Let us look at the first of these. Taking the electronegativity of carbon as 2.5 and that of chlorine as 3.0, we conclude that the charge on the carbon atom in carbon tetrachloride is $+1.0\ e$. As opposed to this, Gordy[25] has estimated from quadrupole coupling data that the charge is only $+0.48$. Similarly, using 4.0 as the electronegativity of fluorine and 2.1 for hydrogen we obtain $+2.05$ as the carbon charge in fluoroform. Schwartz, Coulson, and Allen,[16] using empirically corrected Hartree-Fock results, find a charge of only 0.53 on this atom. Furthermore, if the charge of the carbon is as high as 2+, the assumption that the shift in energy varies linearly with charge is almost certainly wrong.[17] Gordy's formula, however, applies only to the ionic character of the σ part of the bond. In carbon tetrachloride there is a partial cancellation of the charge transferred from carbon to chlorine in the σ bond by a back-donation of electrons in the π bond. Thus the effective ionic character of the bond is substantially less than would be predicted by the formula $(X_A - X_B)/2$.

Looking now at the second point mentioned above, we note that the electronegativity[25] of a methyl group is 2.33 while that of a CCl_3 group is 2.58. Using Gordy's rule, then, the ionic character of a bond between one of these groups and a chlorine would be 0.34 for the methyl and 0.21 for CCl_3. The corresponding charges on the chlorines are -0.34 for CH_3Cl and -0.21 for CCl_4. Because of the changing electronegativity of the central atom the charge removed by the chlorines is not proportional to the number of chlorines. (In carbon tetrachloride, the charges are even less than indicated here, because of the π bonding.) Similar conclusions are drawn from the theoretical calculations of Schwartz, Coulson, and Allen. They show that for the fluorinated methanes the charge on the fluorines drops from -0.212 for CH_3F to -0.208 for CHF_3. In the binding energy shifts there is some compensation for this effect. Although the charge increases less than in direct proportion to the number of fluorines, the binding energy probably increases more than in direct proportion to the charge.

Summarizing this section, we have seen that there is a linear correlation between the binding energy shifts and the electronegativity of the ligands. We have seen a plausible argument that there should be such a linear correlation. However, to obtain a satisfactory agreement between the experimental values and theoretical estimates we must use ionic characters that are rather smaller than those obtained from Gordy's formula. This formula applies only to the σ bonds and we must reduce the ionic character from the predicted value to account for back-bonding in the π bond.

Acknowledgments. I would like to thank David A. Shirley and Charles S. Fadley for many thoughtful discussions and J. M. Hollander for making the electron spectrometer available to me. I am indebted to Charles Butler for assistance in constructing various pieces of apparatus needed in these experiments. I am pleased to acknowledge fellowship support from the John Simon Guggenheim Memorial Foundation. I would also like to thank Drs. Pople, Basch, and Schwartz for providing me with results of their calculations prior to publication.

Nonaqueous Silver Nitrate Solutions. Raman Spectral Studies in Acetonitrile

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Abstract: The Raman spectra of $AgNO_3$-CH_3CN solutions (0.01 to 9 mol/l.) have been investigated with He-Ne and Ar^+ ion lasers as excitation sources. In the symmetrical NO_3^- stretching frequency region, two frequencies, 1036 and 1041 cm^{-1}, are observed. The concentration dependence of the relative intensities of these two frequencies is examined from the viewpoint of ion-ion interactions. The band contours of C≡N and C—C stretching frequencies of CH_3CN have also been examined. As $AgNO_3$ is added, these bands resolve into two components and the variations of their relative intensities with concentration are understood, largely, through marked solvation interaction in the solute-solvent system.

Studies of Raman and infrared spectra of nitrates in aqueous solutions have been extensively used to explore the types of interactions arising in electrolyte systems. Recently, the splitting and the intensity of the NO_3^- bands in 1200-1500- and 750-cm^{-1} regions have been reviewed[1] to define spectroscopic guidelines to the disposition of the solvent molecules around the ions, and ion-ion association interactions in aqueous nitrates. The present paper reports the results of a Raman spectral investigation of $AgNO_3$ in an aprotic solvent, CH_3CN, to evaluate these criteria for nonaqueous electrolytes.

