

Ab Initio Localized Electron Calculations on Solvated Electron Structures

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Abstract: Ab initio molecular orbital calculations using a localized split-valence (31) s-orbital to represent the electron in a cavity model and using the standard 6-31G* basis for solvent molecules are remarkably successful in calculating the structure of solvated electrons. Calculated structures for hydrated electrons are in good agreement with experiment. Structures are predicted for ammonia-, methylamine-, ethylamine-, dimethylamine-, dimethyl ether-, and propane-solvated electrons. Solvation energies for the localized electron correlate moderately well with experimental λ_{\max} values and an $e^-(\text{H}_2\text{O})_6$ cluster is calculated to be bound relative to a free electron and six water molecules. Spin densities and Fermi contact terms are discussed. The bonding in solvated electrons is found to involve some donation to OH or NH antibonding orbitals, but bond and atom spin polarization play a major role in electron solvation.

Solvated electrons have been extensively studied by a variety of methods,¹ but their structures were unknown until the advent of new methods of analysis of electron spin echo modulation patterns, second moment line shapes, and forbidden proton spin-flip transitions in disordered systems such as electrons in glassy matrices.² The results of these investigations revealed surprising details about the geometries of solvated electrons. In particular, the "OH bond orientation" found for hydrated electrons and the 30° or 60° rotation of the OH bond in ethanol solvated electrons represent unexpected departures from a simple "dipole orientation" model.² Perhaps the most successful theoretical treatment of the solvated electron is Newton's combination of the semicontinuum model³ with ab initio methods,⁴ but even this does not successfully reproduce the geometry of the hydrated electron.

Our recent work using "inadequate" basis sets to mimic the behavior of radical anions in condensed phases^{5,6} has demonstrated that artificially curtailing the extent of the most diffuse functions in a basis set can be an effective method of simulating the cavity effect in condensed phases. This effect relies on the inability of an LCAO calculation to use regions of space other than those described by the basis functions. This approach has strong conceptual similarities with the localized or "solvated anion" model for solvated electrons,⁷ which in turn relates to Ogg's original cavity model.⁸ Kevan's results support this model, and he has pointed out the similarity between his structure for the hydrated electron and the X-ray structure of potassium fluoride dihydrates.⁹ However, Golden and Tuttle,^{10a} in one of a series of papers in

which they outline their view of the solvated electron,^{10b} have questioned the validity of Kevan's interpretation and have pointed out that the treatment used could give rise to a bogus cavity, even if none existed. Nevertheless, the cavity model remains popular and can account for many aspects of the physical behavior of solvated electrons. It has received spectacular support from the recent X-ray structure of $e^- \text{Cs}^+ (18\text{-crown-6})_2$ by Dye et al.¹¹ We have, therefore, combined the cavity model with our "inadequate" basis set approach to investigate solvated electron structures. Newton⁴ also used a cavity model with a split-valence s-orbital to describe the solvated electron. The exponent of the more diffuse function was, however, 0.01 a_0^2 , a value more compatible with gas-phase calculations. For comparison, the exponent of the Rydberg functions used to describe dipole-bound CH_3CN^- was 0.005,⁵ and the standard diffuse-function exponents for the anion-optimized 6-31+G* basis set¹² are 0.0438 for carbon, and 0.0639, 0.0845, and 0.1076 for nitrogen, oxygen, and fluorine, respectively. The carbon exponent was optimized for the methyl anion, which has an electron affinity of 0.08 eV,¹³ so that this exponent essentially provides a Rydberg orbital. We, therefore, decided to investigate the behavior of a far more compact s-orbital representation of the solvated electron in order to produce a model which successfully treats at least the short-range effects operating in solvated electrons without resorting to external potentials. It should be emphasized that the calculations reported here are not appropriate to the gas phase. Addition of diffuse functions would of course result in "better" calculations, but they would then begin to approximate gas-phase behavior. The small basis set used here has been deliberately restricted in order that (a) the electron is localized (i.e., we are using a solvated anion model) and (b) the solvent molecules do not possess adequate diffuse functions to form loosely bound radical anions. In effect, the small basis set is restricting the extent of the electron density in the same way as the spherical potentials used in calculations on macroscopic solvent effects.¹⁴ This simple trick allows a highly cost-effective simulation of condensed-phase behavior.

The results are particularly encouraging with respect to structure determination, especially as the calculations can be performed with the standard GAUSSIAN 82 or any other comparable program package.

(1) See, for instance: The Proceedings of the Fifth and Sixth International Conferences on Excess Electrons and Metal-Ammonia Solutions. *J. Phys. Chem.* **1980**, *84*, 1065-1298. *J. Phys. Chem.* **1984**, *88*, 3699-3906.

(2) Kevan, L. *Acc. Chem. Res.* **1981**, *14*, 138. Kevan, L. *J. Phys. Chem.* **1981**, *85*, 1628 and references therein.

(3) Feng, D. F.; Devan, L. *Chem. Rev.* **1980**, *80*, 1 and references therein.

(4) (a) Newton, M. D. *J. Phys. Chem.* **1975**, *79*, 2795. (b) Rao, B. K.; Kestner, N. R. *J. Chem. Phys.* **1984**, *80*, 1587.

(5) Clark, T. *Faraday Disc. Chem. Soc.* **1984**, *78*, 203.

(6) Clark, T. *J. Chem. Soc. Chem. Commun.* **1984**, 93.

(7) See, for instance: Atkins, P. W.; Symons, M. C. R. *The Structure of Inorganic Radicals*; Elsevier: Amsterdam, 1967; Chapter 4. Symons, M. C. R. In *Electron-Solvent and Anion-Solvent Interactions*, Kevan, L., Webster, B. C., Eds.; Elsevier: Amsterdam, 1976; pp 325-6. *Chem. Soc. Rev.* **1976**, 337.

(8) Ogg, R. A., Jr. *J. Am. Chem. Soc.* **1946**, *68*, 155.

(9) Beurskens, G.; Jeffrey, G. A. *J. Chem. Phys.* **1964**, *41*, 917.

(10) (a) Golden, S.; Tuttle, T. R., Jr. *J. Phys. Chem.* **1984**, *88*, 3781. (b) See, for instance: Tuttle, T. R., Jr.; Golden, S. *J. Chem. Soc., Faraday Trans. 2* **1979**, *75*, 474, 1146. Tuttle, T. R., Jr.; Golden, S. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 138, 889, 1421. Tuttle, T. R., Jr.; Golden, S. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 1581. Tuttle, T. R., Jr.; Golden, S. *J. Phys. Chem.* **1980**, *84*, 2457. Tuttle, T. R., Jr.; Golden, S.; Lwenje, S.; Stupak, C. M. *J. Phys. Chem.* **1984**, *88*, 3811.

(11) Dawes, S. B.; Ward, D. L.; Huang, R. H.; Dye, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 3534.

(12) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294.

(13) Ellison, G. B.; Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 2558.

(14) See, for instance: McCreery, J. H.; Cristoffersen, R. E.; Hall, G. G. *J. Am. Chem. Soc.* **1976**, *98*, 7191.

