$$e^2q_{zz}Q/h(\text{sample}) = e^2q_{zz}Q/h(\text{reference}) + \frac{e^2Q\Delta q}{a_0{}^3h}\left\langle \Psi_p{}^*\right| \sum_i \frac{3z_i^2 - r_i^2}{r_i^5} \left|\Psi_p\right\rangle \quad (2)$$

where Δq is the change in occupancy of the 2p-orbital relative to the reference. The field gradient expectation value is calculated by using a Slater-type orbital ($Z_C = 1.72$) and an analytical expression.[10b] Equation 2 is valid for comparisons between molecules having the same C–H bond distance; otherwise, $e^2q_{zz}Q/h$(reference) must be scaled; errors in $e^2q_{zz}Q/h$(reference) accumulate at the rate of 1 kHz per 0.001 Å difference in bond length.[10a,c] Also, we assume that the two C–H bond lengths are equally affected by deuterium substitution. We emphasize that the reference is used to account for the contribution to eq_{zz} from the charge distribution associated with an aliphatic C–H bond.

According to the second term of eq 2, for d(C–H) = 1.1 Å, an extra occupancy of the carbon 2p-orbital of –0.5 e should reduce the deuterium quadrupole coupling constant by 30.6 kHz. Small changes in d(C–H) matter little: for d(C–H) = 1.09 Å and 1.11 Å, reductions of 30.9 and 30.2 kHz, respectively, are predicted.

The reference molecule is a three-ring aromatic compound, (9,9-$^2H_2$)fluorene.[17] The C^2H_2 unit is incorporated into a relatively rigid molecule, thus, reducing the potential for motional averaging affecting the value of $e^2q_{zz}Q/h$(reference).[18] Spectra were obtained at 38.5 MHz at 300 and 198 K with solid-state deuterium NMR and at 77 K with ADLF spectroscopy (Figure 1).

As noted above, the model is most conveniently applied when the C–^{2}H bond distances in the reference and sample are equal. Recently, McKean has developed a linear correlation between the $\nu_{CH}{}^{is}$ stretching frequency and bond distance.[19,20] The slope of the correlation is –0.0001 Å per cm^{-1}, making possible precise, relative assessments of the C–H bond distances (Table I).

Acquisition of solid-state deuterium NMR spectra at 76.7 MHz for *cis*-(μ-C^2H_2)(μ-CO)[FeCp(CO)]$_2$ proved to be difficult due to an extremely long deuterium T_1. Therefore, the Cp ring positions were partially deuteriated to reduce the deuterium T_1 at the C^2H_2 unit.[21-23] The solid-state deuterium NMR spectrum of *cis*-(μ-C^2H_2)(μ-CO)[FeCp^d(CO)]$_2$ is shown in Figure 2.

The observed deuterium NMR parameters (Table I) are simply not compatible with the assignment of a large excess charge on carbon in this, the first application of solid-state deuterium NMR techniques to the determination of charge structure in an organometallic complex. Rather, we find that the bridging methylene carbon has zero charge relative to the reference aliphatic carbon atom within limits that we estimate to be 0.17 e based on an assumed uncertainty of 0.010 Å in the C–H bond distances.

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Chloride Ion Pairs in Water

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The study of ions in water by statistical mechanical methods has made a significant contribution to our understanding of solution chemistry and biological processes in saline solutions. Integral equation methods have been used recently by Pettitt and Rossky[1] to study solvent-averaged forces and the effective interactions or the potentials of mean force (PMF) for the alkali halides in water at infinite dilution. Integral equations revealed that the PMF's of unlike charged ions in water display clear minima in the ion-contact and solvent-separated regions. The presence of such minima and maxima is not predicted by continuum solvent theory. It is a direct result of explicitly molecular correlations.[1,2] The striking result obtained from the approximate integral equation theory for the PMF between negatively charged ions is that the ions display a stable contact minimum whereas only a modest minimum was found for positive charge pairs.[1] Of particular significance is the Cl^-–Cl^- pair whose approximate PMF indicates the possibility of a substantial minimum at the ion-contact pair distance. A short dynamical simulation has indeed confirmed the plausibility of such a contact minimum, apparently due to the formation of bridging hydrogen bonds between water molecules and the ion pair.[3] However, no quantitative estimates of this free energy have been reported.

In this communication, we report a quantitative study of the Cl^-–Cl^- PMF in water with use of an umbrella sampling method[4] and the same Hamiltonian as that used in the integral equation study.[1] The system studied here consists of two chloride ions and 295 water molecules in a rectangular box with periodic boundary conditions and lengths of 25.4, 18.6, and 18.6 Å in the x,y,z directions, respectively. Sampling was performed with microcanonical molecular dynamics, and the equations of motions were integrated by the Verlet algorithm with a time step of 1.5×10^{-15} s.[5] The water intermolecular potential employed was the rigid TIPS model of Jorgensen[6] and the SHAKE procedure was used to constrain the internal geometry of the water molecules.[5] The interactions in the system were truncated by using previously studied switching functions.[7] The water–water switch used a distance parameter of 9.3 Å and the ion–water parameter was 12.0 Å.

