Absorption Spectra of Trapped Electrons in Nonpolar Glasses: Oscillator Strengths and Threshold Behaviors[†]

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Received: October 13, 2000

Trapped electrons were generated by photoionization of TMPD (*N*,*N*,*N*′,*N*′-tetramethylparaphenylenediamine) and the absorption spectra measured in 2-methylpentane (2MP), 3-methylpentane (3MP), *cis*-decalin (CD), methylcyclohexane (MCH), and deuterated methylcyclohexane(dMCH) glasses at 77 K. The low energy absorption fits the Wigner 3/2 power law for threshold photodetachment, consistent with a ground S state with binding energy of 0.48 ± 0.02 eV and a final continuum P state. For all solvents studied, the maximum absorption cross-section is located at ca. 0.7 eV with an extinction coefficient of 2.7×10^4 M^{-1} cm^{-1} (determined by comparison to TMPD cation). From the spectral distribution of the absorption (from 0.5 to 3.3 eV), experimental oscillator strengths were determined to be 0.65(2MP), 0.63(3MP), and 0.76(CD). Various local field corrections to these experimental oscillator strengths are discussed.

Introduction

The absorption spectra of trapped electrons offer numerous insights into the interaction of excess electrons with the matrix, and serve as the principal measurable quantities of these important initial products of ionizing radiation. Unfortunately, most of the information the absorption spectra hold remains elusive. Many questions are difficult to answer even with the vast amount of experimental and theoretical results available.[1−50] Herein, we utilize the absorption spectra of trapped electrons in nonpolar glasses to re-address the following questions: (1) Is the terminal state of the absorption free or bound? (2) What is the binding energy of the trapped electron? (3) What is the oscillator strength of the transition and what is its significance? (4) To what extent is electronic polarization of the solvent responsible for forming the trapping potential?

Much of the current knowledge of trapped electrons comes from decades of studies in water and polar solvents.[1−5] Experimentally, changes of spectral properties with time,[5−14] temperature,[4,15−17] and nature of the solvent[1,3,4] have been reported. This vast amount of experimental data has spawned numerous theoretical studies employing fits to model potentials,[18−19] quantum mechanical simulations,[20−29] and various sum rules.[30−32] While no theory claims to explain all of the data, these studies have explained many of the time-dependent properties of electron solvation in polar solvents. Unfortunately, the conclusions cannot be easily transferred to nonpolar systems. The overwhelming influence of dipolar orientation in forming and deepening the traps does not manifest itself in nonpolar solvents. Additionally, the absorption of the trapped electron in nonpolar systems is primarily in the infrared, where few time-resolved laser studies of the absorption spectrum have been performed.[33−36]

Nonpolar glasses offer a number of advantages over polar solvents. At liquid nitrogen temperatures, the electron traps are stable and absorption can be measured by steady-state methods. A large literature exists in which γ radiation was used to produce trapped electrons, which were subsequently studied by optical absorption,[4,14,15,35,37−48] electron spin resonance,[4,15,38,45,49,50] photoconductivity,[4,46−48] and chemical scavenging.[4,37,38,41−43] Yet the problems posed above still remain.

Herein, we utilize similar measurements of absorption spectra but have attempted in a few selected systems to obtain accurate measurements of the spectra in the region of threshold absorption and accurate experimental oscillator strengths. The functional form of the threshold spectra suggests that the transition is bound → free with a ground-state binding energy equal to the threshold energy. The experimental spectrum and its moments are found to resemble the predictions from the bound → free absorption of a particle in a spherical well. The appropriate local field correction to the oscillator strength could not be decided and accordingly, no decision could be made as to whether the corrected oscillator strength lies below unity. A corrected value of the oscillator strength below unity is considered a measure of the contribution to the binding energy from electronic polarization.

Experimental Section

The absorption spectrum of the hydrocarbon glass at 77 K, with 10^{-3} M TMPD (*N*,*N*,*N*′,*N*′-tetramethylparaphenylenediamine) was recorded as a baseline. The TMPD was then photoionized to produce trapped electrons. Spectra of trapped electron and TMPD cation absorption were recorded after several minutes, to avoid effects of recombination during acquisition.