Table I. Total (au) and Relative (kcal mol⁻¹) Energies for Hydrated Electrons

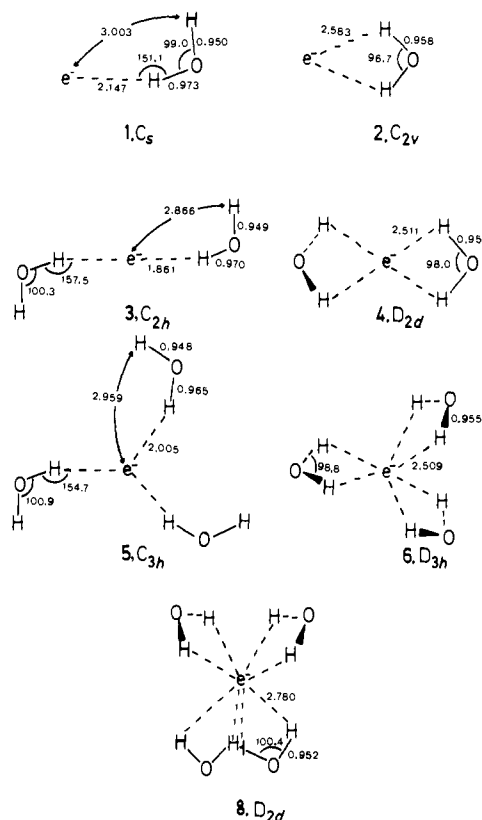
species		tot. energy	rel energy
H ₂ O		-76.010 75 ^a	
e ⁻ (H ₂ O)	1	-75.910 35	0.0
e ⁻ (H ₂ O) ₂	2	-75.909 99	0.2
e ⁻ (H ₂ O) ₃	3	-151.945 26	0.0
e ⁻ (H ₂ O) ₃	4	-151.943 54	1.1
e ⁻ (H ₂ O) ₃	5	-227.977 86	0.0
e ⁻ (H ₂ O) ₄	6	-227.974 62	2.0
e ⁻ (H ₂ O) ₄	7	-304.011 18	0.0
e ⁻ (H ₂ O) ₄	8	-304.001 77	5.9

^aReference 16.**Method**

All calculations used the GAUSSIAN 82 series of programs¹⁵ modified for the CYBER 175 and 845 computers by A. Sawaryn and T. Kovář. The unrestricted Hartree-Fock (UHF) formalism was used throughout, but all S² values are less than 0.751, so that spin contamination is not a problem. The standard 6-31G* basis set¹⁶ was used for all real atoms. The electron was represented by a 31 split s-orbital. The inner 3-Gaussian function was simply the inner 1s function from the 6-31G* basis set¹⁶ for hydrogen but was used unscaled (i.e., it is less compact than the corresponding hydrogen basis). The outer s-function used an exponent of 0.09, which places it between the diffuse functions used for oxygen and fluorine in 6-31+G*.¹² This combination was found to give good results in preliminary calculations and was, therefore, used throughout. In retrospect a 13, rather than a 31, split would probably have been more appropriate to this problem, but the practices common to atom-based calculations die hard. Six Cartesian d-functions were used throughout. These were found to be important in describing the electron-solvent interaction. Preliminary work with the 3-21G basis gave poor results. Diffuse functions were also added to the heavy atoms and to the hydrogens in trial calculations, but they gave a tendency for the solvent molecules to form σ* radical anions rather than solvating the electron. Increasing the diffuse exponents cured this tendency but then gave results equivalent to those obtained by using the unmodified 6-31G* basis. Geometry optimizations used the standard Murtaugh-Sargent¹⁷ routines from GAUSSIAN 82. These were found to be more effective than the alternative procedures. In most cases SCF-damping was necessary in order to achieve convergence. Typically, a damping factor of 0.5 (50% mixing of the density matrix from the last cycle into the new one) gave rapid convergence. This damping was switched off near convergence.

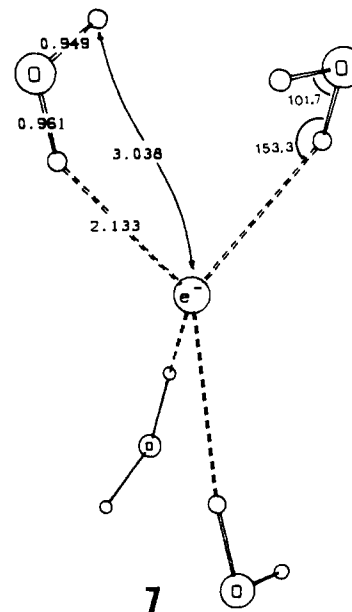
Results

Hydrated Electrons. Table I shows the total and relative energies obtained for electron mono-, di-, tri-, and tetrahydrates 1-8. Two models were investigated: the "OH bond orientation" structures 1, 3, 5, and 7 and the "dipole orientation" geometries 2, 4, 6, and 8. In all cases the dipole-oriented isomers were found to be less stable than their bond-oriented counterparts. For e⁻(H₂O)₄ the difference is found to be almost 6 kcal/mol⁻¹, suggesting that the bond-oriented structure for an electron with six water molecules in the first solvation shell is favored by almost 8 kcal/mol⁻¹ over the dipole-oriented equivalent. One remarkable feature of the bond-oriented structures is the relative constancy of the structure of the e⁻-H₂O moiety in e⁻(H₂O)_n from n = 1, 4. Apart from the abnormally short e⁻-H distance found for 3, the values found for this parameter vary only in the range 2.005-2.147 Å. Similarly, the e⁻-H-O angles, which are roughly inversely proportional to the e⁻-H distance, are all in the range 151-158°. In all cases the OH bond adjacent to the electron is slightly longer than the more distant one, suggesting a degree of normal hydrogen bonding to the electron. The HOH angles of the water molecules are in the range 99-102°, smaller than the 105.5° angle found for unperturbed water at 6-31G*.¹⁸ This angle does, however, increase steadily with increasing number of



solvating water molecules. A narrowing of the HOH angle was also found by Newton⁴ for the hydrated electron.

The constancy in these calculations has two important consequences: structure 7 can be compared with the experimental geometry for e⁻(H₂O)₆,² and calculations for larger solvent



molecules can be expected to reproduce at least the main features of the experimentally observed structure if only one solvent molecule is considered. Experimentally² the hydrated electron is surrounded by six water molecules with six protons at a distance of 2.1 ± 0.1 Å and six more distant protons about 3.6 Å from the electron. Structure 7 reproduces the shorter e⁻-H distance well but gives a longer e⁻-H distance of only 3.04 Å. A 180° e⁻-H-O angle would, however, only give a long e⁻-H distance of 3.42 Å with the H₂O geometry calculated for 7. Presumably both the e⁻-H-O and the HOH angle are widened in the experimental structure. Nevertheless, considering that no long range interactions have been considered and that a calculation for e⁻(H₂O)₄ is being

(15) Binkley, J. S.; Whiteside, R. A.; Raghavachari, K.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Frisch, M. J.; Pople, J. A.; Kahn, L. R. *GAUSSIAN 82 Release A*; Carnegie-Mellon University: Pittsburgh, 1982.

(16) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(17) Murtaugh, B. A.; Sargent, R. W. H. *J. Comput. Chem.* **1970**, *13*, 185.

(18) Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. *Carnegie-Mellon Quantum Chemistry Archive*, 2nd ed.; Carnegie-Mellon University: Pittsburgh, 1981.

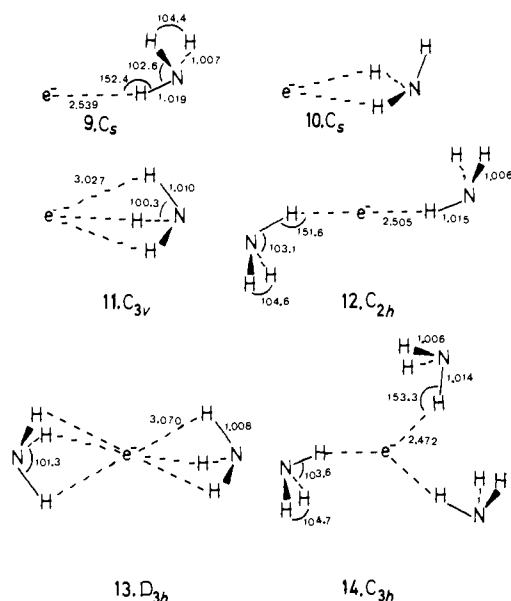
Table II. Total (au) and Relative (kcal mol⁻¹) Energies for Ammonia-Solvated Electrons

species		tot. energy	rel. energy
NH ₃		-56.184 36 ^a	
e ⁻ (NH ₃)	9	-56.072 32	0.0
	11	-56.071 31	0.6
e ⁻ (NH ₃) ₂	12	-112.271 62	0.0
	13	-112.269 77	1.2
e ⁻ (NH ₃) ₃	14	-168.470 06	

^a Reference 16.

compared with the experimental e⁻(H₂O)₆ system, the success of the calculations in correctly predicting the e⁻-H "bond" distance and, qualitatively at least, the bond orientation is remarkable.