To facilitate sampling we chose a bias potential, U_B, such that it consisted of an approximation to the negative of the free energy surface, U_A, plus a loose harmonic constraint, U_H, used primarily for control. The use of a bias potential that approximates the negative of the PMF means that we are sampling from a nearly flat distribution and therefore only the difference between the guessed bias and the true PMF need to be explicitly calculated. For U_A we have used the negative of the PMF obtained from integral equation estimates.[1] The harmonic potential was then used to constrain the chloride ions to a certain separation region. The form of the harmonic potential used is

$$U_H(r) = \frac{1}{2}k_x(x - x_0)^2 + \frac{1}{2}k_{yz}(y^2 + z^2) \qquad (1)$$

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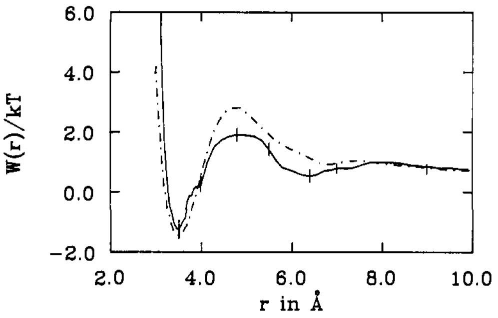

Figure 1. Potential of mean force of Cl^-–Cl^- ion pair in water at 300 K. Solid line is obtained from eq 4; dot-dash line is from ref 1. Error bars were obtained by averaging over the first and last half of the data for each simulation window.

where r is the distance between the two chloride ions, x,y,z are the cartesian coordinates, and x_0 is the center of the window on the x axis. Thus the ions are constrained along the longest axis and near to the center of the box. The force constant k_{yz} is selected to confine the ion to the x axis and k_x and x_0 were chosen so that successive simulation windows overlapped. For a given window, the unbiased estimates of the probability $P(r)$ can be obtained by[4]

$$\langle P(r)\rangle = \langle P(r)e^{\beta U_B(r)}\rangle / \langle e^{\beta U_B(r)}\rangle \tag{2}$$

A radial distribution function $g(r)$ can be obtained from $P(r)$ as follows

$$g(r) = \frac{\langle P(r)\rangle}{V(r)} \tag{3}$$

where $V(r) = \pi\Delta r\rho^2$ is the volume of a disk, centered on the x axis, and ρ is the distance from the circumference of a disk to the x axis. The interionic potential of mean force $W(r)$ is then given by

$$W(r) = -kT \ln [g(r)] + C \tag{4}$$

The entire $W(r)$ from different simulations was combined by a standard matching procedure.[8]

The resultant Cl^-–Cl^- PMF at 300 K was obtained by eq 4 over the range of $3 < r < 10$ Å. A total of 15 windows were used, and each window was sampled for 24 ps following 2 ps of equilibration. In Figure 1 the resulting PMF is shown and compared to the result from previous integral equation studies.[1] By performing sampling at distances large enough to approach the continuum limit we fix the absolute energy of the simulated results (see eq 4). Both estimates of the PMF display a clear minimum in the ion-contact region near 3.5 Å and a very shallow minimum near 6.5 Å.

The computer simulation yields a barrier height to dissociation from the contact well of 3.3 kT, only slightly smaller than the integral equation result of 4.2 kT. The difference is similar to the difference in the hydration energy of −190 kcal/mol computed by integral equations[1] as compared to −143 kcal/mol from MC calculations by J. Chandrasekhar et al.[9]

The umbrella sampling technique in this work has been used to obtain an independent estimate of the PMF of chloride ion pair in water. These results quantify the qualitative free energy surface of like anion pairing predicted by approximate integral equation methods.[1] When like ions approach each other, water molecules form bridging hydrogen bonds with sufficient probability to account for the predicted contact stabilization. Anomalous NMR relaxation rates in dilute alkali–halide aqueous solutions have been interpreted as due to anionic associations,[10] the strongest being in alkali fluoride solutions. In agreement with this integral equations have predicted an even deeper contact stabilization for F^- pairs compared to Cl^- pairs in water.[1] It is clearly of interest to use the same method as described above to obtain the PMF between cations as well, in particular, the sodium ion pair in water. Because there is no highly directional hydrogen bond between water and sodium ions, integral equation techniques have predicted there is no substantial sodium–sodium ion-contact pair minimum in water.

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Double Quantum Based ^{6}Li,^{13}C NMR Correlation Spectroscopy

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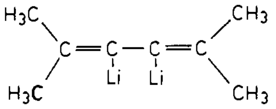
Among the various two-dimensional NMR pulse methods[1] those used for scalar chemical shift correlations are of particular importance for the unequivocal assignment of resonance frequencies. While the existence of a scalar spin–spin coupling is a necessary requirement for these techniques to be applicable, the assignment or even the observation of line splittings in the one-dimensional spectrum is not essential. This feature is of great value in cases where scalar couplings are not resolved due to line-broadening effects[2] or where complex multiplet structures prevent an unequivocal analysis.

With respect to scalar interactions the NMR spectroscopy of lithium–organic compounds profits from the use of the isotope lithium-6 with spin $I = 1$ and a small quadrupolar moment.[3] Line splittings due to ^{13}C, ^{6}Li spin–spin coupling are thus usually well resolved in the ^{13}C NMR spectra of lithium-6 enriched systems, and their analysis allows the recognition of lithiated carbon atoms in a particular structure.[3] However, two-dimensional scalar ^{6}Li,^{13}C chemical shift correlations become desirable if several lithiated centers exist, leading to a number of ^{13}C multiplets, or in situations where the ^{13}C multiplet structure is not easily deciphered.

We met such a case with 3,4-dilithio-2,5-dimethyl-2,4-hexadiene (**1**), a compound recently synthesized by addition of lithium to



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tetramethylbutatriene.[4] X-ray results[5] have shown that **1** has a crystal structure which is characterized by a Li_8 cluster with four "inner" and four "outer" lithium atoms surrounded by two "inner" and two "outer" ligands (Figure 1a).

In a recent NMR investigation[6] a ^{6}Li,^{6}Li COSY experiment provided evidence that the same structure also exists in THF

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