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Does the Basicity of ^{129}Xenon Affect Its NMR Chemical Shift?

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^{129}Xe has a nuclear spin of $^1/_2$ and gives a single sharp peak whose NMR chemical shift is so sensitive to its environment that it has been proposed as a probe of the reaction field model of medium effects in pure solvents[1-3] and a variety of heterogeneous systems[4] including zeolites and biological structures.[4-6] Recently, a close correlation was shown between the ^{129}Xe shift and the ^{13}C shift of methane in 16 solvents of diverse polarities, and since the ^{129}Xe shift was 27 times more sensitive, it was recommended as the preferred reference probe for van der Waals shift studies.[7] If, in fact, this technique is successful for isolating dispersion force contributions from all other interactions, it provides a standard against which they can be referenced. However, if the ^{129}Xe shift can be affected by acid–base interactions, this must be taken into consideration when it is used as an environmental probe of systems (such as zeolites) which carry strongly acidic sites. Furthermore, if the ^{129}Xe shift is acid-sensitive, it might be used to calibrate the strengths of very strong acids, both liquid and solid.

To test this possibility, we have compared the ^{129}Xe chemical shifts in some very strong acids as solvents with those in their methyl esters and other nonacidic media. Table 1 lists our results along with those for 36 solvents used by Stengle and colleagues[6] to establish normative solvent effects on the ^{129}Xe chemical shift. Figure 1 plots the shifts in all the solvents *versus* the Rummens[8] refractive index function employed by Stengle[1,2,4,5] as the criterion of reaction field interactions.

The sharp differentiation of the ^{129}Xe shift in the very strong protonic acids CF_3SO_3H, point 2 ($H_0 \sim -14$),[9] and CH_3SO_3H, point 3 ($H_0 = -7.86$),[10] from their esters, points 5 and 6, in contrast to the less acidic $Cl_2CHCOOH$, point 4 ($H_0 = -0.75$),[10] shows that a specific effect, either hydrogen bonding or even protonation, is perturbing the xenon nucleus in addition to the usual nonspecific dispersion force effects. Not only does this deserve consideration as a contribution to solvent effects in strongly acidic media, but it may also be of potential value in determining the strengths and distribution of acidic sites in solid acids[11,12] where this type of interaction has so far been ignored.[4] Although we were easily able to determine the ^{129}Xe shift in "magic acid" ($HSO_3F–SbF_5$), we were unable to determine the refractive index with a Bausch and Lomb Abbé refractometer. It appeared to be off-scale below the end of the instrument's range at 1.3000, but the prism surfaces may have been etched by traces of HF. The value for magic acid interpolated from the line drawn on Figure 1 through the strong acids is 1.092. Also, we were unable to measure the ^{129}Xe shift in H_2SO_4 ($n_{10}^{20} = 1.429$)[13] because its high viscosity prevented solution of a sufficient quantity of ^{129}Xe for NMR detection.

Table I. ^{129}Xe NMR Chemical Shifts and Refractive Indices of Various Acidic and Nonacidic Solvents

entry no.	solvent	^{129}Xe NMR chemical shift[a,b] (ppm)	solvent refractive index (n_D^{20})
1	fluorosulfuric acid–antimony pentafluoride (1:1) [magic acid]	233	(1.092)[c]
2	trifluoromethanesulfonic acid	220	1.3270
3	methanesulfonic acid	213	1.4300
4	dichloroacetic acid	210	1.4663
5	methyl chloroacetate	180	1.4220
6	methyl methanesulfonate	183	1.4140
7	methyl trifluoromethanesulfonate	181	1.3260
8	*n*-hexane	160	1.3750
9	acetonitrile	175	1.3440
10	methanol	148	1.3286
11	water	196	1.3330
12	methyl chloride	153	1.3389
13	diethyl ether	160	1.3526
14	*n*-pentane	156	1.3577
15	tetramethylsilane	158	1.3586
16	acetone	175	1.3590
17	ethanol	165	1.3614
18	ethyl acetate	168	1.3724
19	*n*-heptane	168	1.3878
20	*n*-octane	171	1.3976
21	1-butanol	176	1.3990
22	2,2,4-trimethylpentane	192	1.3916
23	cyclopentane	158	1.4063
24	*n*-decane	177	1.4121
25	methylene chloride	192	1.4243
26	cyclohexane	165	1.4263
27	ethylene glycol	199	1.4319
28	1-octanol	187	1.4295
29	*n*-hexadecane	186	1.4344
30	chloroform	217	1.4457
31	oleic acid	193	1.4582
32	carbon tetrachloride	222	1.4603
33	olive oil	198	1.4663
34	fluorobenzene	176	1.4659
35	toluene	190	1.4969
36	benzene	195	1.5011
37	pyridine	197	1.5102
38	chlorobenzene	202	1.5246
39	methyl iodide	209	1.5314
40	*m*-dichlorobenzene	207	1.5459
41	nitrobenzene	189	1.5524
42	bromobenzene	219	1.5602
43	bromoform	285	1.5977
44	iodobenzene	248	1.6195
45	carbon disulfide	225	1.6279
46	methylene iodide	335	1.7476

