Optical Absorption of Solvated Electrons in Water and Tetrahydrofuran/Water Mixtures

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Received: August 26, 1998; In Final Form: October 20, 1998

In the past Jou and Dorfman (*J. Chem. Phys.* **1973**, *58*, 4715) have determined the optical absorption spectra of solvated electrons (e_{solv}^-) in binary mixtures of tetrahydrofuran (THF) and water over the entire concentration range. From these experiments they concluded that the position of the absorption maximum and the width at half-height of the band are dominated by water. By additional experiments we show that at least for some mixtures with a mole fraction $X(\text{THF}) \leq 0.50$, we obtain spectra at 298 K which agree almost completely with those of e_{solv}^- in pure water at *elevated* temperatures obtained by Jou and Freeman (*J. Phys. Chem.* **1979**, *83*, 2383). It follows that for this range of composition, excess electrons are obviously hydrated and the large amount of THF of up to $X(\text{THF}) = 0.49$ changes the water structure of the hydrated electron only slightly. The same effect can be produced by a temperature increase of $T = 80$ K in *pure* water. From the spectra we have determined equilibrium ground-state properties of the hydrated electron as a function of temperature and composition of the mixture. Results of quantum-statistical simulations on hydrated electrons show very poor agreement with the experimental results. Therefore, it seems to be presumptuous to take these simulations as a basis to explain the behavior of excess electrons in water on a femtosecond time scale.

I. Introduction

One of the most frequently investigated properties of solvated electrons in polar liquids is their optical absorption spectrum[1,2] which is extremely broad, asymmetric, and structureless. However, changing the temperature and/or pressure can produce very large shifts of the e_{solv}^- spectra, but they almost always retain their shape in the process. This characteristic near-invariance of the line shape which is usually different in different solvents is called *shape stability of the optical profile*.[2] This was observed in many solvents at different temperatures and/or pressures but was almost never noticed by the theoreticians.

Optical spectra were not only determined in the pure liquid but also in binary mixtures of polar components. Jou and Dorfman have measured the spectrum of e_{solv}^- in THF/H_2O mixtures as a function of composition.[3] In this binary liquid system consisting of a weakly polar and a strongly polar compound, Jou and Dorfman observed *one* absorption band with an absorption maximum, $\hbar\omega_{max}$, varying between 0.585 (pure THF) and 1.73 eV (pure water). In Figure 1 we have collected the results of this investigation, i.e., $\hbar\omega_{max}$ and the width at half-height, $W_{1/2}$, of the absorption band as a function of the composition. From these results, Jou and Dorfman concluded that for a THF mole fraction $X(\text{THF}) \leq 0.50$, the spectrum is strongly dominated by water. They pointed out, however, that in this mole fraction range a bulk property like the dielectric constant is dominated just by THF and not by water.[4,5]

Jou and Freeman have determined temperature and isotope effects on the shape of the optical absorption spectrum of solvated electrons in water (H_2O and D_2O).[6] By increasing the temperature from 274 to 380 K, the spectrum of e_{solv}^- is red-shifted from 1.793 to 1.531 eV in H_2O and from 1.828 to 1.552 eV in D_2O.