Ammonia-Solvated Electrons. The ammonia-solvated electron, e⁻(NH₃), was investigated in conformations in which the electron interacts with one, **9**, two, **10**, and three, **11**, protons of the solvent



molecule. As for water, the bond-orientation structure **9** proved to be the most stable. **10** collapsed to **9** on optimization, and **11** proved to be 0.6 kcal/mol⁻¹ less stable than **9**, as shown by the total and relative energies given in Table II. Because of the instability of **10**, only the bond- and dipole-oriented structures **11** and **12** were investigated for e⁻(NH₃)₂. Once again the bond-oriented structure is calculated to be 1.2 kcal/mol⁻¹ more stable than its isomer. The bond oriented structure **14** was the only one investigated for e⁻(NH₃)₃ as there is no geometry for this species in which three equivalent protons per ammonia are defined by symmetry. The trends observed for the hydrated electron are repeated for the ammonia-solvated electron. The HNH angles (102.6–103.6° for angles involving the unique hydrogen and 104.4–104.7° for third angle) are smaller than that found in unperturbed ammonia at 6-31G* (107.2°).¹⁸ These angles increase steadily with increasing number of solvent molecules, but the angle between the two equivalent hydrogens is always larger than the other two. The "bonding" e⁻-N-H angle lies in the range 151.6–153.3°. As for e⁻(H₂O)_n, however, the structure of the e⁻-NH₃ moiety remains remarkably constant through the three bond-oriented species **9**, **12**, and **14**. Also as expected from the hydrated electron results, the unique NH bond is slightly longer than the other two. Unfortunately e⁻(NH₃)₄ proved to be marginally too large for the available core and disk space, but, nevertheless, structures **9**, **12**, and **14** allow an extrapolation to e⁻(NH₃)₆, which should have a short e⁻-H distance around 2.4 Å and two equivalent longer ones at about 3.5 Å.

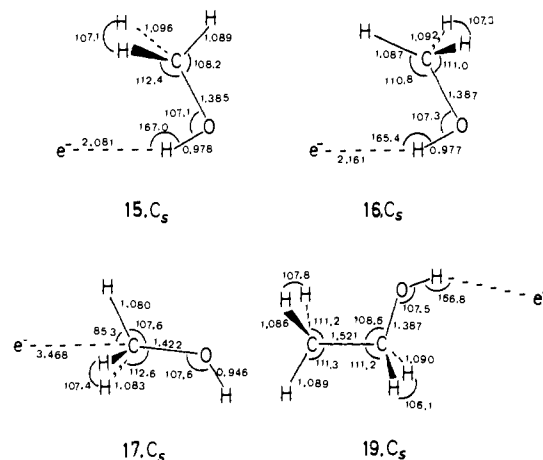
Alcohol-Solvated Electrons. Kevan² has investigated the structures of both methanol- and ethanol-solvated electrons. Unfortunately the methanol experiments are hindered by the presence of the [•]CH₂OH radical produced on irradiation of the matrix, so that only an e⁻-H distance of about 2.3 Å and the fact

Table III. Total (au) and Relative (kcal mol⁻¹) Energies of Electrons Solvated with Organic Molecules

species		tot. energy	rel energy
CH ₃ OH ^a		-115.033 25	
e ⁻ (CH ₃ OH)	15	-114.935 03	0.08
	16	-114.935 15	0.0
	17	-114.916 42	11.9
CH ₃ CH ₂ OH ^a		-154.075 74	
e ⁻ (CH ₃ CH ₂ OH)	18	-153.977 54	0.0
	19	-153.975 57	1.2
CH ₃ NH ₂ ^a		-95.209 83	
e ⁻ (CH ₃ NH ₂)	20	-95.098 30	0.02
	21	-95.093 12	3.3
	22	-95.098 33	0.0
CH ₃ CH ₂ NH ₂		-134.247 73	
e ⁻ (CH ₃ CH ₂ NH ₂)	23	-134.135 04	2.5
	24	-134.131 07	5.0
	25	-134.139 09	0.0
(CH ₃) ₂ NH ^a		-134.238 85	
e ⁻ ((CH ₃) ₂ NH)	26	-134.128 81	
(CH ₃) ₂ O ^a		-154.064 74	
e ⁻ ((CH ₃) ₂ O)	27	-153.949 87	0.0
	28	-153.947 21	1.7
	29	-153.945 42	2.8
CH ₂ (CH ₃) ₂ ^a		-118.263 65	
e ⁻ (CH ₂ (CH ₃) ₂)	30	-118.145 52	

^a Reference 16.

that there are four methanol molecules in the first solvation sphere could be determined. We have investigated the two e⁻(CH₃OH) structures **15** and **16** in which the coordination of the electron is similar to that in water and which differ only in the conformation of the methyl group. As shown in Table III, the eclipsed isomer **16** is calculated to be the more stable, although the barrier of 0.08 kcal mol⁻¹ amounts to essentially free rotation of the methyl group. Kevan² assumed dipole-orientation in his proposed structure of e⁻(CH₃OH)₄, but the electron is calculated to move only slightly inside the line of the OH bond (i.e., toward the dipole) in both **15** and **16**. The e⁻-H distances of 2.08 and 2.16 Å are compatible with Kevan's value of 2.3 ± 0.15 Å, especially considering that e⁻(CH₃OH) is being used as a model for e⁻(CH₃OH)₄.



The third e⁻(CH₃OH) structure considered, **17**, is analogous to the complexes formed prior to the gas-phase S_N2 reaction.¹⁹ In this geometry the localized electron is acting as a nucleophile rather than forming a hydrogen bond. Although **17** is found to be 11.9 kcal mol⁻¹ less stable than **16** (see Table III), it does show the characteristics (such as the long CO bond) of typical S_N2 complexes.¹⁹

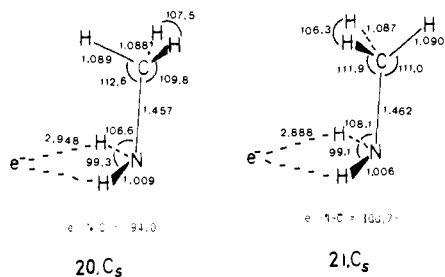
The ethanol-solvated electron presents the most exacting test of structure calculations on solvated electrons. Kevan^{2,20} has found a structure for e⁻(CH₃CH₂OH)₄ in which the OH bond is rotated

(19) See, for instance; Schlegel, H. B.; Mislow, K.; Bernardi, F.; Bottoni, A. *Theor. Chim. Acta* **1977**, *44*, 245.