Difficulties in subtracting absorptions due to TMPD, $TMPD^+$ and any photoproducts limit our spectra to $\lambda > 375$ nm (3.3 eV). The upper wavelength of the Cary 14 spectrometer (modified for computer control by OLIS) limited us to $\lambda < 2550$ nm (0.486 eV). An absorption peak of the quartz prism at 2150−2225 nm and absorptions due to solvent overtones at $\lambda \sim 1720$ nm and at $\lambda > 2300$ nm, limited measurements in these spectral regions. To minimize the overtone absorptions, we employed a 0.75 mm path length cell and a band-pass of 5−7 nm. The 1720

[†] Part of the special issue “Aron Kuppermann Festschrift”.

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10.1021/jp0037706 CCC: $20.00

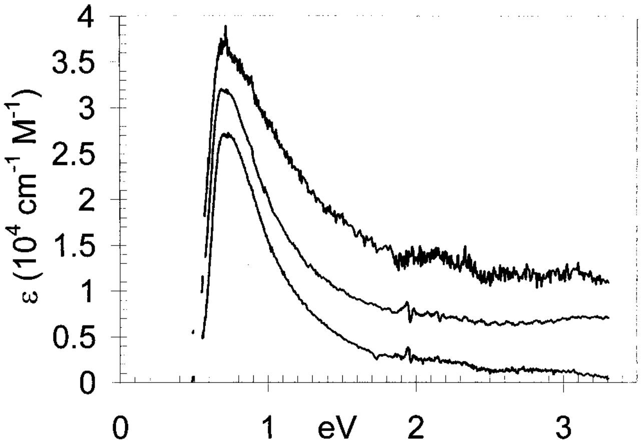

Figure 1. The absorption spectra (extinction coefficient vs energy) of trapped electrons are shown from top to bottom in *cis*-decalin, 2-methylpentane, and 3-methylpentane glasses at 77 K. For clarity, the *cis*-decalin and 2-methylpentane spectra are shifted 1.0 and 0.5 units on the *y*-axis, respectively.

nm peak could be reliably subtracted, but above 2175 nm, only sections around the solvent absorption peaks could be measured. Deuterated MCH exhibits much smaller and broader overtone peaks that were easily subtracted up to 2550 nm.

To ensure accurate baselines for threshold absorption, the baseline and trapped electron spectra were both measured in the infrared and visible without moving the detector or the cell. Then the lead sulfide detector was changed to a photomultiplier tube and the visible and ultraviolet regions measured. The step size between points in the infrared was 5 nm, the band-pass 3−7 nm. The step size in the ultraviolet and visible was 5−10 Å with 5−10 Å band-pass.

Resonant two-photon ionization of TMPD was performed with 308 nm (XeCl excimer) pulses applied at 25 Hz(∼10 mJ per pulse with ∼15 ns pulse width). Approximately 100−200 pulses were typically applied, to produce adequate concentration of trapped electrons(∼1−2 × 10^{-4} M) with minimal TMPD photodegradation. Photobleaching was performed with a tungsten lamp and a 930 or 1100 nm interference filter.

Solvents were purified by passage through 1-m silica gel columns. TMPD and pyrene were repeatedly vacuum sublimed. All chemicals were obtained from Aldrich at the highest purities available. Concentration of TMPD in the room temperature liquid solvent was typically 10^{-3} M, but 10^{-2} M was used when scavenging with pyrene, which competes for the excitation light. No pyrene cation was observed when TMPD was present. The solutions were degassed to approximately 10^{-4} Torr by repeated (5−12) freeze−pump−thaw cycles, before introduction into the evacuated cell. The cell consisted of a stainless steel body with quartz windows separated by a stainless steel ring of width 0.75 mm. The outer edges of the windows were sealed with indium wire compression seals.

The glasses were formed by rapid cooling with liquid nitrogen. The solvents 2MP and 3MP formed clear, crack-free glasses, MCH and dMCH formed cracked glasses, and CD formed extensively cracked glasses that were much less transparent, resulting in the increased noise and decreased spectral range that could be measured for this solvent.

Results

A. Spectral Distribution. Trapped electron absorption spectra are shown in Figure 1, from bottom to top, for 3-methylpentane (3MP), 2-methylpentane (2MP) *cis*-decalin (CD), and in Figure 2 for deuterated methylcyclohexane (dMCH) and methylcyclohexane (dMCH) solvents. For clarity, each spectra after the first is shifted 0.5 units of 10^4 M^{-1} cm^{-1}. Energies above 1.85 eV (670 nm) have been corrected for TMPD cation absorption. Small artifacts of the TMPD cation subtraction are present at 1.9−2.2 eV. Spectra for 2MP, 3MP, and MCH have been previously reported,[39,46] and agree substantially with those reported here.