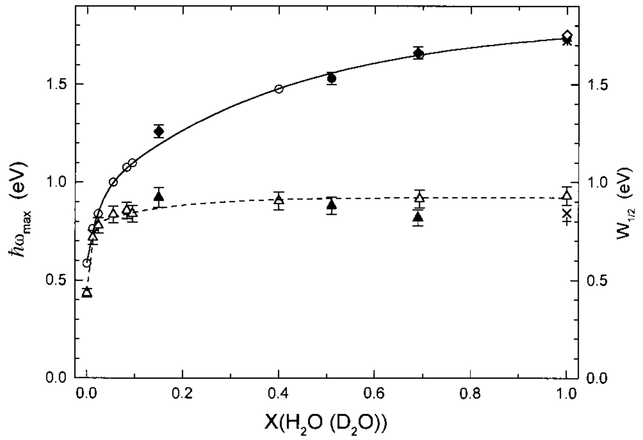

Figure 1. Position of the absorption maximum, $\hbar\omega_{max}$, and the width at half-height, $W_{1/2}$, of the optical absorption band of e_{solv}^- in THF/H_2O (D_2O) mixtures as a function of the mole fraction of water $X(H_2O\text{-}(D_2O))$. $\hbar\omega_{max}$: (○), Jou and Dorfman THF/H_2O, $T = 298$ K (refs 3 and 4); (◇) D_2O, Jou and Freeman $T = 298$ K (ref 6); (*) H_2O, $T = 298$ K (ref 6); (◆) THF/D_2O, $T = 298$ K, this work; (●) THF/H_2O, $T = 298$ K, this work. The solid line connecting the results of Jou and Dorfman serves as a guide. $W_{1/2}$: (△) Jou and Dorfman THF/H_2O (refs 3 and 4); (+) D_2O, Jou and Freeman (ref 6); (×) H_2O (ref 6); (▲) THF/D_2O and THF/H_2O, this work. The dashed line connecting the results of Jou and Dorfman serves as a guide.

If the electron in THF/water mixtures is in fact hydrated for $X(\text{THF}) \leq 0.50$, then one would expect that the optical properties of e_{solv}^- in these mixtures should resemble those of a (slightly disturbed) hydrated electron in pure water. Therefore, we want to answer the question of whether the spectra of the hydrated electron determined by Jou and Freeman at 340 and 380 K, respectively, agree with those of e_{solv}^- in THF/ H_2O (D_2O) mixtures for some suitable compositions in the THF mole fraction range between $X(\text{THF}) = 0$ and 0.50. We have done

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10.1021/jp983520d CCC: $18.00

such experiments because, unfortunately, Jou and Dorfman have not published any spectra of e_{solv}^- in these mixtures.

From these spectra we can get the ground-state properties of e_{solv}^- as a function of composition and/or temperature by applying so-called optical sum rules. The results independent of any model that may be ascribed to e_{solv}^- can be compared with the properties of e_{solv}^- obtained by current methods of quantum-statistical simulations.

II. Experimental Section

Solvated electrons were produced by irradiation of light in the low-energy tail of the CTTS-spectrum of iodide ion I^- according to[7−11]

$$I^- + \hbar\omega \rightarrow I^\bullet + e_{solv}^- \qquad (1)$$

Therefore, potassium iodide (about 5×10^{-3} M, Merck, suprapur 99.5%) was used in THF/H_2O mixtures. The wanted amount of anhydrous KI was filled in a reservoir of the sample cell and dried at the vacuum line (1×10^{-6} mbar). Then the cell was flushed with N_2 and the desired amount of freshly prepared 4-fold distilled H_2O was filled in the vessel. The last two distillation steps were prepared from permanganate in a quartz apparatus. D_2O (Roth, minimum isotopic purity 99.7 atom %D) was used without further purification.

THF was purified by $LiAlH_4$. In a special glass apparatus which was flushed with argon (5.0, Messer-Griesheim), 1 g of $LiAlH_4$ was added to 100 mL of THF. The solution was gently bubbled with argon and refluxed for 4 h in order to make THF free of peroxides. Then it was fractionally distilled through a 50 cm Vigreux column. The middle fraction was degassed and vacuum distilled into a storage bulb containing a sodium mirror made of freshly triple-distilled sodium. From this reservoir the desired amount of THF was vacuum-distilled in the sample cell. The solutions in the cell are made free of O_2 and CO_2 by at least 5 freeze−pump−thaw cycles at the vacuum line. Thereafter, the sample cell with the solution was flushed again with about 1 bar of argon. For the measurements the solution was then transferred to the attached spectrosil cell (Hellma) of 10 mm optical path length. It should be pointed out that before sample preparation, the glass vessel with the quartz cell was cleaned with overheated water vapor for at least 24 h.