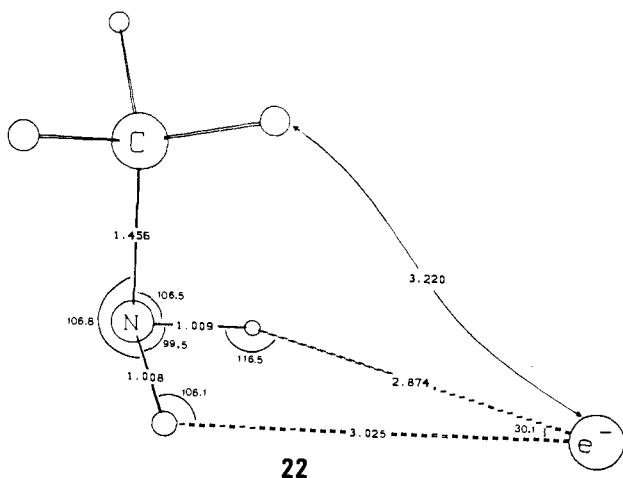
(20) Narayama, M.; Kevan, L. *J. Chem. Phys.* **1980**, *72*, 2891. Narayama, M.; Kevan, L. *J. Am. Chem. Soc.* **1981**, *103*, 1618.

either 30° or 60° toward an eclipsing position with one methylene hydrogen, and in which the electron occupies a position close to the molecular dipole orientation. We have investigated the C_1 structure **18** and the C_s geometry **19** in which the ethanol molecule adopts its normally most stable conformation. Structure **19**, which is found to be 1.2 kcal mol⁻¹ less stable than **18** (Table III), is analogous to $e^-(\text{CH}_3\text{OH})$, **15**, and shows similar structural parameters. **18**, however, shows remarkable similarities to Kevan's proposed $e^-(\text{C}_2\text{H}_5\text{OH})_4$ structure. The OH bond is rotated 101° away from its most stable conformation in unperturbed ethanol to a staggered position *gauche* to the CC bond (see Figure 1). This is a larger rotation than that proposed by Kevan but means that the electron can now occupy a more bond orientation-like position and still give acceptable $e^-\cdots\text{CH}_2$ and $e^-\cdots\text{CH}_3$ distances. The experimental^{2,17} electron-hydrogen distances are 2.2 ± 0.1 Å for the hydroxyl hydrogen and mean values of 3.3 ± 0.1 Å for the two methylene hydrogens and 3.8 ± 0.1 Å for the three methyl protons. The corresponding values for **18** are 2.28, 3.95, and 4.18 Å, respectively. In this case the theoretical model appears to favor the bond orientation rather more than the experimental results suggest is the case in $e^-(\text{C}_2\text{H}_5\text{OH})_4$. The $e^-\text{H}-\text{O}$ angle is, however, a "soft" geometrical parameter (i.e., one for which the potential surface is flat), and a decrease of less than 20° would give the experimental values. Once more, considering the simplicity of the model, the agreement with experiment with respect to the molecular conformation and the "bonding" $e^-\text{H}$ distance is remarkable.

Amine-Solvated Electrons. Electrons solvated with methylamine, ethylamine, and dimethylamine were considered. The three $e^-(\text{CH}_3\text{NH}_2)$ structures, **20-22**, are all relatively similar. The electron interacts with the two amino hydrogens equally in **20** and **21**, which differ only in the conformation of the methyl group,



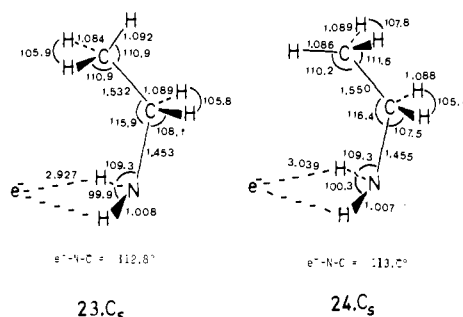
but unsymmetrically in the C_1 structure **22**. The staggered



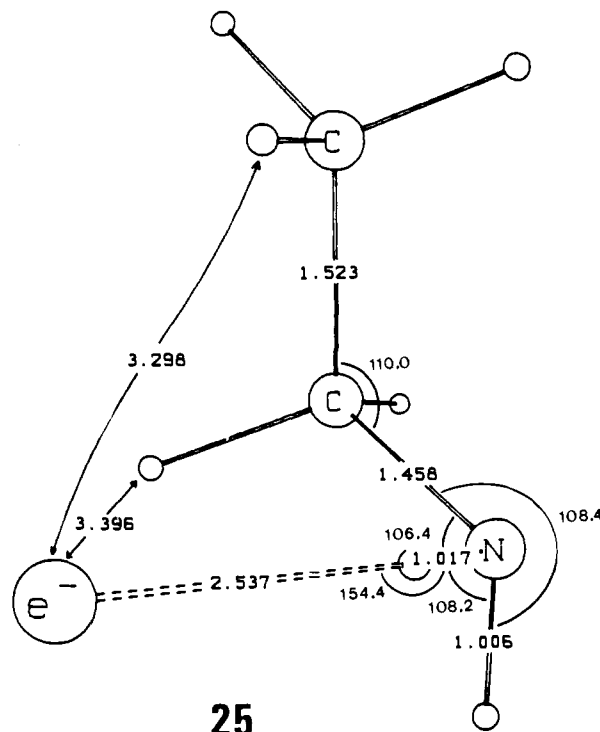
conformation **20** is found to be preferred over the eclipsed isomer **21** by 3.3 kcal mol⁻¹, in contrast to the $e^-(\text{CH}_3\text{OH})$ result. The unsymmetrical structure **22** is, however, suggested to be marginally more stable than **20**, reflecting the preference of $e^-(\text{NH}_3)_n$ for bond oriented structures. The difference in energy between **20** and **22** is, however, extremely small, reflecting once more the ease of such $e^-\text{H}-\text{X}$ angle deformations. In all cases the $e^-\text{H}$ vector lies inside the line bisecting the HNH angle, once more giving a small movement of the electron toward the line of the dipole moment.

The mean calculated electron-hydrogen distances are 2.957 Å for the amino- and 4.105 Å for the methyl hydrogens.

Three structures were investigated for $e^-(\text{CH}_3\text{CH}_2\text{NH}_2)$, the staggered and eclipsed C_s isomers **23** and **24**, and the C_1 structure

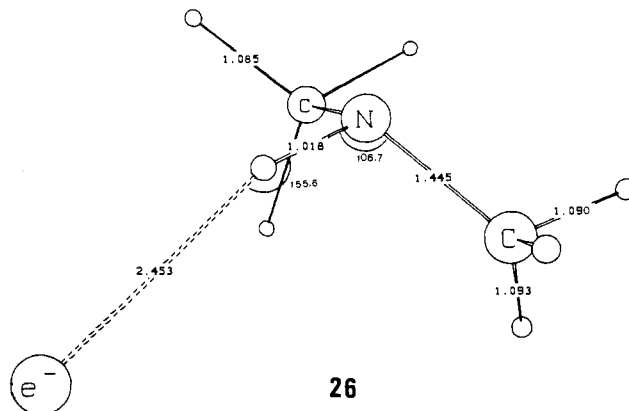


25, which is analogous to $e^-(\text{C}_2\text{H}_5\text{OH})$, **18**. As for the etha-

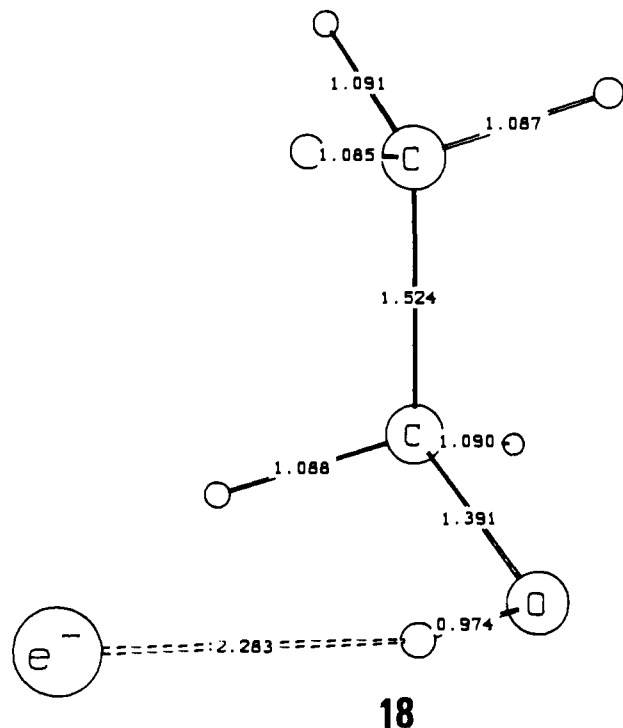


mine-solvated electron, the structure **18**, in which the electron interacts preferentially with a hydrogen *gauche* to the CH_3 group, is found to be most stable. The $e^-\text{H}-\text{N}$ angle is 154°, and once more the electron moves toward a dipole orientation position. The mean electron-hydrogen distances are 3.160 Å for the terminal CH_3 .