Experimental Section

Reagent grade $AgNO_3$ and CH_3CN were purified by the recrystallization, drying, and distillation techniques previously used in this laboratory and described elsewhere.[2,3] The preparation of the

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Table I. Raman Frequencies of $AgNO_3$–CH_3CN Solutions

CH_3CN (25°)	$AgNO_3$–CH_3CN solutions (25°)[a,b]	$AgNO_3$ melt (235°)	$AgNO_3$ powder (25°)	Assignments
			25	
			43	
			101	
	~120[d]	~120	136	
			181	
			195	
			287	
380 (dp)	380–386 (dp)			C—C≡N bend (e)
	705–708 (p)	712 (p)	712	NO_3^- ion
	721–725 (dp)	725 (dp)	731	NO_3^- ion
750 (p)	750–762 (p)			
	823–816 (p)	804 (p)	807	NO_3^- ion
919 (p)	919 (p)			C—C symmetric stretch (a_1), free
	928–931 (p)			C—C symmetric stretch, complex
	1036–1033 (p)	1029 (p)	1027?	NO_3^- ion
	1037–1039 (p)	1038 (p)	1045	
1047[c] (dp)	1048[c] (dp)			CH_3 rocking[d]
	1302 (p)	1275 (p)	1320	NO_3^- ion
	1364 (dp)	1335 (dp)	1350?	NO_3^- ion
1374 (p)	1374–1369 (p)			CH_3 symmetrical bend (a_1)
~1410	~1410			
	1425 (dp)	1420 (dp)	1370	NO_3^- ion
1448 (dp)	1448–1442 (dp)			CH_3 antisymmetric bend (e)
	1646–1632 (p)	1605 (p)	1616	NO_3^- ion
2205 (p)	2205–2200 (p)			
2253 (p)	2253 (p)			C≡N symmetric stretch (a_1), free
	2272 (p)			C≡N symmetric stretch, complex
2294 (p)	2294–2302 (p)			
2730 (p)	2730–2725 (p)			
2845 (p)	2845–2835 (p)			
2885 (p)	2885–2875 (p)			
2945 (p)	2945–2937 (p)			C—H symmetric stretch (a_1)
3004 (dp)	3004–2996 (dp)			C—H antisymmetric stretch (e)

[a] 0.01–9 mol/l. [b] p = polarized, dp = depolarized. [c] Observed as a weak band only with more powerful Ar^+ ion laser. [d] Observed only in solutions of concentrations above 5 mol/l.

solutions (by weight) and the transfer to the Raman sample cells were effected in a dry nitrogen box. The cells were sealed before removal for the Raman spectral studies. The spectra were recorded with a Jarrell-Ash laser Raman spectrometer (Model 25-300) having both He-Ne and Ar^+ ion lasers (55 and 125 mw, respectively) as excitation sources. This spectrometer has a double Czerney-Turner monochromator with a slit servo system which automatically adjusts the width of all slits and thus maintains constant resolution corresponding with wave number. The instrument is capable of resolution of ~0.4 cm^{-1}, in the first order, using a 1180-g/mm diffraction grating. The detector is a cooled ITT-FW 130 phototube, and the signal amplification is accomplished by a photon counting system.

All spectra were scanned three to four times to establish the consistency of the band shapes and positions. Band polarizations were gained with a polaroid in the scattered light path with $\vec{E}$ parallel to the slit, and with a half-wave plate in the path of the incident light oriented in such a way as to have the incident light polarized parallel and perpendicular to the slit in successive measurements. The band contours were examined with a Du Pont curve analyzer, by means of which asymmetric contours may be resolved into Lorentzian or Gaussian components. For quantitative work, the integrated intensity of the 2945-cm^{-1} band of pure CH_3CN was selected as the intensity standard; the integrated intensities in this communication are thus all relative to this standard. Correction of the intensity values for variations in refractive index with change of solution composition was considered;[4] this correction was found to be within the accuracy of the intensity measurements (about 10%).

The Raman spectrum of $AgNO_3$ in the molten state (235°) was reexamined as part of this work, to gain results of comparable quality to spectra of $AgNO_3$–CH_3CN solutions (25°). For this part, an electrically heated metal block was used as a high-temperature Raman cell thermostat in the sample area directly before the slit. The Raman tubes for all measurements were made from Pyrex glass (0.7-cm o.d. and 10 cm long) with optical flats as windows in the conventional manner.