For further experimental details concerning the production of e_{solv}^-, the absorption measurements, and the evaluation of the total absorption to get the absorption spectra of e_{solv}^- we refer to a former study.[11]

III. Results and Discussion

The concentration of e_{solv}^- was on the order of 10^{-6} M. The mean lifetime of e_{solv}^- in THF/H_2O at $T = 298$ K was about 2−6 μs. In Figure 2 we show the e_{solv}^- absorption spectrum in a solution consisting of X(THF) = 0.31 and $X(D_2O)$ = 0.69 at 298 K. The absorbance A at each $\hbar\omega$ has been normalized to the absorption maximum A_{max}. The dashed line represents the best fit to an e_{solv}^- absorption spectrum in pure D_2O at 340 K determined by Jou and Freeman in a pulse radiolytic experiment.[6] The agreement is almost quantitative. By increasing the mole fraction of THF to X(THF) = 0.49 ($X(H_2O)$ = 0.51) a spectrum is obtained which agrees (within the experimental error) with the e_{solv}^- absorption spectrum in pure H_2O at 380 K (see Figure 3). In both cases we have used a Gaussian line shape at the low-energy side and a Lorentzian line shape at the high-energy side of the spectrum with just the parameters published by Jou and Freeman (see Table 1 in ref 6). It was pointed out by Jou and Freeman that for $A/A_{max} < 0.04$ on the Gaussian (low-energy) and for $A/A_{max} < 0.1$ on the Lorentzian (high-energy) side the data were less certain due to the low light intensity at low energy and to the correction for radicals at high energies.[12] The corresponding quantities $\hbar\omega_{max}$ and $W_{1/2}$ have also been taken into account in Figure 1, together with the results for another mixture consisting of X(THF) = 0.85 and $X(D_2O)$ = 0.15 at 298 K.

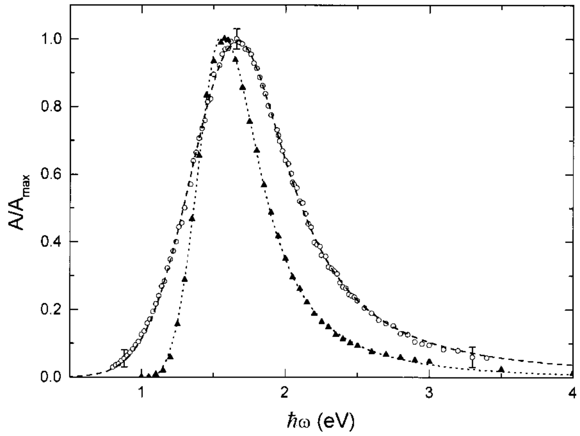

Figure 2. Normalized optical absorption spectrum of e_{solv}^- in a THF/D_2O mixture with X(THF) = 0.31 at T = 298 K (○): $\hbar\omega_{max}$ = 1.66 eV; $W_{1/2}$ = 0.86 eV. The error bars show the maximum calculated error. The dashed line represents the best fit by a Gaussian and Lorentzian line shape to the spectrum of e_{solv}^- in pure D_2O at T = 340 K observed by Jou and Freeman (ref 6). (▲) Taken from the theoretical calculation performed by Gallicchio and Berne (ref 29). The pointed line represents a Gaussian/Lorentzian line shape fit.

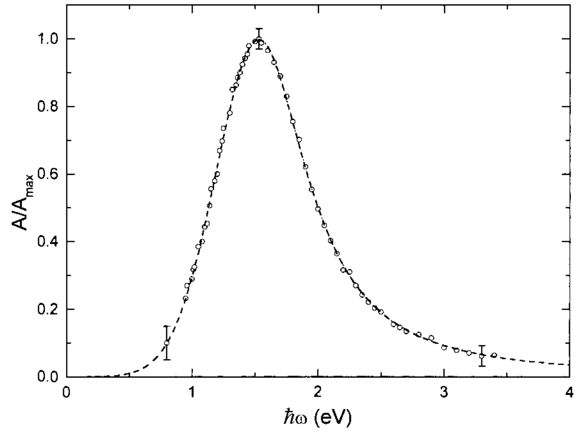

Figure 3. Normalized optical absorption spectrum of e_{solv}^- in a THF/H_2O mixture with X(THF) = 0.49 at T = 298 K (○): $\hbar\omega_{max}$ = 1.53 eV; $W_{1/2}$ = 0.88 eV. The error bars show the maximum calculated error. The dashed line represents the best fit by a Gaussian and Lorentzian line shape to the spectrum of e_{solv}^- in pure H_2O at T = 380 K given by Jou and Freeman (ref 6).