Only the C_s structure **26** was calculated for $e^-(\text{CH}_3)_2\text{NH}$.



Once again the electron interacts strongly with the single amino hydrogen and lies slightly on the dipole orientation side of the NH

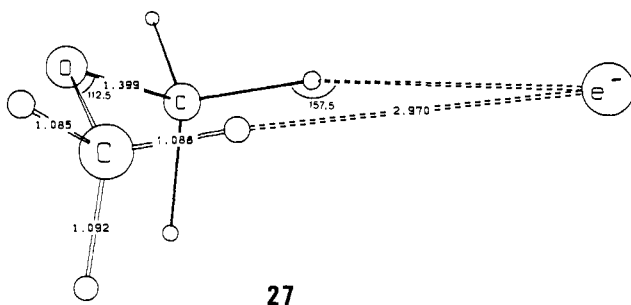


18

Figure 1. The 6-31G* optimized geometry of $e^-(\text{EtOH})$, **18**. Bond angles (deg) are $e^- \text{--} \text{H} \text{--} \text{O} = 162.5^\circ$, $\text{H} \text{--} \text{O} \text{--} \text{C} = 106.8^\circ$, $\text{O} \text{--} \text{C} \text{--} \text{C} = 112.0^\circ$. The $\text{C} \text{--} \text{C} \text{--} \text{O} \text{--} \text{H}$ dihedral angle is 78.0° and the two $\text{H} \text{--} \text{C} \text{--} \text{O} \text{--} \text{H}$ dihedrals are 42.9° and 160.3° .

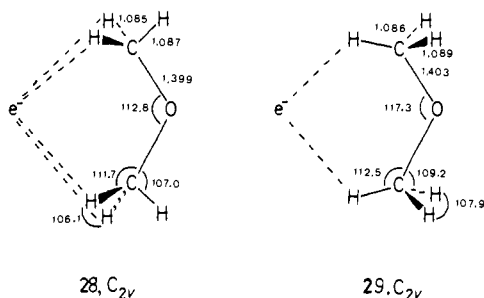
bond vector. The $e^- \text{--} \text{H}$ distance (2.453 \AA) is short in comparison with the other amines and the mean $e^- \text{--} \text{hydrogen}$ distance for the methyl groups is 4.168 \AA .

The Dimethyl Ether-Solvated Electron. The C_s geometry **27**, in which the electron interacts preferentially with two methyl hydrogens, was found to be more stable than the staggered and



27

eclipsed dipole-oriented structures **28** and **29** (Table III), although no species of lower than C_s symmetry were considered. The

28, C_{2v} 29, C_{2v}

electron is close to the plane defined by the CH bonds to the closest hydrogens, but these two bonds are not longer than the others. The oxygen–electron distance is calculated to be 4.430 \AA , and the mean electron–hydrogen distance is 4.031 \AA . The smallest $e^- \text{--} \text{H}$ distance, 2.970 \AA , is larger than those calculated for alcohol- or amine-solvated electrons but smaller than the 3.4 \AA found experimentally² for 2-methyl-tetrahydrofuran-solvated electrons.

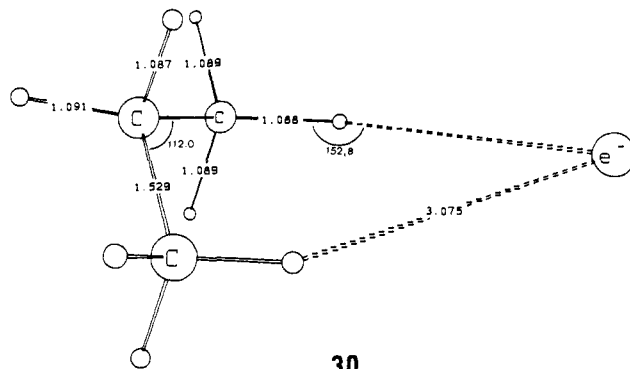
Table IV. Calculated Solvation Energies (kcal mol^{-1})

species	eq 1	$\lambda_{\text{max}}(e^-(s)_n)^a$ (kcal mol^{-1})
$e^-(\text{H}_2\text{O})$	-19.2	40.0
$e^-(\text{H}_2\text{O})_2$	-34.4	
$e^-(\text{H}_2\text{O})_3$	-48.1	
$e^-(\text{H}_2\text{O})_4$	-62.3	
$e^-(\text{NH}_3)$	-11.9	16.9
$e^-(\text{NH}_3)_2$	-21.3	
$e^-(\text{NH}_3)_3$	-30.2	
$e^-(\text{CH}_3\text{OH})$	-20.7	45.6
$e^-(\text{C}_2\text{H}_5\text{OH})$	-20.6	41.0
$e^-(\text{CH}_3\text{NH}_2)$	-12.3	15.5 ^b
$e^-(\text{CH}_3\text{CH}_2\text{NH}_2)$	-14.1	14.7
$e^-((\text{CH}_3)_3\text{NH})$	-13.2	
$e^-((\text{CH}_3)_2\text{O})$	-10.2	12.5
$e^-((\text{CH}_3)_2\text{CH}_2)$	-8.1	$\sim 9^c$

^aUnless otherwise noted from the compilation of Delaire, J. A.; Delcourt, M. O.; Belloni, J. J. *Phys. Chem.* **1980**, *84*, 1186. ^bSeddon, W. A.; Fletcher, J. W.; Catterall, R. *Can. J. Chem.* **1977**, *55*, 2017. ^cEstimated from a value of $14.4 \text{ kcal mol}^{-1}$ at 88 K (Gillis, H. A.; Klassen, N. V.; Teather, G. G.; Lokan, K. H. *Chem. Phys. Lett.* **1971**, *10*, 481).

The $e^- \text{--} \text{H}$ distances in $e^- \text{Cs}^+ (18\text{-crown-6})_2$ range from 3.29 to 4.29 \AA ,¹¹ the smallest being only 11% larger than that calculated here.

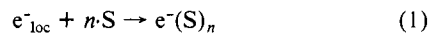
The Propane-Solvated Electron. The propane-solvated electron was only investigated in the C_s geometry **30**, which is very similar to $e^-(\text{O}(\text{CH}_3)_2)$, **27**. The electron-to-methylene carbon distance (4.339 \AA) is actually shorter than the $e^- \text{--} \text{O}$ distance in **27**. The



30

mean $e^- \text{--} \text{H}$ distances lie between 3.5 and 4.2 \AA for the methyl groups in the 3-methylpentane-solvated electron.² The methyl carbon atoms are calculated to be 4.073 \AA from the electron.

Energies. The main disadvantage of the "inadequate" basis set technique, and hence of the present calculations, is that the energies obtained are artificially high because of the basis set constraints, so that in this case direct estimates of the stabilities of solvated electrons are not possible. One reasonable approach is to define energies relative to the localized electron itself (0.13107 au with the basis set used here) and to treat the problem similarly to one of anion solvation. This leads to the energies for the reaction shown in Table IV (where e^-_{loc} is the localized electron and S the solvent).



