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Nuclear Spin–Spin Coupling via Nonbonded Interactions. 4. Importance of Bridgehead Interactions on Vicinal ^{13}C–^{19}F and Long-Range ^{1}H–^{19}F Coupling Constants in 1-Fluorobicycloalkanes

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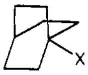
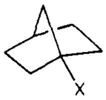
Abstract: Experimental and theoretical techniques were used to investigate the importance of the nonbonded interactions that are associated with the bridgehead carbon atoms in 1-fluorobicycloalkanes to the vicinal ^{13}C–^{19}F and long-range ^{1}H–^{19}F coupling constants. Both of these types of coupling increase dramatically in the series by an amount that is greater than would be expected on the basis of simple additivity of the coupling constant contributions over equivalent three- or four-bond paths. For example, the long-range ^{1}H–^{19}F coupling constants range from 5.6 Hz in 1-fluorobicyclo[2.2.2]octane (**1d**) to 70.6 Hz in 1-fluorobicyclo[1.1.1]pentane (**4d**). By means of a modified molecular orbital study it is demonstrated that nonbonded interactions between the bridgehead carbon atoms provide *positive* contributions to both $J(^{13}C–^{19}F)$ and $J(^{1}H–^{19}F)$ in this series of molecules. In **4d** the nonbonded contributions are shown to be 23 and 64 Hz, respectively, for these two types of coupling constants. Experimental and theoretical results for vicinal ^{1}H–^{13}C and ^{13}C–^{13}C coupling constants in the series of compounds with ^{1}H, $^{13}CO_2H$, and $^{13}CH_2OH$ at the C1 bridgehead position are also included; in these cases it is demonstrated that the nonbonded interactions associated with the bridgehead carbon atoms make *negative* contributions to these coupling constants. These data indicate that the signs of the nonbonded contributions to coupling over n formal bonds in the bicyclic compounds are identical with the experimental signs found for coupling over $n - 1$ bonds in saturated hydrocarbons and fluorocarbons.

The importance of the nonbonded interactions (NBI) involving the bridgehead carbon atoms in the series of bicycloalkanes **1**–**4**



1a–d



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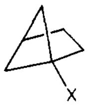
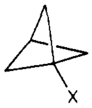


3a–d



4a–d

a, X = ^{1}H, ^{2}H; b, X = $^{13}CO_2H$; c, X = $^{13}CH_2OH$; d, X = ^{19}F

has been the subject of a number of experimental and theoretical investigations. In a previous study in this series,[2] it was shown that in the compounds **1a**–**4a**, **1b**–**4b**, and **1c**–**4c** the coupling between the C4 bridgehead carbon (C3 in **4a**–**4c**) and the nuclear spin of the substituent at C1 are increased by an amount that is less than would be expected on the basis of simple additivity of coupling over the increasing number (zero to three in **1**–**4**, respectively) of essentially equivalent three-bond paths. Furthermore, by means of a modified molecular orbital (MO) procedure[3] in which the interactions (NBI) between the bridgehead carbon atoms were eliminated from the coupling constant calculations, it was shown that these observations were due to increasingly *negative* contributions arising from the nonbonded paths as the distances between the bridgehead carbon atoms decrease in the series **1**–**4**.

In a recent study of 1-fluorobicycloalkanes **1d**–**4d**[4] it was shown, by way of contrast, that the analogous ^{13}C–^{19}F coupling constants between C4 (C3 in **4d**) and ^{19}F increase by an amount that is greater than would be expected on the basis of additivity of the contributions over the three-bond paths. It was concluded that the interactions associated with the bridgehead carbon atoms augment rather than oppose the coupling constants over the three-bond paths.[4]

In the present study the experimental data are extended to include the long-range ^{1}H–^{19}F coupling constants in the series **1d**–**4d** and the long-range ^{1}H–^{13}C coupling constants in the series **2a**–**d** and **3a**–**d**. In addition, all of the experimental data are compared with MO results for the Fermi contact contributions, which are consistent with all of the trends in the four series of compounds. The patterns of signs of the nonbonded contributions and the exceptionally large value of the long-range ^{1}H–^{19}F coupling constant in **4d** are discussed.