From these experimental results it follows, for example, that the mole fraction X(THF) = 0.49 in a THF/H_2O mixture at 298 K has the same effect on the e_{solv}^- spectrum in comparison with the spectrum in pure water at 298 K as a temperature increase from 298 to 380 K in pure H_2O. This means that excess electrons in this mixture are insensitive to the bulk properties (such as the dielectric constant, see Figure 4 of ref 4). e_{solv}^- seems to be rather connected with the local characteristics of the solvent: They behave like more or less “hot” *hydrated* electrons.

The interaction energy of the water system is reduced at 380 K due to the increased thermal motion of the water molecules with a concomitant reduction of hydrogen bonding. Berne and co-workers have estimated by computer simulations that the

TABLE 1: Equilibrium Ground-State Properties of Solvated Electrons: The Mean Static Dipole Polarizability $\langle\alpha(0)\rangle$, the Mean Dispersion in Position $\langle r^2\rangle$, and the Mean Dispersion in Kinetic Energy $\langle T\rangle$ of e_{solv}^- in H_2O (D_2O), THF, and THF/H_2O (D_2O) Mixtures

solvent	T (K)	$\hbar\omega_{max}$ (eV)	$\langle\alpha(0)\rangle^{exp}$ (Å^3)	$\langle\alpha(0)\rangle^{corr}$ (Å^3)	$\langle r^2\rangle^{exp}$ (Å^2)	$\langle r^2\rangle^{corr}$ (Å^2)	$\langle T\rangle^{exp}$ (eV)	$\langle T\rangle^{corr}$ (eV)	refs[a]
H_2O	299	1.72	32.8	34.1	5.99	6.22	1.62	1.47	22[b]
H_2O	274	1.793		29.5		5.69		1.70	6, this work
	274	1.793				5.88		1.61	6, 2
	298	1.725	32.8	32.5		5.94		1.65	6, this work
	340	1.632		38.5		6.41		1.55	6, this work
	380	1.531	46.1	46.5	7.05	6.96	1.36	1.46	6, this work
D_2O	340	1.665	38.0	36.6	6.46	6.30	1.45	1.56	6, this work
THF	155	0.85	114	128	11.05	11.54	0.89	0.87	23, this work
	298	0.585		≈285		≈17.3		≈0.58	extrapolated[c]
THF(0.31)/D_2O(0.69)	298	1.66	39.4	37.0	6.63	6.31	1.38	1.56	this work
THF(0.49)/H_2O(0.51)	298	1.53	46.7	46.3	7.17	6.95	1.30	1.46	this work
THF(0.85)/D_2O(0.15)	298	1.26	58.0	62.0	7.9	8.0	1.17	1.15	this work

[a] First reference: experimental spectrum. Second reference: evaluation of the ground-state properties. [b] Carmichael used a spectrum of Jou and Freeman (*Can. J. Chem.* **1979**, *57*, 591) fitting it by a skewed Gaussian. [c] See refs 11 and 20.

number of hydrogen bonds at 373 K is reduced by about 15% in comparison with room temperature.[13] Obviously, such a large amount of 49 mol % THF produces the same relatively small effect on the structure of the hydrated electron. The spectra show "shape stability",[2] i.e., the shape does not change appreciably by substantial changes in the composition of the solvent. Also in the case of pure water (in D_2O), the absorption band of e_{solv}^- is red-shifted but preserves its shape in the temperature range $274 \leq T \leq 634$ K.[14,15] In summary, in the case of THF/H_2O (D_2O) mixtures, we observe only slightly disturbed hydrated electrons in comparison with pure water. In the following discussion we will estimate some ground-state properties of e_{solv}^- as a function of solvent composition and/or temperature.