These energies contain a large basis set superposition error (BSSE) but nonetheless give at least a qualitative idea of the solvating power of the different solvents. The calculated solvent energies for $e^-(\text{H}_2\text{O})_n$ and $e^-(\text{NH}_3)_n$ are a linear function of the number of solvent molecules, n , as shown in Figure 2. The equations obtained from least-squares fits from the calculated data are

$$E_{\text{solv}}(e^-(\text{H}_2\text{O})_n) = 5.25 + 14.30n \quad (2)$$

$$E_{\text{solv}}(e^-(\text{NH}_3)_n) = 2.83 + 9.15n \quad (3)$$

These equations lead to the localized electron solvation energies of 91.5 and $57.73 \text{ kcal mol}^{-1}$ for $e^-(\text{H}_2\text{O})_6$ and $e^-(\text{NH}_3)_6$, respectively. Furthermore, the extrapolated total energy for

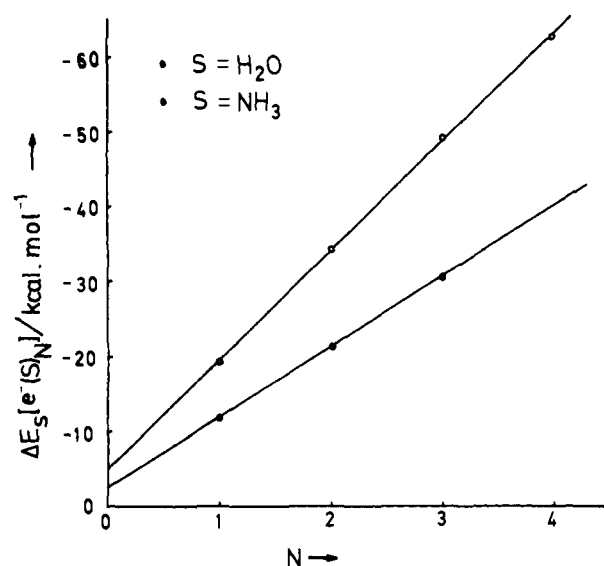


Figure 2. Localized electron solvation energies plotted against the number of solvent molecules, N .

$e^-(\text{H}_2\text{O})_6$ (-456.078 44) predicts that this cluster is bound by 8.75 kcal mol⁻¹ relative to an isolated electron and six separated water molecules. Presumably, an $e^-(\text{H}_2\text{O})_6$ calculation, which is at present beyond our possibilities, would give a wave function which is stable with respect to extension of the basis set, although the compact s -functions used here would be necessary in order to describe the short-range interactions adequately. The smallest $(\text{H}_2\text{O})_n^-$ cluster yet observed appears to be for $n = 11$,²¹ although Kestner and Jortner²² have calculated an $(\text{H}_2\text{O})_6^-$ cluster to be bound by 8.8 kcal mol⁻¹ relative to an electron and six water molecules. Superficially, this result agrees perfectly with our extrapolated energy for $e^-(\text{H}_2\text{O})_6$, but Kestner and Jortner's model was a dipole-oriented cluster with four water molecules in the first solvation shell and two in the second. Rao and Kestner's calculations^{4b} on $e^-(\text{H}_2\text{O})_6$ with all six molecules of water in the first solvation shell lead to a net stability of +20.1 kcal mol⁻¹ relative to $e^- + 6\cdot\text{H}_2\text{O}$.²² This result serves to illustrate the importance of the compact electron basis functions. Rao and Kestner used Newton's very diffuse basis set^{4a} for the electron but, nevertheless, obtained a binding energy almost 30 kcal mol⁻¹ worse than that obtained here for $e^-(\text{H}_2\text{O})_6$. The extrapolated energy for $e^-(\text{NH}_3)_6$ (-337.068 81 au) suggests this cluster to be unbound by 24.7 kcal mol⁻¹ relative to the isolated electron and six ammonia molecules. We emphasize, however, that these energies are essentially Hartree-Fock electron affinities, and should therefore be treated with caution.

Returning to the localized electron solvation energies calculated according to eq 1 and shown in Table IV, we attempt to relate this quantity to an observable variable. If localized electron solvation energies represent a measure of the strength of the electron-solvent interaction independent of the heat of vaporization or surface tension of the solvent, and if the visible/IR absorptions observed for solvated electrons are $s \rightarrow p$ transitions, there should be a correlation between the calculated localized electron solvation energies and the experimental absorption maxima. Such a plot is shown in Figure 3. There is a clear correlation between the two quantities, which is probably more than could reasonably be expected considering the differences in the numbers of solvent molecules in the first solvation shell and the uncertain nature of the electronic absorption in many cases.^{10b} Figure 2 does, however, lend support to the concept of localized electron solvation energies as a measure of electron solvent interactions. These energies show similarities among the hydroxyl solvents ($\Delta E_s = -19$ to -21 kcal

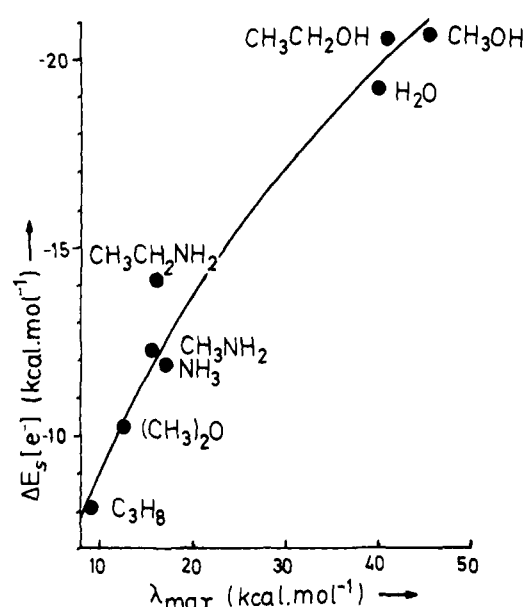


Figure 3. Calculated localized electron solvation energies plotted against experimental λ_{max} values (data taken from Table IV).

mol⁻¹) amines and ammonia ($\Delta E_s = -12$ to -14 kcal mol⁻¹) and the solvents containing no hydroxyl or amino groups ($\Delta E_s = -10$ kcal mol⁻¹). These energies bear little relationship to the dipole moment of the solvent molecules. The magnitude of the solvation energies given by dimethyl ether and propane is perhaps surprising, but there is certainly a large element of BSSE in these energies. We have, however, not corrected for BSSE as it is not unlikely that a similar, but real, expansion effect of the localized electron on solvation in a cavity contributes to the solvation energy.

Spin Densities. The question of spin densities in solvated electrons is somewhat confused. Knight shift experiments on ammonia²³ and methylamine-solvated²⁴ electrons show a very small negative spin density on the amino hydrogens and a larger, positive spin density on nitrogen. ESR spin-echo work on the hydrated electron, however, suggests that the spin density on the hydrogens is positive.²⁵ Unfortunately, ab initio UHF calculations with split-valence basis sets are poor tools for determining spin densities. The results of such calculations are usually extremely basis set dependent and bear little or no relationship to experimental results. Nevertheless, the localized electron model used here does give consistent predictions and may help to resolve the difficulties.

Table V shows the calculated s -spin densities for a variety of solvated electrons with the standard Fermi contact analysis terms calculated by using GAUSSIAN 82. For all atoms shown in Table V there is a change in sign between the total spin density and the Fermi contact term. This change of sign is caused by a spin-phase change between inner and outer components of the s -orbitals in the split-valence basis. Although the spin densities in the outer functions are much larger than those in their inner counterparts, the latter dominate the Fermi contact term because of their proximity to the core.

Two different spin polarization mechanisms determine the spin densities and Fermi contact terms shown in Table V. The first, shown in Figure 4, is the normal spin polarization of an adjacent bond by the localized electron itself (indicated by the large arrow in Figure 4a). In all the calculations reported here 85–90% of the excess spin density is situated in the outer of the two basis functions used for the localized electron. This large concentration of α -electron density polarizes adjacent bonds so that there is an excess of α -electrons on the hydrogen atom and a corresponding

(23) See: Webster, B. C.; Howat, G. *Radiat. Res. Rev.* **1972**, *4*, 259. Kevan, L. *Adv. Radiat. Chem.* **1974**, *4*, 181 and references therein.