Results

(a) CH_3CN Frequencies. The Raman frequencies observed in pure CH_3CN and in $AgNO_3$–CH_3CN solutions are given in Table I. The frequencies observed for the CH_3CN component in the solutions are essentially the same as those for pure CH_3CN. Further, the doubly degenerate modes of pure CH_3CN are not split in the spectra of the solutions. The structure of CH_3CN in the solutions thus appears to be C_{3v} as in pure CH_3CN.[5] This is similar to that found for the solvent in the spectra of the solutions of $ZnCl_2$–CH_3CN[6] and Zn, Cd, and Hg(II) nitrates in CH_3CN.[7]

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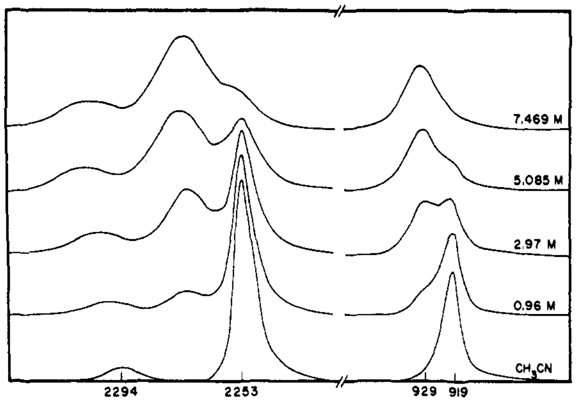

Figure 1. C≡N and C—C bands in $AgNO_3$-CH_3CN solutions.

The values of CH_3CN frequencies were found to decrease gradually with increasing $AgNO_3$ concentrations with the exception of 2294-, 750-, and 380-cm^{-1} lines for which the values increase with concentration. Two bands, at 2272 and 929 cm^{-1}, are seen only in the solution spectra, and not in the spectrum of pure solvent. The intensities of these two bands increase with increasing $AgNO_3$ concentrations, apparently at the expense of 2253- and 919-cm^{-1} bands of pure solvent (*i.e.*, C≡N and C—C stretching frequencies). Normal coordinate calculations[6,8] show that the 2272- and 929-cm^{-1} frequencies arise due to solute-solvent interactions and can be assigned to C≡N and C—C stretching vibrations of CH_3CN which is bound to the cationic species of the solute; *i.e.*, the structure of the solvate is $M^+\cdots N{\equiv}C{-}CH_3$ with C_{3v} symmetry. In Figures 1 and 2, the intensity variations of the 2272-, 2253-, 929-, and 919-cm^{-1} lines are shown as a function of $AgNO_3$ concentration.

(b) Frequencies of NO_3^- Ions. The frequencies in Table I for NO_3^- ions in $AgNO_3$-CH_3CN solutions are those observed in the concentration region ~3 to ~9 mol/l. Below ~3 mol/l. it was not possible to gain satisfactory spectra in the 1200-1500- and 650-850-cm^{-1} regions (ν_2, ν_3, and ν_4 frequency regions of unperturbed NO_3^- ion[9]) with He-Ne or the more powerful Ar^+ ions sources; however, in the 1050-cm^{-1} region (ν_1 region of the unperturbed NO_3^- ion[9]) it was possible to make quantitative observations, with the He-Ne source, down to concentrations as low as 0.01 mol/l. of $AgNO_3$. With the Ar^+ ion laser, excitation of the very weak solvent band (1047 cm^{-1}, dp) vitiated the studies at still higher dilutions.

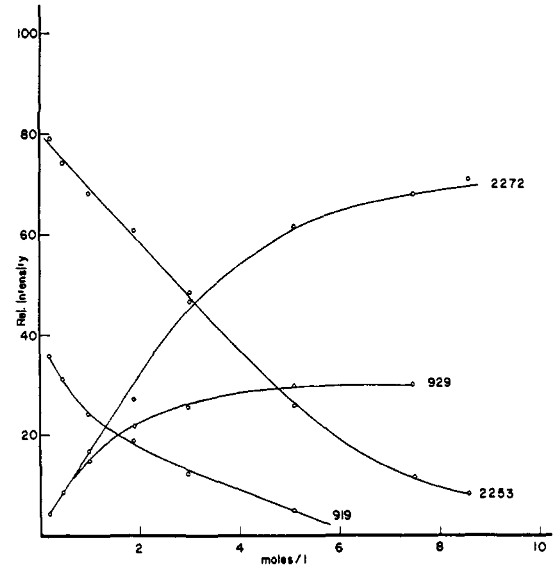

Figure 2. Relative integrated intensities of C≡N and C—C bands in $AgNO_3$-CH_3CN solutions.