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Table I. Comparison of Calculated INDO-FPT MO Results for Selected ^1H-^1H, ^{13}C-^1H, ^{13}C-^{13}C, ^{13}C-^{19}F, and ^1H-^{19}F Coupling Constants in Bicycloalkanes with the Experimental Data[a]

	coupling of X to	a, X = ^1H		b, X = $^{13}CO_2H$		c, X = $^{13}CH_2OH$		d, X = ^{19}F	
compd	atom	exptl	calcd	exptl	calcd	exptl	calcd	calcd	calcd
1	C4	<1[b,c]	0.36[c]	0.29[c]	0.20[c]	0.22[c]	−0.04[c]	3.3[d]	−2.40
	H	*e*	0.80	*e*	0.41	*e*	0.50	5.6 (3)	4.62
2	C4	8.7[c]	8.56	5.42[c]	5.17[c]	4.15[c]	4.25[c]	7.9[d]	14.20
	H	1.0–1.6[f]	1.20	<0.7	0.40	<0.7	0.36	1.9 (3)	1.91
3	C4	*e*	13.75[c]	8.49[c]	8.42[c]	7.81[c]	6.46[c]	23.6[d]	17.48
	H	8[g]	7.94	4.6 (1)	4.62	3.1 (1)	3.17	20.5	6.30
4	C3	*e*	17.55[c]	*e*	11.87[c]	*e*	9.62[c]	42.5[d]	41.07
	H	18[h]	28.27[c]	*e*	16.01	*e*	14.03	70.6	72.12

[a] All values are in hertz. [b] The ^{13}C-^2H coupling constant was not observed in the ^{13}C NMR spectrum of the 1-deuteriobicyclo[2.2.2]octane; see Experimental Section. [c] Reference 2. [d] Reference 4. [e] Value was not reported. [f] Ramey, K. C.; Lini, D. C.; Moriarty, R. M.; Gopal, H.; Welsh, H. G. *J. Am. Chem. Soc.* 1967, *89*, 2401. [g] Srinavasan, R.; Sonntag, F. I. *Ibid.* 1967, *89*, 407. [h] Wiberg, K. B.; Connor, D. S. *Ibid.* 1966, *88*, 4437.

Table II. Changes ΔJ in the Calculated Coupling Constants in the Series 1–4 due to Elimination of the NBI between the Bridgehead Carbon Atoms, which are Separated by a Distance R

	a, X = ^1H		b, X = $^{13}CO_2H$		c, X = $^{13}CH_2OH$		d, X = ^{19}F			
compd	$\Delta J_{HH'}$	ΔJ_{CH}	ΔJ_{CH}	$\Delta J_{CC'}$	ΔJ_{CH}	$\Delta J_{CC'}$	ΔJ_{HF}	ΔJ_{CF}	R, Å	θ,[a] deg
1	−0.47	−0.47	−1.85	−0.12	−1.59	0.06	−11.90	8.68	2.567	180
2	1.88	−3.46	0.99	−1.63	0.63	−1.19	2.12	9.76	2.317	151.5
3	7.35	−7.53	4.61	−3.91	3.31	−2.77	10.61	16.66	2.172	174.7
4	24.76	−30.12	14.09	−17.31	12.63	−12.39	64.24	23.13	1.844	180

[a] The angle θ is measured between the C1–H and C1–C4 lines in the parent hydrocarbon.[2] All coupling constants are in hertz.

Results and Discussion

The experimental coupling constant data from ref 2 and 4, data from the literature, and those obtained in this study (see Experimental Section) are entered in Table I. It should be noted that the long-range ^1H–^1H and ^1H–^{19}F coupling constants in the table parallel the experimental trend for ^{13}C–^{19}F coupling constants, wherein the values increase substantially more in the series than would be expected for coupling over essentially equivalent four-bond (three-bond for ^{13}C–^{19}F coupling) paths.