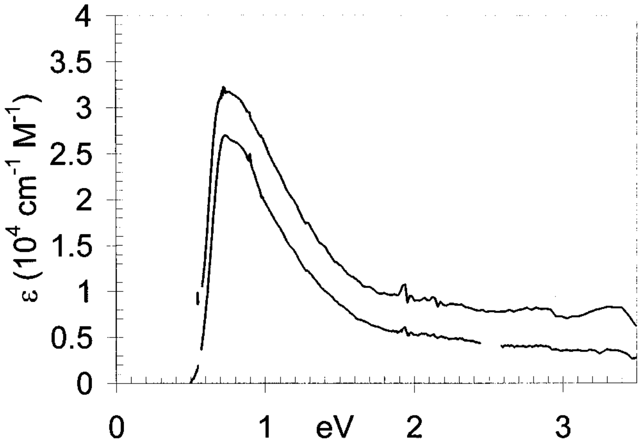

Figure 2. The absorption spectra (extinction coefficient vs energy) of trapped electrons are shown from top to bottom in methylcyclohexane and deuterated methylcyclohexane glasses at 77 K. For clarity, the methylcyclohexane spectrum is shifted 0.5 units on the *y*-axis.

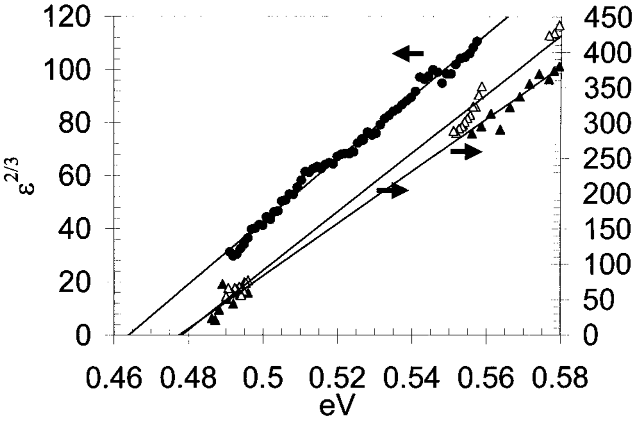

Figure 3. The extinction coefficient of the electron absorption raised to the 2/3 power vs photon energy in the threshold region in deuterated methylcyclohexane(●), 2-methylpentane(△), and 3-methylpentane(▲).

It will be noted from Figure 2 that the high energy absorption in methylcyclohexane falls off much more slowly than in other hydrocarbon glasses. This can also be observed in the spectra of Shida, Iwata, and Watanabe[39] in the γ-irradiated glasses. The near quantitative similarity between our spectra and theirs suggests that the origin of this absorption is not in cation radicals produced on γ irradiation or during TMPD photoionization. The photobleaching of this spectrum was found to be homogeneous, suggesting that any species responsible must disappear by reaction with released electrons. We remain unsure as to the origin of the tail and are wary of assigning it to a trapped electron since it does not appear in any other reported solvent systems. Accordingly, in what follows, we only use these methycyclohexane spectra in Figure 2 for their behavior below 1 eV.

B. Threshold Absorption. In Figure 3 we plot the absorption cross-section raised to the 2/3 power versus energy for 2MP, 3MP, and dMCH. A linear fit is predicted in the threshold region by the Wigner[51] law for a photodetachment process involving

TABLE 1: Threshold Energies, Experimental Oscillator Strengths, Moments of the Spectral Distribution, Peak Extinction Coefficients, ϵ, and Their Method of Determination

solvent[a]	threshold (eV)	f_{exptl}	$\langle\alpha\rangle$ (Å^3)	$\langle r^2\rangle$ (Å^2)	$\langle T\rangle$ (eV)	ϵ at peak (10^4 M^{-1} cm^{-1})	method of ϵ determination[b]
3MP	0.48	0.63	80	9.9	1.54	>2.7, <2.8	D, PB
2MP	0.48	0.65	80	10.0	1.64	>2.7, <3.7	D, PB
CD		0.76	84	11.1	1.99	>2.6, <2.9	D, PB
dMCH	0.47					>2.1, <3.5	D, PB
MCH	~0.49					>2.7, >2.7, <2.7, <3.5, ~2.7	SD, D, SPB, PB, TE

