V_0$ data, which compares favorably with $a$ = 2.2 Å derived from mobility data via eq 1, despite the fact that the latter calculation involves the sum of *single*-scattering events and the $V_0$ model considers *multiple*-scattering events. $V_0$ data are not yet available for polar fluids.

The *localized* state of electrons in polar fluids has provoked considerable theoretical attention in the past

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(49) Critical reviews of the theory can be found in ref 16–18, 22, 31. Restrictions on space, not interest, preclude discussion on the ~25 model calculations currently in print. The references that follow are selective, not exhaustive.

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decade following the primal theories whose roots lay in polaron physics.[31] It is now the general consensus of both theoretical and experimental evidence that the most accurate model is one in which both the short-range and the long-range electron–medium interactions are explicitly considered for an electron localized in a discrete molecular cluster in the polar fluid, where short-range effects dominate.[23] This is also intuitively reasonable, since the local fluid does possess a dynamical structure and we thus expect the electron–molecular coupling to be sensitive to the order, fluctuations, and correlations that precede any adiabatic act of electron injection. Strictly continuum theories naturally cannot project the short-range effects.

Although early structural models neglected the long-range polarization interactions, they nevertheless contributed ideas to which more recent *semicontinuum* models have appealed. Any molecular approach for polar fluids must take into account the anisotropic polarizability and thus angular-dependent intermolecular forces within the coordination layer. Polymeric species of the type $(H_2O)_n^-$, where $2 < n < 6$, and variations of molecular orbital calculations have been employed to calculate the $E_{\max}$ values of electrons in clusters with dimeric, tetrahedral, octahedral, and spherical symmetry.

Although many-electron ab initio techniques have been used to treat the cluster or short-range part of the problem,[31,53,54] the long-range polarization of the fluid must be folded into the calculation in a more empirical way. How to treat the boundary between the cluster and continuum is a continual point of discussion. Nevertheless, the spirit of a semicontinuum calculation is as follows. (1) Create a cavity (R) in the fluid following electron injection, and then allow the dipoles comprising the inner walls of the cluster (or the $N$ molecules of the first coordination shell) to align in the field of the electron. (2) During this rotation to achieve thermal equilibrium, a countereffect from the repulsive dipole–dipole interactions will come into play to determine the optimum cavity size. (3) Finally the continuum, defined as all fluid *outside* the coordination shell, is polarized in response to the field of the electron. The total energy is then minimized in a variational calculation on R. In principle the *free energy* $G$ rather than $E_T(R)$ should be used in establishing the most stable localized states, in order to include the entropy changes. Of course, subtle and important differences do appear for each calculation within the semicontinuum framework, which we cannot explore here.

Inspection of selected theoretical results in Table II leads us to conclude that all the semicontinuum calculations of electrons in four- or six-membered clusters lead to essentially similar properties for $e^-_s$. And yet, despite much musing, these models cannot yield the line width and skewed line shape of the optical band. This remains a perplexing and unsolved problem which cannot justifiably appeal to the dominance of bound–continuum transitions nor to unrealistic potentials to circumvent the issue. Furthermore the absence of a marked density dependence on the profile of the band seems to deemphasize the role of higher excited bound states.

What remains to be done? Model calculations often treat a single cavity and do not allow for coupling of the electronic states of electrons in neighboring sites, and when a distribution of cavity sizes *is* considered, the species nevertheless remain energetically independent. Furthermore, the role of the fluid is assessed independently of the electronic part of the problem and therefore density and configurational fluctuations do not explicity participate in determining the Franck–Condon envelope (hence line width and line shape) for the electric dipole transition. Perhaps if we return to the role of the fluid disorder and consider, for example, asymmetric modes in the cavity vibration and solvent exchange in the floppy cluster, fluctuations in the correlation of electronic and molecular motion, and hopping or tunnelling between trapping sites, we may gain some insight into the line shape and line width.

A unified treatment of the electron and its vibrationally active environment of $N$ molecules is the motivation behind a recent calculation[48] of the electronic band shape $I(\omega)$ of $e^-_s$ in glassy ethanol and anthracene, based on quantum theory and statistical mechanics. Through the Fourier transform of the time–correlation function[55] of the electronic dipole moment operator $\langle F(t)F(0)\rangle$, the band shape is given by:

$$I(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \mathrm{d}t\, e^{i\omega t}\langle F(t)F(0)\rangle \tag{3}$$

Contributions to $I(\omega)$ arise from the electron–dipole transition and corresponding Franck–Condon envelope (which also carries some inhomogeneous line broadening as a consequence of intermolecular interactions in the fluid) and from the rotational and translational motion of the molecules. The latter promote electron migration via cavity or molecular orbitals through local fluctuations in the solvent structure. Preliminary results are rather encouraging for $e^-_s$, where $N = 6$ and bound–bound transitions were assumed. The line width and line shape have been reproduced successfully to a point that has hitherto escaped the more phenomenological models, even though the dynamical liquid structure and collective effects have been previously recognized as playing an important role.

In a future paper we will pursue our theme and examine in detail the picosecond dynamics of electron solvation and laser-induced transitions of the localized electron within its cluster trap, in the context of the molecular dynamics of fluids.

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