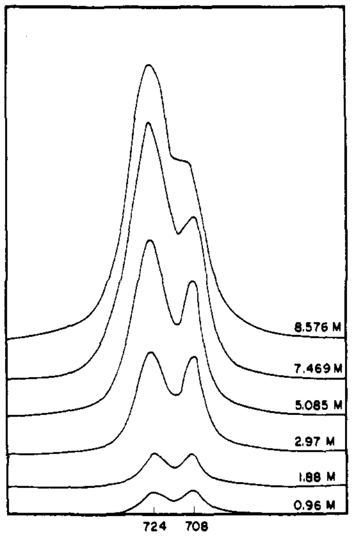

Figure 3. NO_3^- bands in the 700–750-cm^{-1} region in $AgNO_3$–CH_3CN solutions.

From the results for concentrations above ~3 mol/l., nine of the observed frequencies can be attributed to NO_3^- ion vibrations, six polarized (708, 816, 1033, 1039, 1302, and ~1632 cm^{-1}) and three depolarized (725, 1364, and 1425 cm^{-1}). The frequencies in the 1200-1500-cm^{-1} region are not concentration dependent and their intensities increase more or less linearly with increasing $AgNO_3$ concentration. The frequencies of the polarized lines at ~816 and ~1632 cm^{-1} increase with decreasing $AgNO_3$ concentration. Relative to the polarization, the 725-cm^{-1} line remains depolarized for all concentrations (~3 to ~9 mol/l.), whereas the depolarization ratio of the 708-cm^{-1} line changes from 0.75 at ~3 mol/l. to 0.55 at ~8.5 mol/l. This is probably due to the existence of two coincident Raman lines. The intensity variations with concentration of the 708- and 725-cm^{-1} bands are shown in Figure 3; the behavior is not unlike that reported for aqueous $Ca(NO_3)_2$ solutions[10] in the 750-cm^{-1} region.

The changes with concentration in the 1050-cm^{-1} region are quite marked and have not been previously noted. Above ~3 mol/l., the broad band with a peak at ~1039 cm^{-1} has a very noticeable asymmetry on the low-frequency side; this band can be resolved into two components, an intense band at ~1039 cm^{-1} and a less intense band at ~1033 cm^{-1}. This asymmetry shifts to the higher frequency side for concentrations less than 3 mol/l. At the lowest concentration (0.0098 mol/l.) only one polarized band, at 1041 cm^{-1},

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[10] D. E. Irish and G. E. Walrafen, *J. Chem. Phys.*, **46**, 378 (1967).

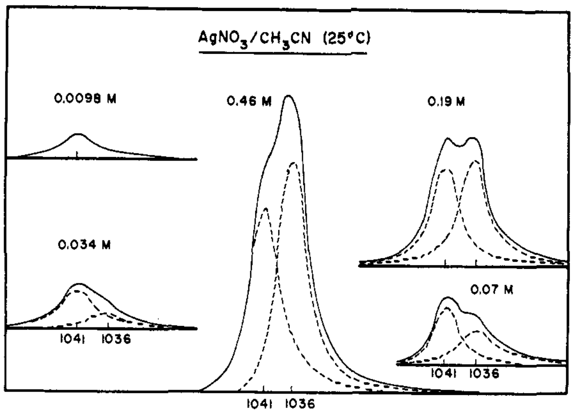

Figure 4. NO_3^- bands in the 1050-cm^{-1} region in $AgNO_3$–CH_3CN solutions at low concentrations.

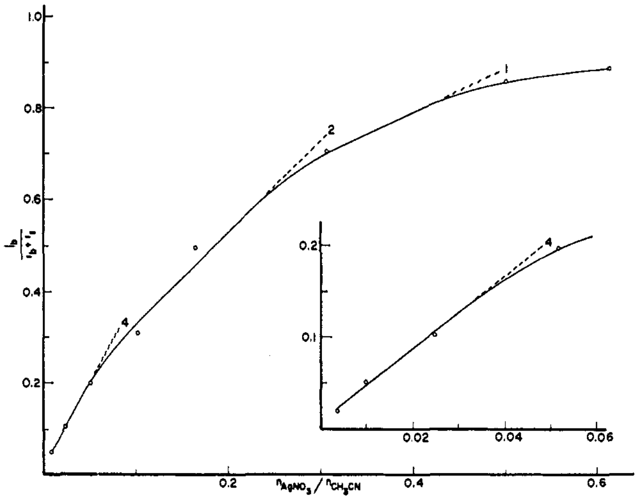

Figure 5. Graph of $I_b/(I_b + I_f)$ *vs.* n_{AgNO_3}/n_{CH_3CN}.

is observed. With increasing concentrations of $AgNO_3$, it is seen that a new line appears, approximately at 1036 cm^{-1}, and increases in intensity until at ~0.2 mol/l., the relative intensities of these two lines are virtually equal. The band contour in the 1050-cm^{-1} range shows two well-defined band peaks at these concentrations. Above ~0.2 mol/l., the 1036-cm^{-1} band is the dominant component of the overall band contour. These features are shown in Figure 4.