(24) Holton, D. M.; Edwards, P. P.; McFarlane, W.; Wood, B. *J. Am. Chem. Soc.* **1983**, *105*, 2104.

(25) Narayana, P. A.; Bowman, M. K.; Kevan, L.; Yudanov, V. F.; Tsvetkov, Y. D. *J. Chem. Phys.* **1975**, *63*, 3365.

(21) Haberland, H.; Langosch, H.; Schindler, H.-G.; Worsnop, D. R. *J. Phys. Chem.* **1984**, *88*, 3903.

(22) Kestner, N. R.; Jortner, J. *J. Phys. Chem.* **1984**, *88*, 3818 (see, also: ref 4b).

Table V. Spin Densities and Fermi Contact Terms (au)

atom ^a		s-spin density ^b	Fermi contact term
e ⁻ (H ₂ O)	H _(inner)	0.096	-0.005
	O	-0.015	0.135
e ⁻ (H ₂ O) ₄	H _(outer)	0.045	-0.002
	H _(inner)	0.040	-0.004
e ⁻ (NH ₃)	O	-0.004	0.056
	H _(outer)	0.008	-0.001
e ⁻ (NH ₃) ₃	H _(inner)	0.090	-0.005
	N	-0.018	0.093
e ⁻ (NH ₃) ₃	H _(outer)	0.019	-0.001
	H _(inner)	0.049	-0.003
e ⁻ (CH ₃ OH)	N	-0.010	0.052
	H _(outer)	0.010	-0.001
e ⁻ (CH ₃ OH)	H _(OH)	0.118	-0.002
	O	-0.008	0.118
e ⁻ (C ₂ H ₅ OH)	C	-0.008	0.011
	H _(CH₃)	0.012	-0.007
e ⁻ (C ₂ H ₅ OH)	H _(OH)	0.114	-0.004
	O	-0.008	0.096
e ⁻ (C ₂ H ₅ OH)	C _(CH₂)	-0.007	0.007
	C _(CH₂)	-0.007	0.007
e ⁻ (C ₂ H ₅ OH)	C _(CH₃)	-0.005	0.013
	H _(CH₂)	0.011	-0.001
e ⁻ (C ₂ H ₅ NH ₂)	H _(CH₃)	0.009	-0.001
	H _(NH₂)	0.047	-0.003
e ⁻ (C ₂ H ₅ NH ₂)	N	-0.009	0.065
	C _(CH₂)	-0.006	0.008
e ⁻ (C ₂ H ₅ NH ₂)	C _(CH₃)	-0.005	0.015
	H _(CH₂)	0.011	-0.001
e ⁻ ((CH ₃) ₂ NH)	H _(CH₃)	0.010	-0.001
	H _(NH)	0.097	-0.004
e ⁻ ((CH ₃) ₂ NH)	N	-0.007	0.071
	C	-0.006	0.007
e ⁻ (O(CH ₃) ₂)	H _(CH₃)	0.005	0.000
	H	0.019	-0.001
e ⁻ (O(CH ₃) ₂)	O	0.000	0.000
	C	-0.004	0.029
e ⁻ (CH ₂ (CH ₃) ₂)	H _(CH₃)	0.019	-0.001
	H _(CH₂)	0.003	0.000
e ⁻ (CH ₂ (CH ₃) ₂)	C _(CH₃)	-0.004	0.026
	C _(CH₂)	-0.002	0.001

^aData applies to the most stable structure calculated for a given formula. In cases where the hydrogens on a given group are not equivalent, a mean value is given. ^bThe sum of the spin densities on all the s-type functions in the atomic basis. The s-component of the Cartesian d-functions is not included.

β -excess on the atom X. Because, however, the outer localized electron basis function is relatively diffuse, the spin polarization of the XH bond also occurs in the most diffuse basis functions of atoms X and H. The more compact inner functions, which overlap poorly with the outer s-function of the electron, are largely unaffected. This spin polarization of the XH bonds, therefore, occurs in the more diffuse regions of the basis set.

The second spin polarization effect, shown in Figure 4b, can occur for each atom and is responsible for the change of sign between inner and outer basis functions. Consider a doubly occupied orbital, indicated by the shaded area in Figure 4b, surrounded by a more diffuse orbital with a net α -spin, indicated by the larger arrow. Spin polarization will result in the α -component of the doubly occupied orbital becoming more diffuse while the β -component becomes more compact, as shown on the right-hand side of Figure 4b. The result is an excess of spin of opposite sign to that causing the perturbation close to the nucleus. This effect should occur in any system in which the unpaired electron occupies diffuse orbitals and especially in radical anions.

Table V shows that the total spin density, which is dominated by the contribution from the outer basis functions, is largely determined by the polarization mechanism shown in Figure 4a. The Fermi contact term, which reflects the situation close to the nucleus, is, on the other hand, determined by the atom spin polarization shown in Figure 4b. These polarization mechanisms are particularly important for the solvated electron, in which relatively little direct delocalization of the excess spin to the solvent

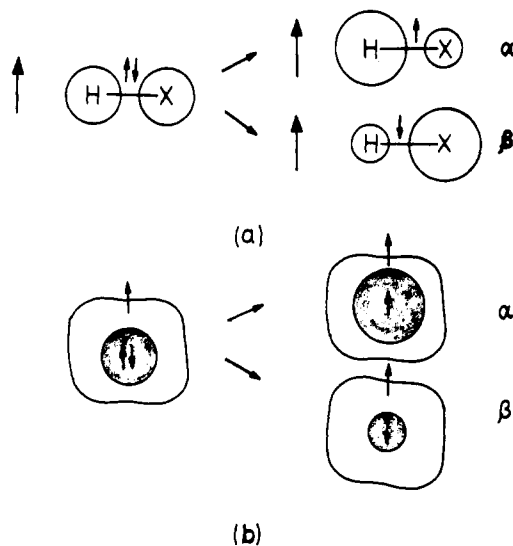


Figure 4. Schematic representation of (a) bond spin polarization and (b) atom spin polarization. The large arrow in (a) represents a perturbing spin. The doubly occupied σ_{HX} orbital is spin-polarized as shown by the α and β orbitals on the right-hand side. The shaded doubly occupied orbital in (b) is spin-polarized by the excess α -spin in diffuse regions to give the compact β - and more diffuse α -orbitals shown on the right.

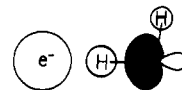


Figure 5. The interaction of a localized electron with a σ^*_{OH} orbital.

occurs. Although it is difficult to judge without comparable spin-restricted calculations (which do not converge), spin polarization must play a significant energetic role in stabilizing solvated electrons.

The Fermi contact terms given in Table V are pleasingly consistent with the Knight shift data^{23,24} in that the amino hydrogens are predicted to have a very small negative value and the nitrogens substantial positive values. Note, however, that the total spin density on the amino hydrogens is relatively large and positive, as it is for the hydroxyl hydrogens in hydrated and alcohol-solvated electrons. The balance between direct spin delocalization and bond spin polarization, which both produce positive spin density at the hydrogen adjacent to the solvated electron, and atom spin polarization, which produces negative spin density close to the nucleus, determines the coupling, which will in any case be very small because of the conflicting effects.

Discussion

The present calculations can be seen to support Kevan's interpretation of his spin-echo results² although this is something of a circular argument. The calculations are based on a cavity model, and Golden and Tuttle's criticism¹⁰ of Kevan's work is essentially that his results do not unequivocally indicate the existence of a cavity. Nevertheless, this work does demonstrate a consistency in the cavity model through the good agreement between theory and experiment and does resolve many of the theoretical problems pointed out by Feng and Kevan.³ The calculations also allow a qualitative picture of the "bonding" in solvated electron systems, which is, however, necessarily biased by the model toward a "solvated anion" picture of the solvated electron.