[a] The ^{129}Xe NMR chemical shifts were referenced to pure xenon gas extrapolated to zero xenon gas pressure, where $\delta_{[Xe]=0} = 0$ ppm. [b] Entries 10–46 were taken from ref 6. [c] The refractive index of magic acid was estimated on the basis of its ^{129}Xe NMR chemical shift in relationship to the ^{129}Xe NMR chemical shift dependence on the refractive index of acids 2–4 in the above table.

Other workers have tried to detect the *basic behavior* of xenon toward strong Brönsted and Lewis acids. Gillespie and Pez[14] used solubility in the superacidic $HSO_3F–SbF_5–SO_2$ system as a criterion of basicity by which Xe, Ne, O_2, N_2, H_2, NF_3, and CO were considered to be nonbasic but CO_2 and SO_2 to be basic. Christe[15] was unable to obtain an adduct in the $HF–SbF_5–Xe$ system although he isolated and characterized $SH_3^+SbF_6^{\ominus}$.

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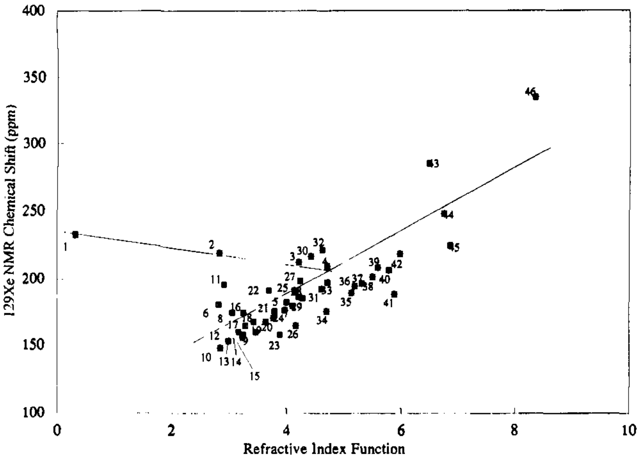

Figure 1. Rummens van der Waals function, $[(n^2-1)/(2n^2+1)]^2 \times 100$, *versus* the ^{129}Xe NMR chemical shift (ppm) for 46 solvents: (1–9) this report, (10–46) from ref 6.

However, strong evidence for Xe as a Brönsted base in solution is that of Olah and Shen,[16] who used the suppression of H–D exchange from D_2 in HF–SbF_5 as evidence for the protonation of Xe, Cl_2, Br_2, and CO_2, while H_2, N_2, and O_2 were not considered to be protonated in this medium. The gas-phase proton affinities[17] of some very weak bases are CH_4 (132.0), CO_2 (130.9), CF_4 (~126), Xe (118.6), N_2 (118.2), Kr (101.6), H_2 (101.3), O_2 (100.9), and Ar (88.6) kcal/mol, showing that in the limit XeH^+ can be made. Whatever may be the nature of the interactions reported here for Xe with CF_3SO_3H, CH_3SO_3H, and $Cl_2CHCOOH$ and that inferred for magic acid, they represent a dramatic departure from the previous correlation with reaction field theory and must be taken into account when it is used in the future.

Approximately 2.5 mL of each solvent was transferred into a 10-mm heavy-walled NMR sample tube in an argon-filled glovebox. Each NMR sample tube was placed on a vacuum line and subjected to a freeze–pump–thaw cycle. Xe gas (>99%, National Specialty Gas Co.) was admitted into the vacuum line, and the NMR sample tubes were sealed by a propane–oxygen flame under 1 atm of Xe_g pressure. The ^{129}Xe NMR spectra were determined on a GE-GN300 NMR spectrometer operating at a center band frequency of 83.0266 MHz with a 33333-Hz spectral sweep width. A signal-to-noise ratio greater than 10 was obtained for all the samples studied employing a 30° pulse angle, a 2-s pulse delay, and between 500 and 1000 transients. The ^{129}Xe NMR chemical shifts were referenced to free xenon gas, extrapolated to zero concentration and taken as 0 ppm as described in ref 6.

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