Also included in Table I are the calculated MO results based on the finite perturbation theory (FPT) formulation[5] in the semiempirical INDO (intermediate neglect of differential overlap) approximation of self-consistent-field (SCF) molecular orbital theory.[6,7] Molecular geometries were based on the electron diffraction results for **1a**–**4a**;[8] bond lengths and bond angles for the carboxyl group were taken from the compilation of Sutton,[9] those for the hydroxymethyl group conform to a standard geometrical model,[10] and the C–F bond lengths were taken to be 1.36 Å.[10] Calculated values for the series **1b**–**4b** and **1c**–**4c** are average values weighted with respect to the barriers hindering internal rotation.[2] The energies from the INDO MO calculations were used in these integrations. All computations were performed on a Control Data Corp. CYBER 175 digital computer.

In view of the approximations of the theoretical methods and uncertainties of the details of the molecular geometries in these molecules, the calculated results are in very good agreement with the experimental data. In a few cases the calculated values are within the experimental error of the measurements. Although a major disparity occurs for the ^1H–^{19}F coupling constants in **3d**, wherein the calculated result is off by a factor of 3, the important point is that the experimental trends are consistently reproduced in all of the series of molecules. In particular, it is gratifying that the very large coupling constants of 42.5 Hz for $J(^{13}C$–$^{19}F)$ and 70.6 Hz for $J(^1H$–$^{19}F)$ in **4d** are in good agreement with the predicted values. Two of the calculated coupling constants are predicted to be of negative sign in the 1-substituted bicyclo[2.2.2]octanes **1c** and **1d**. A sign determination for the ±3.3 Hz ^{13}C–^{19}F coupling constant in **1d** would be a useful additional check of the theoretical methods.

Two different trends appear in the coupling constants of the various series of Table I; the ^{13}C–^1H and ^{13}C–^{13}C coupling constants increase substantially from the bicyclo[2.2.2]octane to the bicyclo[2.2.1]heptanes as the first three-bond path becomes available for transmission of the coupling. However, for these types of coupling constants the calculated and experimental values for coupling over the two three-bond paths in **3** and the three three-bond paths in **4** are not increased by factors as large as 2 and 3, respectively. As a consequence, it must be concluded that the NBI give rise to contributions of negative signs for these types of coupling constants. The second trend to be noted in Table I is that which occurs for the long-range ^1H–^1H coupling in **1a**–**4a** and ^{13}C–^{19}F and ^1H–^{19}F coupling in **1d**–**4d**. In these cases the coupling constants over equivalent three- and four-bond paths are much larger than would be expected on the basis of additivity. The calculated results are consistent with this observation, and it must be concluded that the NBI contributions substantially augment the couplings associated with the bonding paths. It is interesting to note that the larger values found for the long-range H–H coupling constants in bicyclic molecules led to the suggestion that the overlap of the rear lobes of the carbon hybrid orbitals may be an important factor in the transmission of coupling information.[3,11]

To determine the importance of the NBI's associated with the bridgehead interactions in these molecules a modified INDO-FPT MO procedure was adopted.[2,3] Elements of the Fock matrices associated with orbitals centered on C1 and C4 (C3 in **4a**–**4d**) were set equal to zero in each SCF cycle (neglect of nonbonded interactions, NNBI). Entered in Table II are the differences $\Delta J_{NN'}$ obtained on subtracting the coupling constants obtained with NNBI from the results of the unmodified calculations in Table I. As a consequence, the $\Delta J_{NN'}$ provide a qualitative measure of the importance of the NBI contributions to each of the six types of coupling constants as the bridgehead carbon atoms get closer together in the series of compounds. Also included in Table II are the internuclear separations between the bridgehead carbon

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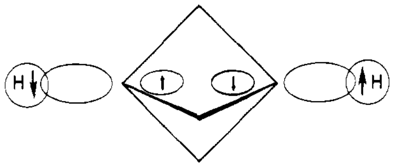

Figure 1. Schematic representation by means of a valence-bond or Dirac vector model description of the mechanism for long-range coupling via the bridgehead carbon atoms in bicyclo[1.1.1]pentane. The spin-pairing schemes implicit in this model imply that the nonbonded contributions to the vicinal H–C coupling, which are associated with orbitals on the bridgehead carbons, will be of negative sign, whereas those associated with the long-range ^1H–^1H coupling will be positive in sign.

atoms and the angle θ that the H–C1 bond makes with the C1–C4 (C1–C3 in **4**) internuclear lines of the parent compounds.[12]