Brodsky and Tsarevsky[16,17] were the first to apply optical sum rules in the analysis of the absorption spectra of e_{solv}^- in order to get some equilibrium ground-state properties of the solvated electron. Lateron, Golden, and Tuttle[2,18] also used this many-particle theory, which is independent of any model for the solvated electron (for example, such as an excess electron in a solvent cavity).[19] In the following, we summarize the relevant results for the evaluation of the e_{solv}^- spectra[11,20]

$$S(-2) = n_0 \frac{c}{C_0} \int_0^\infty \gamma(\omega)\omega^{-2}\, d\omega = \langle\alpha(0)\rangle$$

$$S(-1) = n_0 \frac{\hbar c}{C_0 e^2} \int_0^\infty \gamma(\omega)\omega^{-1}\, d\omega = \frac{2}{3}\langle r^2\rangle$$

$$S(0) = n_0 \frac{m_e c}{C_0 e^2} \int_0^\infty \gamma(\omega)\, d\omega = 1 \qquad (2)$$

$$S(+1) = n_0 \frac{m_e \hbar c}{C_0 e^2} \int_0^\infty \gamma(\omega)\omega\, d\omega = \frac{4}{3}\langle T\rangle$$

$$\text{with } C_0 = 2\pi^2 N_A/\ln 10$$

$\gamma(\omega)$ is the molar decadic extinction coefficient of e_{solv}^- at the absorption frequency, ω, and n_0 is the refractive index of the system considered to be independent of ω. N_A is Avogadro's constant, and c is the light velocity in a vacuum. The equation for $S(0)$ in eq 2—the sum of the oscillator forces—represents the Thomas−Reiche−Kuhn sum rule.[21] This rule was verfied by Golden and Tuttle for solvated electrons in a variety of polar solvents, especially in H_2O/D_2O, thus supporting the many-particle theory.[2] Golden and Tuttle originally introduced *thermalized* spectral moments for e_{solv}^- in a condensed medium by averaging the sum rules over a Boltzmann distribution of initial states. Under conditions of usual experimental interest, these corrections are, however, negligibly small. With the assumption that the TRK sum rule is valid also in the case of THF/H_2O-(D_2O) mixtures (which is at least justified for $X(\text{THF}) \leq 0.50$), one very easily obtains by the application of these sum rules (2) the mean static dipole polarizability, $\langle\alpha(0)\rangle$, the mean squared dispersion in position, $\langle r^2\rangle$, and the mean dispersion in kinetic energy, $\langle T\rangle$, of e_{solv}^- in the *ground state*.

In Table 1 we have listed values of $\langle\alpha(0)\rangle$, $\langle r^2\rangle$, and $\langle T\rangle$ for solvated electrons in H_2O and in D_2O at different temperatures,[6,22] in THF,[23] and in THF/H_2O(D_2O) mixtures. The quantities with the superscript exp are obtained directly from the experimental spectra in the restricted experimental spectral range, whereas the quantities marked by corr are obtained from the experimental spectra which were fitted and *extended* by a Gaussian and Lorentzian shape function[24] beyond the experimentally observed spectral range (in order to approach the required integration limits 0 and ∞). For instance, the obtained quantity $\langle r^2\rangle$ determines the equilibrium radial probability density $\rho(r) = (3/2\pi\langle r^2\rangle)^{3/2} \exp\{-3r^2/2\langle r^2\rangle\}$ of the solvated electron about its mean position.[2,25] $\langle P^2\rangle = (2m_e\langle T\rangle)$ fixes the corresponding conjugate momentum distribution of the solvated electron. It was already pointed out by Brodsky and Tsarevsky that the shape stability of the e_{solv}^- spectrum with respect to variation of external conditions suggests that only small fluctuations in $\langle r^2\rangle$ and $\langle T\rangle$ exist.[16]

In principle, all these quantities can be calculated by current methods of quantum-statistical simulations of solvated electrons. In the case of e_{solv}^- in methanol, we have already shown the discrepancies between the simulated quantities[26] and the equilibrium ground-state properties obtained from the experimental spectra with the aid of the above sum rules.[11] In Table 2 we compare the theoretically simulated results for e_{solv}^- in H_2O at 300 and 373 K[13,27,28] with those obtained from the 298 and 380 K spectra. The scatter of the data due to the application of different methods and approximations in evaluating the experimental spectra is by far smaller than the differences between theory and experiment. Not only are the calculated ground-state properties of the hydrated electron in strong contradiction to the experimental values, but also the simulated optical absorption spectra which neither show the typical asymmetry[13,27] nor the red shift with increasing temperature[13] (see also the critical notes in ref 2). In any case, in these simulations the absorption is only due to bound-state/bound-state transitions ($2p_i \leftarrow 1s$) of an excess electron in a cavity-type entity ($i = x, y, z$). Bound-