[a] 3MP = 3-methylpentane, 2MP = 2-methylpentane, CD = *cis*-decalin, dMCH = deuterated methylcyclohexane, MCH = methylcyclohexane. [b] D = direct comparison to TMPD cation, PB = photobleached comparison to TMPD cation, SD = direct comparison to TMPD cation with pyrene scavenger, SPB = photobleaching comparison to TMPD cation with pyrene scavenger, and TE = time extrapolation by power law of TMPD cation and trapped electron absorptions. No corrections have been made for refractive index.

a terminal P state. This will be detailed in Discussion, section A. Reliable fits could not be obtained in MCH and CD due to excessive noise in the spectrum at these energies. The thresholds determined by the intercept on the energy axis are listed Table 1. Considerable care was taken to avoid baseline shifts, which act to vertically shift the lines, but the error that remains limits the accuracy of the threshold energies to ±0.02 eV.

The only previous measurements of absorption in the threshold region in saturated hydrocarbon glasses are those of Shida, Iwata, and Watanabe.[39] Although their threshold absorptions are similar to ours, they report too few points to establish a functional form.

C. Extinction Coefficients. The determination of the extinction coefficients was performed by comparison to TMPD cation absorption. TMPD cation has a well-established extinction coefficient of 19 300 M^{-1} cm^{-1} at 632 nm in 3MP glass.[52] Direct comparison of trapped electron to TMPD cation absorption during the first spectral acquisition allows a lower bound on the extinction coefficient to be determined. The value is a lower bound because of scavenging by low concentration impurities produced by the irradiation. A photobleaching spectrum determines an upper bound on the extinction coefficient. The loss of electrons should equal the loss of TMPD cations, but any impurities that capture electrons will cause loss of electron absorption to exceed loss of TMPD cation absorption. Since the extinction coefficient is determined by the ratio of the loss of electron absorption to the loss of cation absorption, photobleaching provides an upper bound in the case of any unaccounted scavenging.

To minimize unobservable scavenging, the scavenger pyrene was added in some experiments. The direct and photobleached comparison was made by including pyrene anion in the calculation of the extinction coefficient. The extinction coefficient of pyrene anion was determined, by comparison to TMPD cation, to be 6.5×10^4 M^{-1} cm^{-1} at 492 nm via scavenging all electrons. This value is higher than previously reported values in liquid tetrahydrofuran, based on chemical preparation methods.[53,54] The most likely error in our determination is the failure to capture all the electrons, but this would make our value too low. A more recent report of pyrene anion absorption in 2,2,4-trimethylpentane at room temperature suggests $\epsilon = 4.8 \times 10^4$ M^{-1} cm^{-1} at 494 nm,[55] also lower than our value. The difference may originate from some sharpening of the line in the glassy solid. The value obtained for the trapped electron extinction coefficient using pyrene agrees with the values obtained without scavenging, suggesting that in the glass, our pyrene anion extinction coefficient is correct.

The upper and lower bounds determined for the extinction coefficient at peak absorption are reported for each solvent in Table 1, along with the method of determination as described above. The value of 2.7×10^4 M^{-1} cm^{-1} was determined by equating upper and lower bounds in methylcyclohexane, and was consistent with bounds established in the other solvents. The lower bounds are probably closer to the true value, since under the excitation conditions employed, the impurity concentration is expected to be quite small. Photobleaching mobilizes the electrons, increasing the chance that they will be captured by an impurity and thereby making more suspect the estimated upper bounds. Numerous trials were necessary to achieve the best set of bounds for each solvent.

Hamill[41] has reported the extinction coefficient of trapped electron absorption in 3MP glass as lying between 2.2 and 3.0×10^4 M^{-1} cm^{-1}, with the upper value preferred. His methods involved photobleaching to transfer electrons from biphenyl anions to solvent traps and back. His results should be corrected for a later determination of biphenyl anion's extinction coefficient.[54] This leads to a range of extinction coefficients of $2.6-3.2 \times 10^4$ M^{-1} cm^{-1}, which encompasses the preferred value reported here of 2.7×10^4 M^{-1} cm^{-1}.