The signs of the NBI contributions $\Delta J_{NN'}$ in Table II are completely consistent with the observations made on the basis of the calculated and experimental data in Table I; the bridgehead interactions provide increasingly negative contributions to the ^{13}C–^1H and ^{13}C–^{13}C coupling constants in the series **1–4** but increasingly positive contributions for the ^{13}C–^{19}F coupling constants. Furthermore, both the ^1H–^1H and ^1H–^{19}F coupling constants, which involve four formal bonds in compounds **2a–4a** and **2d–4d**, have ΔJ values that are also increasingly positive. In fact, for the bicyclo[1.1.1]pentane compounds it seems clear that the NBI contributions dominate the coupling constants. For example, it is estimated that the contribution of the bridgehead interactions to the ^1H–^{19}F coupling constant in **4d** is 64 Hz!

The trends of negative NBI contributions for ^1H–^{13}C and ^{13}C–^{13}C coupling constants and positive NBI contributions for ^1H–^1H coupling constants are consistent with a simple valence-bond[13,14] or Dirac vector model description.[15] For example, consider such a description for bicyclo[1.1.1]pentane **4a** as depicted in Figure 1. In the covalent bonds the electron spins will be antiparallel, and if the overlap between the orbital on C1 and C3 is substantial, the exchange integral would be negative and the electron spins antiparallel. Therefore, NBI contributions of negative sign are expected for $\Delta J(^1H$–$^{13}C)$ and positive signs for $\Delta J(^1H$–$^1H)$. A positive sign for $\Delta J(^{13}C$–$^{19}F)$ would also be consistent with this type of argument if it is noted that directly bonded ^{13}C–^{19}F coupling constants have negative signs.[16] However, this simple model fails entirely for the sign of the NBI contributions to the ^1H–^{19}F coupling constants in Table II. Alternatively, it is instructive to examine the pattern of signs of geminal and vicinal coupling constants in aliphatic compounds; geminal ^1H–^1H,[17] ^1H–^{13}C,[18] and ^{13}C–^{13}C[19] coupling constants are negative, whereas the corresponding vicinal coupling constants are positive.[17-19] However, geminal and vicinal ^1H–^{19}F[20,21] and ^{13}C–^{19}F[21] coupling constants have positive signs. Thus, it appears that the signs of the nonbonded contributions in all of the coupling constants over n formal bonds in the bicycloalkanes can be interpreted in terms of the analogous type of coupling over $n - 1$ bonds in the corresponding saturated hydrocarbon or fluorocarbon. It should be noted that the bicyclo[2.2.2]octane compounds are unique in the series as the various coupling constants involve one more formal bond than the remaining compounds in the series. In Table II it may be noted that the NBI associated with ^1H–^1H, ^{13}C–^1H, and ^1H–^{19}F coupling over five formal bonds are all negative. In the subsequent members of the series, there is at least one four-bond path and the NBI in each of these cases are positive, in conformity with the signs of the corresponding vicinal coupling constants. Furthermore, in compounds **2–4** the vicinal ^1H–^{13}C and ^{13}C–^{13}C NBI are of the same (negative) sign as the corresponding geminal coupling constants in aliphatic hydrocarbons. On the other hand, the NBI for the vicinal ^{13}C–^{19}F couplings in Table II are positive, in conformity with the sign of $^2J_{CF}$ in fluorocarbons.[20,21]

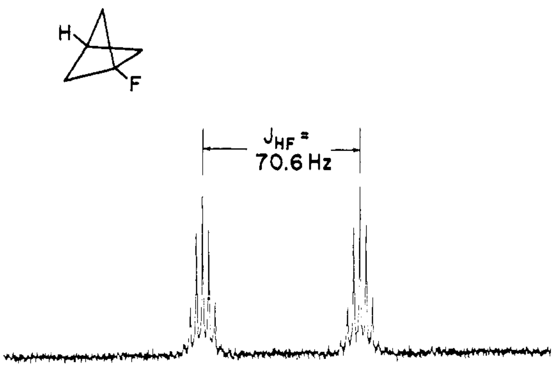

Figure 2. Fluorine-19 NMR spectrum of 1-fluorobicyclo[1.1.1]pentane. The fluorine is split into a doublet of septets with coupling constants of 70.65 and 2.80 Hz, respectively.