TABLE 2: Equilibrium Ground-State Properties of Solvated Electrons in H_2O as a Function of T: Comparison between Theory and Experiment (see text)

	theory								
	Schnitker and Rossky[a] $T = 300$ K	Berne and co-workers[b]		Gallicchio and Berne[c]			experiment		
		$T = 300$ K	$T = 373$ K	$T = 298$ K	$T = 340$ K	$T = 373$ K		$T = 298$ K	$T = 380$ K
$\langle r_g^2 \rangle$/Å^2 [d]	5.76	3.57[e]		3.57[e]			$\langle r^2 \rangle$/Å^2	5.94	6.96
0.25 R^2/Å^2 [f]	2.89	2.73[g]	2.70[g]	~3.15[h]	~3.26[h]	3.36[h]			
$\langle T \rangle$/eV	2.13	0.87 ± 0.35	0.83 ± 0.35	~1.63[i]	~1.63[i]	~1.63[i]	$\langle T \rangle$/eV	1.65	1.46
$\langle \alpha(0) \rangle$/Å^3							$\langle \alpha(0) \rangle$/Å^3	32.45	46.45
$\hbar\omega_{max}$/eV	2.4[j]	1.72	1.72	1.64	1.57	1.51	$\hbar\omega_{max}$/eV	1.725	1.531

[a] Reference 27. [b] Reference 13. [c] reference 29. [d] r_g, radius of gyration; $\langle r_g^2 \rangle$ characterizes the Gaussian electron distribution function in the ground-state (see, e.g., ref 28). [e] Reference 28. [f] $R^2(t) = \langle |r(t) - r(0)|^2 \rangle$ is the real time displacement correlation function (see refs 27 and 28); the radius has been estimated from $0.5\sqrt{R^2(\hbar/2k_BT)}$. We used the squared value for comparison with $\langle r_g^2 \rangle$. [g] With many body polarization. [h] Estimated from Figure 5 of ref 29. [i] Estimated from the velocity correlation function $\langle v(t) \cdot v(0) \rangle$ in Figure 6 of ref 29 (see text). [j] Rossky, P. J.; Schnitker, J. *J. Phys. Chem.* **1988**, *92*, 4277.

state/continuum transitions were not considered. Besides, Wallqvist, Martyna, and Berne[13] determined an oscillator strength of 0.9 or greater for the $2p_i \leftarrow 1s$ transitions. There is obviously not enough oscillator strength for more highly excited states to reproduce just the characteristic high-frequency tail of the spectrum. However, as the TRK sum rule has been verified for e_{solv}^-, it follows immediately that all optical transitions have to be included in the spectrum, also transitions into the continuum.

In a recent paper Gallicchio and Berne applied the maximum entropy analytic continuation method to calculate the optical absorption spectra of the hydrated electron from equilibrium-path integral Monte Carlo data.[29] The spectrum is now slightly red-shifted with increasing temperature and shows, in fact, an indication of a high-frequency tail (see Figure 2 for $T = 340$ K). However, its width is by far too small (about 0.48 eV at $T = 340$ K in comparison with $W_{1/2}^{exp}$ (D_2O) = 0.82 eV and $W_{1/2}^{exp}$ (H_2O) = 0.86 eV) and the slope of the low-energy side line shape is too steep. But the most important difference seems to be that the shape stability of the spectra at 298, 340, and 373 K is *violated* (see Figure 4a of ref 29). There is another decisive point. Gallicchio and Berne have calculated the real-time velocity correlation function $\langle \vec{v}(t) \cdot \vec{v}(o) \rangle$ of hydrated electrons at three different temperatures. They pointed out that the initial value of the velocity correlation function ($t \rightarrow o$) is the mean square velocity, a measure of the average kinetic energy of the electron. From Figure 6 of ref 29 we obtain the values for $\langle T \rangle$ given in Table 2 which agree quite well with the experimental values. Taking into account the fact that according to Wallqvist, Martyna, and Berne[13] the TRK sum rule is approximately fulfilled (see above), then we can apply the sum rules (eq 2) on the spectra calculated by Gallicchio and Berne (like that in Figure 2). In this case, however, we obtain again those disagreeing values for $\langle T \rangle$ which were published in the past by Berne and co-workers[13] (see Table 2). On the one hand this result shows that the sum-rule $S(+1)$ works well, on the other hand it demonstrates that the simulations of Gallicchio and Berne are obviously not consistent.