D. Spectral Moment Analysis. For the purposes of extracting from the experimental spectra various ground-state properties of the trapped electron via use of sum rules,[30−32] we present in Table 1 the ω^n ($n = -2, -1, 0, 1$) moments of the spectra. The spectral moments have each been multiplied by the appropriate constants to provide, *were these gas-phase spectra*, the ground-state polarizability, $\langle\alpha\rangle$,[56] ground-state radius squared, $\langle r^2\rangle$, the oscillator strength, f_{exptl}, and the ground-state kinetic energy $\langle T\rangle$, assuming spherical symmetry.

$$\langle\alpha\rangle = \frac{c}{A}\int_0^\infty \mathrm{d}\omega\ \omega^{-2}\epsilon(\omega)$$

$$\langle r^2\rangle = \frac{3\hbar c}{2Ae^2}\int_0^\infty \mathrm{d}\omega\ \omega^{-1}\epsilon(\omega)$$

$$f_{\text{exptl}} = \frac{mc}{Ae^2}\int_0^\infty \mathrm{d}\omega\ \epsilon(\omega) \tag{1}$$

$$\langle T\rangle = \frac{3m\hbar c}{4Ae^2}\int_0^\infty \mathrm{d}\omega\ \omega^{1}\epsilon(\omega)$$

$$A = 2\pi^2 L/(1000 \ln 10)$$

In eqs 1, ϵ is the decadic extinction coefficient in units of M^{-1} cm^{-1} and L is Avogadro's number. All other symbols have their usual significance. We emphasize again that in eqs 1 *no corrections have been made for the presence of the dielectric medium.*

Discussion

A. Wigner Law for Cross Sections at Threshold. The Wigner power law for photodetachment has often been utilized

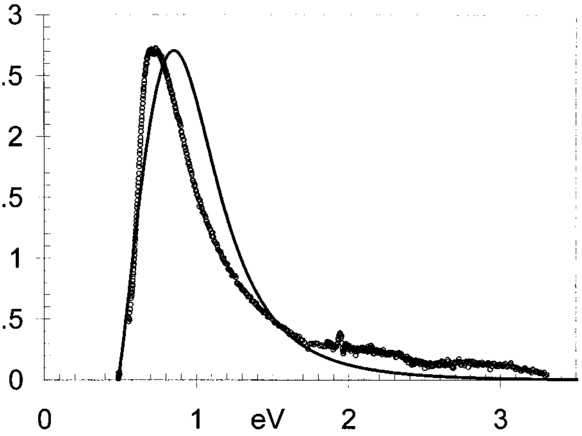

Figure 4. A comparison of the experimental absorption spectrum of trapped electrons in 3-methypentane(○) with a bound S → continuum P spectrum of an electron in a spherical well(solid line). The well parameters were chosen to match the experimental peak extinction coefficient and threshold energy, and the absorption was scaled to match the experimental oscillator strength.

for the analysis of threshold absorption.[51,57−67] For particles bound in potentials which vanish at infinity faster than $1/r^2$, Wigner has shown that the detachment cross section, $\sigma(E)$, to a final state of angular momentum l will behave in the limit $E \rightarrow E_{\text{threshold}}$ as $(E - E_{\text{threshold}})^{l+1/2}$. This threshold law has been successfully utilized in the interpretation both of atomic and molecular anion photodetachment processes.[60−64] Unfortunately without knowledge of the potential, there are no general guide rules to the energy range of applicability of the threshold power law dependence,[51,57−59,65−67] but empirically many photodetachment studies[60,62] show Wigner threshold fits up to energies approaching ca. one-half of the difference between threshold and the energy of the cross-section maximum.

Assuming that the trapped electron absorption is from a bound S state into an allowed P continuum, the cross section would be expected to increase as the 3/2 power of energy above threshold. The more convenient plot of $\sigma(E)^{2/3}$ vs E in Figure 3 shows that the predicted linearity is maintained up to ca. one-fourth to one-third of the difference between threshold and the energy of the cross section maximum. The threshold energies listed in Table 1 are the binding energies, if the transition assignment as bound to free is correct. The 3/2 power law supports this, but it must be noted that a power law fit over a limited range of data is not very sensitive, and other exponents can also linearize the data to within its uncertainty.

B. Comparison of Experimental Spectra to a Spherical Well Model. The distinctive broad, asymmetric absorption spectrum of trapped electrons is reminiscent of the bound-to-free transitions of a particle in a spherical well potential that supports only a single bound state. This has been earlier pointed out by Funabashi,[19] who found good fits to experimental spectra, especially in polar solvents, albeit he did not fit the absolute extinction coefficients at the peaks. In nonpolar solvents, the absence of permanent dipole alignments makes the assignment of the transition as bound to free even more reasonable.