The magnitudes of the values of ΔJ in Table II follow an exponential increase with the bridgehead separation R. This dependence was noted in the previous study[2] in this series and was attributed to the exponential dependence of the overlap integrals, which are the most important terms entering the off-diagonal elements of the Fock matrices.

Some additional comments should be made about the very large value of 70.6 Hz for the ^1H–^{19}F coupling constant in 1-fluorobicyclo[1.1.1]pentane (**4d**). This is substantially larger in magnitude than the experimental values observed in those cases in which the hydrogen and the fluorine are sterically constrained to be in close proximity ("through-space" effects, which are typically less than 12 Hz in magnitude).[22] The 70.6-Hz value in **4d** is also larger than any known vicinal H–F coupling constant, including the 21-Hz value in fluoroacetylene.[23] Since the C–C triple bond of acetylene is 0.64 Å shorter than the distance between the bridgehead carbons of bicyclo[1.1.1]pentane, the σ-bonding electrons must be less effective in transmitting the coupling information than the nonbonded paths. It is also interesting to note that the INDO MO results of this study indicate that the NBI contribute 12 kcal mol^{-1} to the stability of 1-fluorobicyclo[1.1.1]pentane, whereas the NBI stabilize the parent hydrocarbon **4a** by only 2.8 kcal mol^{-1}.

Experimental Section

The coupled ^{19}F spectrum of **4d** was measured at 84.26 MHz on a JEOL FX90Q FT NMR spectrometer, with $CDCl_3$ as solvent and internal lock: spectral width 400 Hz, data points 16K, digital resolution 0.05 Hz. The spectrum, which consists of a doublet of septets, is depicted in Figure 2. The ^1H NMR spectrum of **3d** in $CDCl_3$ was recorded on the same instrument at 89.56 MHz: spectral width 500 Hz, data points 16K, digital resolution 0.06 Hz; the bridgehead proton signal appeared as a perturbed doublet. The ^1H NMR spectra of **3b** and **3c** were similarly obtained at 89.56 MHz; the signals of the bridgehead protons appeared as complex multiplets from which the ^1H–^{13}C coupling constants were determined by normal selective proton-decoupling experiments.

The ^1H NMR spectra of **2c**, **1d**, and **2d** were obtained at 250 MHz on a Bruker Instruments WM-250 FT NMR spectrometer. The resonances of the bridgehead protons are complex multiplets from which the heteronuclear coupling constants could not be determined in the one-dimensional experiments. Therefore, a homonuclear J-resolved two-di-

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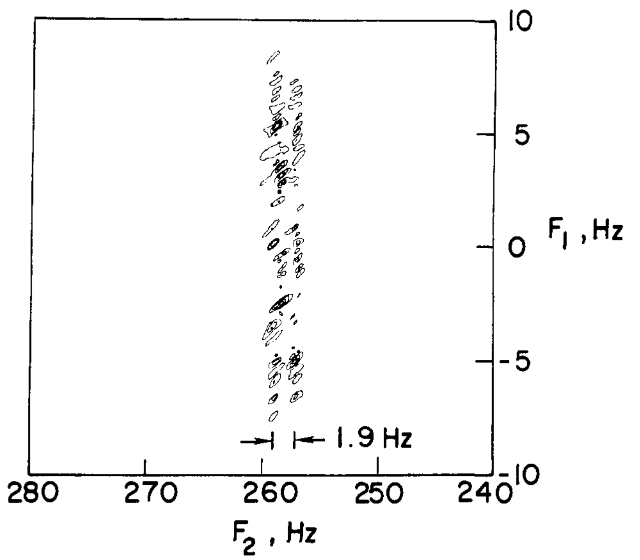

Figure 3. Two-dimensional contour plot associated with the H4 proton of 1-fluorobicyclo[2.2.1]heptane. The interproton coupling constants occur along the F_1 axis, and the $^1H-^{19}F$ coupling constant is measured along the F_2 axis. The center of this doublet corresponds to δ 2.08.