The published results of the simulations are always considered as proof for the existence of an excess electron in a *solvent cavity*. In our opinion, the ansatz of the electron/molecule interaction potential already contains this information, which is only transformed by these quantum-statistical simulations into the cavity picture. This means, for instance, that the possiblity of a *solvent*–anion complex (SAC) as proposed, for instance, by Golden and Tuttle[2] is not included in the potential used in the simulations. In this context, we should refer for comparison to the spectra of a *solute*–anion type species such as M_{solv}^- in THF or other solvents where M is an alkali metal. The asymmetric and featureless optical absorption spectrum resembles those of e_{solv}^- and can be described approximately by a Gaussian/ Lorentzian line shape.[20] The spectrum depends on the cation M^+ and corresponds to a two-electron transition.[30,31]

Kajiwara, Funabashi, and Naleway[32] and Brodsky and Tsarevsky[33] introduced a model based on a short-range spherical well potential with only *one* bound state. With a few parameters matched to the absorption spectra, the shape and the width of the band are well reproduced by *bound-continuum* transitions of the excess electron.[34] Delahay has studied the photoionization spectra of e_{solv}^- in hexamethylphosphoric triamide[35] and pointed out that the simple model of a particle in a finite box fits the photoionization spectra quite well.[36] Thompson[37] argued, however, that such a model cannot be taken too seriously due to the *long-range* Coulombic interactions responsible for the localization of the electrons. In the meantime, there is no doubt that the effective many-particle interaction which gives rise to the localization of excess electrons is rather a short-range interaction.[13] However, the other limiting case of a very short-range interaction, i.e., an excess electron in a *zero-radius* potential (as proposed by Brodsky and Tsarevsky[16]) could be definitely excluded by us.[11] It seems to us that a remark by Kestner at Colloque Weyl IV should be revived for future theoretical work:[38] "If a Coulombic tail does not exist we must provide some theoretical reasons for its vanishing. It seems likely that the best model will appear closer to a particle in a box than a Coulombic potential."

IV. Conclusions

An important conclusion which can be drawn from this study is that optical spectroscopy provides an essential and sound means of discriminating among models of e_{solv}^-. A long story can be written on the theoretical description of the solvated electron and its absorption spectrum starting with the work of Ogg[39] and later on with the fundamental work of Jortner.[40] But to be correct, we have to say that up to now we do *not* know (exactly) on which transitions the experimentally observed absorption spectrum of solvated electrons in polar liquids is based. Therefore, it is presumptuous that some of the members of the femtosecond research community assert that the absorption spectra of the solvated electron in water are understood.[41] They simply modeled the hydrated electron by a two-level system comprised of an s ground state and of three nondegenerate p excited states based on the above-mentioned quantum-statistical simulation work. An extreme case of such an arbitrary interpretation is given in Figure 2a of ref 42 where the spectrum is composed of three energetically equidistant $2p_i \leftarrow 1s$ transitions and a gound-state/continuum transition. Although we do not know which states (except for the s ground state) are involved in the optical transition(s) leading to the equilibrium absorption band a lot of additional electron states are postulated in femtosecond investigations.[42,43] Moreover, new species such as *wet* and *presolvated* electrons are created besides the solvated electron.[41,44] Such terms are ambiguous and should be avoided. In principle, the lack of knowledge on the electron/water system is hidden behind additional electron states and such species. A recent femtosecond study on ultrafast relaxation dynamics of electrons in a water jet has shown that at present no other transient states than hot solvated electrons are necessary to understand ultrafast dynamics within a time resolution of about 100 fs.[45] In other words, there is a *continuous* transition of the hot hydrated electron to the well-known equilibrated hydrated electron in the course of time similar—except for the time scale—to the case of excess electrons in alcohols at low temperatures observed qualitatively 20 years ago.[46]

Acknowledgment. This work has been supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie. A.N.A. gratefully acknowledges support by a grant from the Deutscher Akademischer Austauschdienst (DAAD).

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