The results found for molten $AgNO_3$ (235°) and crystalline $AgNO_3$ (powder) are also reported in Table I. The present work confirms the results previously reported by Walrafen and Irish[11] for molten $AgNO_3$. Inspection of the results shows that the frequencies of $AgNO_3$ melt correspond well with the NO_3^- frequencies for the concentrated $AgNO_3$–CH_3CN solutions (*i.e.*, ~3 to ~9 mol/l.). The frequencies of crystalline $AgNO_3$ are in accord with those already reported by James and Leong.[12]

Discussion

From an analysis of the concentration dependence of the relative intensities of the 2253- and 2272-cm^{-1} bands (C≡N frequency of "free" and "bound" CH_3CN, respectively) an insight can be gained relative to the solute–solvent interactions in the solution. The ratio of solvent to solute is 2000 at a concentration of ~0.01 mol/l. of $AgNO_3$, 100 at ~0.2 mol/l., 10 at ~2 mol/l., and about 1.5 at ~9 mol/l. The intensity (I) of a Raman line is proportional to the molar concentration (n) of the scattering compound; *i.e.*, $I = kn$, the constant k being the molar scattering factor. The intensity measurements, within the experimental limits of accuracy, show that the intensity of the 2272-cm^{-1} absorption at the highest concentration (~8.6 mol/l.) is nearly the same as that of 2253-cm^{-1} band of pure CH_3CN. From this it is apparent that the molar scattering factors of bound and free CH_3CN are nearly equal; accordingly, it can readily be shown that a measure of the number of solvent molecules bound to the solvate through inner-sphere or primary solvation is given by the expression

$$\frac{I_b}{I_b + I_f} = N\frac{n_{AgNO_3}}{n_{CH_3CN}} \qquad (1)$$

where I_b and I_f are the intensities of the 2272- and 2253-cm^{-1} bands, n_{AgNO_3} and n_{CH_3CN} are the concentrations (mol/l.) of $AgNO_3$ and CH_3CN, and N is the average number of molecules of the solvent which are coordinated by the solute through solvation forces in the primary layer. Inspection of eq 1 shows that the value of N follows from the slope of the graph of $I_b/(I_b + I_f)$ *vs.* n_{AgNO_3}/n_{CH_3CN}, and this is illustrated in Figure 5. The value of N is found to vary with concentration, being about four in the dilute concentration range (less than ~0.5 mol/l.), about two in the moderate concentration range (~0.5–~5 mol/l.), and decreasing to about one at higher concentrations (greater than 5 mol/l.). Solvates of stoichiometry $AgNO_3 \cdot 2CH_3CN$ and $AgNO_3 \cdot CH_3CN$ have been crystallized[13] from $AgNO_3$–CH_3CN solutions of concentrations ~5 mol/l. and ~8 mol/l. respectively, *i.e.*, from solutions where the slope of the graph in Figure 5 is about two and one, respectively. Diffusion studies for $AgNO_3$[14] in these solutions (0.1–5 mol/l.) are understood if the diffusing entity is a solvated kinetic unit of $AgNO_3 \cdot 2CH_3CN$ stoichiometry. These studies give strong support to the observation of the present work, namely, that N is a measure of the solvent bound in the primary solvation sheath and that the decrease of N with increasing $AgNO_3$ concentration is a consequence of the competition of ion–solvent and ion–ion interactions in these solutions.