The major interaction, apart from the spin polarization discussed above, is essentially hydrogen bonding, as would be predicted by the "solvated anion" model.⁷ The localized electron donates to the σ^*_{OH} or σ^*_{NH} orbitals of the solvent. This leads to a singly occupied molecular orbital of the general form of that shown for e⁻(H₂O) in Figure 5.

The orbital is, however, concentrated on the outer s-functions and, therefore, leads to a strong spin polarization of the bonding orbitals, resulting in a small negative spin density on the hydrogen

atoms. This phenomenon, which has been observed in Knight shift experiments,^{23,24} has been interpreted²⁶ in terms of donation to the ammonia 3s (Rydberg) orbital. It is, however, the main tenant of the "inadequate" basis set technique that Rydberg-type orbitals are removed from the MO-manifold by the effect of the condensed phase. These two interpretations actually vary only in nomenclature. The ammonia 4a₁ (σ^*_{NH}) orbital in a valence-only basis has the same symmetry as the Rydberg 3s, which would be the 4a₁ in a full basis set. The choice of the 3s was largely dictated by the observation of a small negative spin density on the amino-hydrogens, suggesting that these atoms were close to a node. The spin polarization effect outlined above explains these results without involving either a node near hydrogen or a total negative spin density on the hydrogen atoms. The antibonding 4a₁ orbital, which becomes as diffuse as it is allowed to be by the restrictions on the basis set, takes over the role that the Rydberg 3s would play in the gas phase.

The relatively high solvation energies calculated for e⁻(O-(CH₃)₂) and e⁻(CH₂(CH₃)₂) arise from electrostatic and spin polarization of the methyl groups and from the BSSE effect discussed above.

The calculational technique outlined here has the advantage of simplicity but suffers from the use of a localized electron basis

(26) See, for instance: Smith, D. R.; Symons, M. C. R.; Wardman, P. J. *Phys. Chem.* 1979, 83, 1762.

set, which makes energy comparisons with free electrons difficult. The following conclusions arise from this work: a) Compact basis functions are essential in describing solvated electrons. Diffuse functions should be avoided in the absence of external potentials or other means of localizing the electron. b) The essential features of the geometry and an estimate of the solvating power of a given solvent are given by calculations on an electron interacting with a single solvent molecule. c) It must be recognized that total spin densities do not reflect experimentally measured coupling constants or Knight shifts. The spin density near the core is determined by spin polarization not by direct spin delocalization.

Although at present crude, the calculations reported here are suitable for inclusion in a semicontinuum type of scheme^{3,4} and are, therefore, open to improvement. An exciting prospect suggested by this technique, however, is that solvated electron reactions may for the first time be amenable to calculation.

Acknowledgment. Helpful discussions with Prof. M. C. R. Symons, Dr. B. P. Roberts, and Prof. J. A. Pople are gratefully acknowledged. Thanks are also due to Prof. P. v. R. Schleyer for his support and the staff of the Regionales Rechenzentrum Erlangen for their cooperation.

Supplementary Material Available: The optimized Z matrixes and Cartesian coordinates for the most stable e⁻(H₂O)₄, e⁻(NH₃)₃, and e⁻S (S = organic solvents) structures (9 pages). Ordering information is given on any masthead page.

Magnetic Properties in Terms of Localized Quantities. 5. Carbocations

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Abstract: The IGLO method (individual gauge for localized molecular orbitals) for the calculation of magnetic susceptibility and chemical shift tensors χ and σ is applied to a number of small- to medium-sized carbocations. There are two classes of cations: (a) cations where intramolecular charge delocalization is possible to a large extent, i.e., aromatic, so-called "nonclassical", and allylic cations (here the agreement between theory and experiment is good); and (b) cations with a localized charge, which have strong interactions with solvents and counterions, and where we cannot expect that under experimental conditions isolated cations are present. For these ions chemical shifts calculated for the isolated species are by far more deshielding than those observed experimentally. The IGLO method is shown to provide a useful tool for the elucidation of molecular structures. For cations with unknown geometry, like C₄H₇⁺ or C₇H₁₁⁺, we have calculated NMR parameters for various proposed structures. For C₄H₇⁺ that is assumed to be either a bicyclobutonium or a bisected cyclopropylcarbinyl ion, our calculations indicate that the assumption of a bisected cyclopropylcarbinyl geometry is not consistent with the observed NMR data. Though higher in energy at the SCF level, a bicyclobutonium structure leads to a much better agreement between calculated and observed chemical shift data for C₄H₇⁺. The methyl-substituted C₄H₆CH₃⁺ cation definitely has the structure of a methylbicyclobutonium ion. Concerning the structure of the 2-norbornyl cation a final decision is possible. Its experimental NMR spectra are in good agreement with those computed for the nonclassical structure and very different from that calculated for several classical geometries.

I. Introduction

During the past 30 years an impressive amount of experimental information on NMR chemical shift data of carbocations under stable ion conditions either in solution or in the solid state¹⁻⁴ has been accumulated. Ab initio calculations on carbocations have been restricted to potential energy hypersurfaces or to the de-

termination of equilibrium geometries^{5,6,17} and references therein. Theoretical calculations of chemical shift tensors have so far been missing, with the exception of ref 7, although cations present a

(1) Young, R. N., *Prog. NMR Spectrosc.* 1979, 12, 261-286.
 (2) Olah, G. A.; Donovan, D. J. *J. Am. Chem. Soc.* 1977, 99, 5026.
 (3) *Carbocation Ions*; Olah, G. A.; Schleyer, P. v. R., Ed.; Wiley: New York, 1968-1976; Vol. I-V.
 (4) (a) Yannoni, C. S.; Macho, V.; Myhre, P. C. *J. Am. Chem. Soc.* 1982, 104, 907-909. (b) Yannoni, C. S.; Macho, V.; Myhre, P. C. *J. Am. Chem. Soc.* 1982, 104, 7380-7388. (c) Myhre, P. C.; Kruger, J. D.; Hammond, B. L.; Lok, S. M.; Yannoni, C. S.; Macho, V.; Limbach, H. H.; Vieth, H. M. *J. Am. Chem. Soc.* 1984, 106, 6079-6080.

(5) (a) Kollmar, H.; Smith, H. O. *Chem. Phys. Lett.* 1970, 5, 7. (b) Dyczmons, V.; Staemmler, V.; Kutzelnigg, W. *Chem. Phys. Lett.* 1970, 5, 361. (c) Dyczmons, V.; Kutzelnigg, W. *Theor. Chim. Acta* 1974, 33, 239. (d) Zurawski, B.; Ahlrichs, R.; Kutzelnigg, W. *Chem. Phys. Lett.* 1973, 21, 309. (e) Hehre, W. J. In *Modern Theoretical Chemistry*; Schaefer, H. F., III, Ed.; Plenum: New York, 1977. (f) Koehler, H.-J.; Lischka, H. *J. Am. Chem. Soc.* 1979, 101, 3479.
 (6) (a) Levi, B. A.; Blurock, E. S.; Hehre, W. J. *J. Am. Chem. Soc.* 1979, 101, 5537. (b) Yoshimine, M.; McLean, A. D.; Liu, B. *J. Am. Chem. Soc.* 1983, 105, 6185-6186. (c) Goddard, J. P.; Osamura, Y.; Schaefer, H. F., III *J. Am. Chem. Soc.* 1982, 104, 3258-3262. (d) Raghavachari, K.; Haddon, R. C.; Schleyer, P. v. R.; Schaefer, H. F., III *J. Am. Chem. Soc.* 1983, 105, 5915-5917. (e) Haddon, R. C.; Raghavachari, K. *J. Am. Chem. Soc.* 1983, 105, 118-120.