In Figure 4, we compare the bound S → continuum P spherical well spectrum with the experimental spectrum in 3-methylpentane. The theoretical spectrum was scaled by a factor of 0.63 to match the experimental oscillator strength. The two parameters of the spherical well potential were then chosen to provide a best fit to the experimental threshold energy and maximum cross-section. For this fit, the radius was found to be $b = 3.37$ Å and the well depth $V_0 = 1.95$ eV. While the spherical well spectrum is slightly broader and peaks at a somewhat higher energy, the general agreement with the experimental spectrum for this simple model is surprisingly good.

In this regard, it should be noted that a spherical well with a depth of 1.95 eV is consistent with the solution to the electrostatic problem of the potential felt by an electron inside a spherical cavity of radius b due to its polarization of a surrounding dielectric (i.e., $V_0 = e^2/(4\pi\epsilon_o b)\,(1 - 1/n^2)$). Taking $n = 1.4$ and a cavity radius $b = 3.37$ Å, provides a well depth $V_0 = 2.1$ eV, a value not too disparate from the fitted value of 1.95 eV.[68] Additionally, the spectral moment analysis of 3MP suggests an average kinetic energy of 1.5 eV, which added to the binding energy of 0.48 eV gives an average potential depth of 2.0 eV.

Consistent with the overall agreement of the spectrum in 3MP and the predictions of the spherical well model, we also find agreement between the predicted and experimental spectral moments. Using eqs 1, the spherical well model predicts $\langle\alpha\rangle = 84$ Å^3, $\langle r^2\rangle = 10.5$ Å^2, and $\langle T\rangle = 1.40$ eV. These values compare favorably with those derived from the experimental spectrum of $\langle\alpha\rangle = 80$ Å^3, $\langle r^2\rangle = 9.9$ Å^2, and $\langle T\rangle = 1.54$ eV(see Table 1). We should keep in mind that the absolute value of these moments have not yet included local field corrections. The above comparisons, however, remain valid.

C. Local Field Corrections. The absorption of light by an impurity in a dielectric material is determined (in dipole approximation), by the square magnitude of the electric vector at the position of the impurity, $\mathbf{E}_l$. The ratio of $\mathbf{E}_l$ to the field averaged over the entire dielectric, $\mathbf{E}$, is referred to as the local field correction. There is some ambiguity in the literature not only as to what value to take for this ratio, but even as to its pertinence in calculating the absorption oscillator strength.

For a pure nonpolar dielectric comprised of point particles, a variety of derivations (both classical and quantum mechanical) indicate that, at least for cubic crystals and likely also for more disorganized materials, the appropriate ratio is the Lorentz−Lorenz or so-called virtual cavity value[69−76] of

$$(\mathbf{E}_l/\mathbf{E})_{\mathrm{L}} = (\epsilon/\epsilon_0 + 2)/3 \tag{2}$$

For the case of an impurity imbedded in nonpolar dielectrics, the ratio $(\mathbf{E}_l/\mathbf{E})$ at the position of the impurity is less well established. A common classical correction is due to Onsager and Bottcher[69,77−79]

$$(\mathbf{E}_l/\mathbf{E})_{\mathrm{OB}} = \frac{(\mathbf{E}_l/\mathbf{E})_{\mathrm{C}}}{1 - \dfrac{2\alpha_{\mathrm{I}}}{3(\epsilon/\epsilon_{\mathrm{o}})b^3}((\epsilon/\epsilon_{\mathrm{o}}) - 1)(\mathbf{E}_l/\mathbf{E})_{\mathrm{C}}}$$
$$(\mathbf{E}_l/\mathbf{E})_{\mathrm{C}} = \frac{3(\epsilon/\epsilon_{\mathrm{o}})}{2(\epsilon/\epsilon_{\mathrm{o}}) + 1} \tag{3}$$

where α_{I} is the polarizability of the impurity and b is the cavity radius in which it resides. In the case that $\alpha_{\mathrm{I}}/b^3 \ll 1$, eq 3 reduces to $(\mathbf{E}_l/\mathbf{E})_{\mathrm{C}}$ which is often called the real cavity ratio.

Equation 3 has recently been recommended by Schuurmans, de Vries, and Lagendijk[80,81] on the basis of both quantum mechanical[80] and classical arguments[81] for use when the impurity is of a substitutional type. On the other hand, for interstitial type impurities these authors have argued for a modification of eq 3 that replaces $(\mathbf{E}_l/\mathbf{E})_{\mathrm{C}}$ by $(\mathbf{E}_l/\mathbf{E})_{\mathrm{L}}$. Accordingly, for an interstitial impurity, if $\alpha_{\mathrm{I}}/b^3 \ll 1$, these authors suggest using eq 2 for the local field correction.