mensional FT NMR technique[24] was used to obtain the $^1H-^{13}C$ and $^1H-^{19}F$ coupling constants. The data were collected by the Hahn spin-echo pulse sequence[25] using a 16-phase cycle[26] to cancel pulse errors. The 90° pulse–τ–180° pulse–data acquisition period–recovery period used τ values from 0.01 to 1.42 s, incremented in units of 0.0111 s to give spectral widths of +22.52 to −22.52 Hz along the F_1 axis. The recovery period was at least 8 s to prevent the formation of spurious peaks. The usual F_2 spectral width was 360 Hz, which was collected into a 2K word file with an acquisition time of 2.84 s. After zero-filling along both the F_1 and F_2 axes, the digital resolution was 0.18 Hz per point. The total data collection times for the two-dimensional spectra were 42 h. The data were manipulated with Bruker Instruments' FTNMR 2D computer program.[27] After a 45° tilt of the two-dimensional data, the contour plots of the bridgehead hydrogens showed the complicated splitting pattern due to the interproton coupling along the F_1 axis, and the coupling to the heteroatoms is given along the F_2 or chemical shift axis. A simplified diagram of the type of data obtained by this two-dimensional technique applied to 1-fluorobicyclo[2.2.1]heptane (**2d**) is given in the contour plot of Figure 3. The bridgehead proton produces a very complicated splitting pattern as two vertical rows of peaks along F_1 due to coupling to the other ten protons in the molecule. The rows are separated by the long-range $^1H-^{19}F$ coupling constant of 1.9 Hz, which is centered on the chemical shift of the multiplet at δ 2.08.

The coupling constant between the bridgehead hydrogen and the carboxyl ^{13}C in **2b** was found to be less than 0.7 Hz by comparison of the spectra of the labeled and unlabeled compounds. A more refined value of the line width of the bridgehead carbon C4 in the proton-decoupled ^{13}C NMR spectrum of 1-deuteriobicyclo[2.2.2]octane (**1a**) gave a value $J(^1H-^2H) \leq 0.15$ Hz, from which it follows that $J_{CH} < 1$ Hz.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research, to the National Science Foundation for assisting in the purchase of the 250-MHz NMR spectrometer, and to the Australian Research Grants Committee. S.R.W. acknowledges the award of the Carl S. Marvel Fellowship for 1980–1981. Services of the University of Arizona Computer Center were essential to the completion of this work.

Registry No. 1a (X = H), 280-33-1; **1b**, 73948-77-3; **1c**, 73948-81-9; **1d**, 20277-22-9; **2a**, 279-23-2; **2b**, 73948-78-4; **2c**, 73948-82-0; **2d**, 78142-52-6; **3a**, 285-86-9; **3b**, 73948-79-5; **3c**, 73948-83-1; **3d**, 78142-55-9; **4a**, 311-75-1; **4b**, 73948-80-8; **4c**, 73948-84-2; **4d**, 78142-58-2; **1a** (X = D), 59346-71-3.

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Electron Spin-Echo Studies of the Solvation Structure of O_2^- in Water

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Abstract: The solvation structure of O_2^- in D_2O frozen solutions has been determined with use of electron spin-echo modulation at 4.2 K. The modulation has been analyzed with use of a Fourier transformation technique combined with direct simulation of the modulation. The analysis indicates that the first solvation shell waters have an H–O bond dipole orientation toward O_2^- and that each O_2^- is surrounded by four water molecules. The distance between the center of O_2^- and the nearest deuteron of a water molecule is 0.24 nm and the deuteron has an isotropic coupling of 0.4 MHz, while the distance to the next nearest deuteron on the same water molecule is found to be 0.34 nm. This solvation structure is discussed in terms of probable bonding interactions and is compared with that of solvated electrons in aqueous matrices.

The solvation of the superoxide ion, O_2^-, in bulk solution and on surfaces is of current chemical importance because of (a) the dependence of solvent–molecule orientation on anion size,[1] (b) the existence of O_2^- on catalytic oxide surfaces,[2] and (c) the reactivity of O_2^- in various biological reactions.[3] Thus, we are currently investigating the solvation structure of O_2^- in frozen solutions[4] and on surfaces.[5] This has been made possible by advances in the analysis of electron spin-echo modulation spectrometry.[6] The first study of O_2^- solvation was in frozen solutions of dimethyl sulfoxide.[4] There we showed that the analysis of

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