Only one frequency in the 1050-cm^{-1} region is expected for the NO_3^- ion, namely, that due to the symmetric stretching mode. Except at the lowest concentration (0.0098 mol/l.) two Raman lines are observed in this spectral region, at 1036 and 1041 cm^{-1}, respectively, for concentrations less than 3 mol/l., 1039 and 1033 cm^{-1} for concentrations greater than 3 mol/l. At the lowest concentration of 0.0098 mol/l., the one polarized line at 1041 cm^{-1} may be assigned to comparatively free NO_3^- ions; *i.e.*, the anion–cation interactions are solvent-separated interactions.[1,15] The presence of only a 1353-cm^{-1} band in the ir spectrum of the 0.02 mol/l. solution[13] is further

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support for this assignment, and the value of four for N is thus understood, for example, as the Ag^+ is more or less completely surrounded by solvent molecules and thus "solvent shielded" from the NO_3^- ion. The 1036-cm^{-1} line which is observed at higher concentrations is assigned to NO_3^- ions in a different force field, *i.e.*, perturbed in some way by the cations. The increase in the intensity of 1036-cm^{-1} line compared to that of the 1041-cm^{-1} line as the solute concentration is increased is understood as due to the direct interactions of the NO_3^- ions with cations. Penetration of the primary solvation sphere, with the displacement of a solvent molecule by the NO_3^- ion, leading to the formation of a contact ion pair (or inner-sphere complex), as suggested elsewhere,[1,15] would be the equivalent of second type of NO_3^- species in these solutions. The presence of two kinds of NO_3^- ions for solutions of concentrations above 3 mol/l. is evident from the observation of the asymmetric shape of the band at ~1039 cm^{-1}.

The value α, the fraction of free NO_3^- ions in the solution, for concentrations less than ~0.5 mol/l., was calculated from the integrated intensity values of the 1036- and 1041-cm^{-1} bands, and the results are shown in Table II, together with the values of α calculated from the Wishaw-Stokes conductance equation[16] and earlier conductance studies.[17] The agreement between the α values calculated from two different methods suggests that a study of the region of the most intense band of NO_3^- ion species, *i.e.*, the 1050-cm^{-1} region, opens the way to spectroscopic investigations of ion-ion association in the dilute solution region, *i.e.*, in a concentration range where spectroscopic and conductance approaches can be interfaced and in which the concepts of interionic attraction theory of electrolytes are still applicable. This has hitherto been denied, since the previously established criteria, *i.e.*, the 750- and 1300-1500-cm^{-1} regions, are the regions of weaker activity so that measurements at high dilutions are virtually impossible.

Table II. α, the Fraction of Free NO_3^- Ions in $AgNO_3$-CH_3CN Solutions

Concentration, M	0.03	0.05	0.1	0.2	0.25	0.50
α_{Raman}	0.72	0.63	0.56	0.48	0.46	0.44
$\alpha_{\text{conductance}}$	0.64	0.59	0.51	0.44	0.43	0.42

Acknowledgments. This work was made possible, in large part, by support received from the National Science Foundation and the U. S. Department of Interior, Office of Saline Water. Dr. Barry G. Oliver is thanked for the calculations of α from the electrical conductance data and helpful discussions.

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Nature of Solvent Effects on the Proton Chemical Shifts of Nonpolar Solutes[1]

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Received January 10, 1970

Abstract: Chemical shifts of nonpolar solutes in various solvents are referenced relative to external hexamethyldisoloxane by utilizing a spinning coaxial sample technique. From a graphical analysis, values for the various factors which contribute to the solvent shifts are deduced. Values for van der Waals terms agree quantitatively with the binary collision model of Bernstein. Solvent anisotropy contributions for benzene and carbon disulfide are compared with the theoretical estimations of Schug. Furthermore, gas-phase shifts of nonpolar molecules are predicted from the graphs.

Most nmr studies are conducted on compounds dissolved in some solvent. It is well known that each solvent perturbs the chemical shift of a solute differently. Recently, Laszlo and coworkers[2] have shown qualitatively that the proton shifts of internal standards (such as tetramethylsilane, cyclohexane, and other nonpolar molecules) are affected dramatically by different solvents. However, quantitative examination of the data were not ventured by these authors since they themselves employed internal standards only. In order to study these systems in more detail we referenced the data of Laszlo[2] to an external standard basis, utilizing spinning coaxial sample techniques described herein. Additional solvents and nonpolar solutes were added to the scheme in order to broaden the study.

Experimental Section

Proton spectra were recorded with a Varian A60-A spectrometer operating at a probe temperature of 39 ± 1°. The spectra were calibrated using a Hewlett-Packard Model 200AB wide range oscillator and a Hewlett-Packard Model 523DR frequency counter. All compounds were used as obtained from commercial sources. When possible, solvents were stored over molecular sieves. Samples were prepared by adding a trace of each solute to the sol-

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(1) Presented at Metro Chem 69, Regional Meeting of the New York and North Jersey Sections of the American Chemical Society, New York, N. Y.

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