All of the derivations of these ratios assume that the impurity (and the dielectric particles) are essentially points. The question therefore arises as to how one should average the "local field" over a rather diffuse bound state wave function of a weakly bound electron. For absorption of bound S states to continuum P states, much of the magnitude of the transition amplitude (especially in the vicinity of its maximum, i.e., at low electron kinetic energies) is expected to arise from portions of the wave function distant from the impurity center. Accordingly, in such cases it may be most appropriate to consider taking the ratio $(\mathbf{E}_l/\mathbf{E})$ equal to unity as has been earlier suggested for the absorption by "diffuse" impurity centers in crystals.[82-84]

We will return to the question of what value to take for $(\mathbf{E}_l/\mathbf{E})$, but turn our attention first to how these corrections relate to the absorption oscillator strength.

D. The Absorption Oscillator Strength. In early papers, Dexter and Heller[85] and later Dexter[86] have calculated, in dipole approximation, the absorption by an impurity point particle in a dielectric. It is assumed that the dielectric itself absorbs at such sufficiently higher energies than the impurity, that even when all interparticle interactions are included, the lowest system excitation ($0 \rightarrow f$) remains identifiable as the impurity absorption.

In their calculation of the ($0 \rightarrow f$) optical transition matrix element, they utilize system wave functions that include excitations of both the dielectric and the impurity to first order in van der Waals interactions(V_{VW}). To terms linear in the polarizability of the dielectric, they show that the transition matrix element in the interacting system can be expressed as the product of $(\mathbf{E}_l/\mathbf{E})_L$ with the transition matrix element that does not include the V_{VW} interactions. From here it follows, that in the usual expression for the dipole absorption cross section[87]

$$\sigma = 4\,\pi^2\alpha_F\omega\,(\mathbf{E}_l/\mathbf{E})^2/n|\langle\phi^0{}_f(\omega)|\mathbf{e}\cdot\mathbf{r}|\phi^0{}_0\rangle|^2\,\rho(\omega) \qquad (4)$$

(where $\mathbf{e}$ is the polarization vector, α_F is the fine structure constant, and $\rho(\omega)$ is the density of final states), that if we choose $(\mathbf{E}_l/\mathbf{E}) = (\mathbf{E}_l/\mathbf{E})_L$, then the wave functions $\phi^0{}_f(\omega)$ and $\phi^0{}_0$ should be those of the impurity in a dielectric NOT subject to the van der Waals interactions. Other interactions may remain.

It should be noted that the treatment by Dexter is for a substitutional impurity. From the analysis of de Vries and Lanendijk,[81] it is plausible to assume that for an interstitial impurity, a real rather than a virtual cavity correction would have emerged from the Dexter treatment, with the same constraints on the interpretation of $\phi^0{}_f(\omega)$ and $\phi^0{}_0$. These considerations affect the interpretation of the absorption oscillator strength.

It will be recalled that if u_o and $u_f(\omega)$ are the exact many particle eigenstates of Z oscillators, then $|\langle u_f(\omega)|\mathbf{e}\cdot\mathbf{r}|\,u_o\rangle|^2\,\rho(\omega)$ defines a differential oscillator strength,[88]

$$df/d\omega = (2m/\hbar)\omega|\langle u_f\,(\omega)|\mathbf{e}\cdot\mathbf{r}|u_o\rangle|^2\,\rho(\omega) \qquad (5)$$

whose integral over all frequencies, ω, gives an oscillator strength f equal to Z. Consider a situation where the lowest optical transition of the system is identifiable as essentially the transition of a single oscillator(i.e., the impurity), which, had it been isolated would have given $f = 1$. In the interacting system, a partial integration of $df/d\omega$ over the energy of this lowest transition would then provide a partial oscillator strength less than unity, having lost strength to the higher frequency excitations.[89]

Accordingly, in eq 4 use of $(\mathbf{E}_l/\mathbf{E}) = (\mathbf{E}_l/\mathbf{E})_L$ or $(\mathbf{E}_l/\mathbf{E})_C$, if there remain impurity-lattice interactions in the wave functions $\phi^0{}_0$ and $\phi_f(\omega)$ other than V_{VW}, then the partial oscillator strength of a low-frequency impurity absorption, that was unity when isolated, would now be expected to be less than unity. The deviation serves as some measure of the strength of these "other" interactions, such as might occur if the impurity carried a net charge.

It is with these considerations in mind that one should interpret the usual equation for the oscillator strength of impurity absorption which is often simply written as

$$f = [n(\mathbf{E}/\mathbf{E}_l)^2]\,f_{\mathrm{exptl}} \qquad (6)$$

where the integral over ω in f_{exptl} (see eq 1) spans only the "impurity absorption".

In Table 1, we list some experimental oscillator strengths for the trapped electron in various solvents. For refractive index $n \sim 1.4$, if we utilize the Lorentz field correction of eq 2, $n(\mathbf{E}/\mathbf{E}_l)^2$ equals 0.8, or if we utilize the cavity correction of eq 3,[90] $n(\mathbf{E}/\mathbf{E}_l)^2$ equals 1.0. Accordingly, for the branched alkanes, f is either lowered to 0.55 or remains at 0.64. Note that the same factor of 0.8 and 1.0 would also apply to the moments of the spectral distribution in Table 1. In either event, there would be implied a significant interaction between the electron and the dielectric that is not accommodated by the local field corrections. In the spherical well model, these interactions would be interpreted to be those responsible for the formation of the trapping potential, namely induced polarizations of the surrounding dielectric. For *cis*-decalin this loss of oscillator strength is reduced, but f remains significantly less than unity.

However, arguments can be advanced for $(\mathbf{E}_l/\mathbf{E}) = 1$ for a transition from a diffuse center into continuum P states (see the discussion at the end of Section B). In this case, the experimental oscillator strength in eq 6 would be multiplied by $n \sim 1.4$ (as must also the spectral moments), and the predicted oscillator strength becomes now ca. 0.9 for the branched alkanes and ca. 1 for *cis*-decalin. Such multiplication of the experimental oscillator strength by n has been utilized by a number of workers who have analyzed trapped electron spectra.[6,32,91] The implication of an oscillator strength ~ 1 would be a prediction of a much smaller involvement of matrix polarization in forming the trapping potential. This would tend to support the notion of electrons bound to preformed sites. This view has both proponents[19,26,92] and antagonists,[4,5,15,49,93] but cannot now be decided on the basis of oscillator strengths. Better theories must first be developed for the local field corrections before firm conclusions can be drawn from the experimental oscillator strengths.

Conclusions

Experimental absorption spectra of trapped electrons in low-temperature hydrocarbon glasses were obtained over a spectral range from threshold to ca. 3 eV above threshold. Major attention was given to the determination of accurate cross-sections and threshold energies in some of the solvents. These were analyzed to address questions regarding the assignment of the transition and the nature of the electron trap.

The threshold absorption was found to fit well the Wigner power law for photodetachment, suggesting that the transition is from a bound S to a continuum P state, and that the threshold energy is the binding energy. In all solvents this energy is 0.48 ± 0.02 eV.

The maximum cross section occurs at about 0.22 eV above threshold, suggesting a rather diffuse bound state wave function. The cross section at the absorption maximum is $2.7 \pm 0.2 \times 10^4$ M^{-1} cm^{-1}. This, together with the spectral distribution, permitted the determination of experimental oscillator strengths of 0.64 in the branched alkanes and 0.76 in *cis*-decalin.

The spectral distribution fit reasonably the simple model of a spherical well of range ca. 3.5 Å and depth of 2 eV. The depth is consistent with classical estimates for the potential energy of an electron in a cavity of 3.5 Å radius that polarizes a dielectric of refractive index 1.4.

The experimental oscillator strengths require local field corrections to convert them to the oscillator strengths that appear in the sum rules. A number of corrections are discussed. Both virtual and real cavity corrections give corrected oscillator strengths of ca. 0.5−0.8. If the local field is taken equal to the average field, as might apply for a sufficiently diffuse center, the corrected oscillator strengths come close to unity.

It is argued that any lowering from unity in these corrected oscillator strengths must reflect the importance of interactions between the electron and the dielectric that are not accommodated by the local field corrections. It is precisely these interactions, if they exist, that would lead to the self-trapping of the electron by its polarization of the surrounding dielectric. Unfortunately, the theoretical status of the appropriate local field corrections leaves this question unanswered.

Acknowledgment. This research was supported in part by the U.S. Department of Energy, Division of Chemical Sciences, Office of Basic Energy Sciences.

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