CHAPTER 2

The Xenon Chemical Shift and Chemical Shift Anisotropy

CYNTHIA J. JAMESON

University of Illinois, Chicago, USA
Email: cjjames@uic.edu

2.1 Scope and Emphasis

This review will focus on (a) understanding observed Xe chemical shifts at an electronic structural level and (b) using that level of understanding to deduce what the observed Xe chemical shift is telling us about the physical system of interest. The goal is to use the theoretical understanding of the observations in model systems in order to interpret more general Xe observations in complex systems, such as those mentioned in extensive reviews by Fraissard in this book and elsewhere. Hyperpolarized Xe uniquely permits the observation of the Xe chemical shift under conditions that are in the limit of no Xe–Xe interactions. Thus, we discuss ''a single Xe atom'' as a probe of physical systems separately. On the other hand, in observations of the Xe chemical shift under variable-loading thermally polarized Xe conditions, the anisotropy of the inner spaces becomes more obvious when Xe–Xe interactions dominate the intermolecular Xe shift tensor. We use first principles calculations to make predictions for static geometries and grand canonical Monte Carlo (GCMC) simulations and molecular dynamics (MD) simulations to do the averaging that makes possible predictions of a general nature and comparison with specific experimental observations. In this chapter we limit interpretation to systems which have well-characterized

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New Developments in NMR No. 4
Hyperpolarized Xenon-129 Magnetic Resonance: Concepts, Production, Techniques and Applications
Edited by Thomas Meersmann and Eike Brunner

Published by the Royal Society of Chemistry, www.rsc.org

structure and morphology, and observations in the slow exchange (with the gas) limit.

2.2 The Xe Chemical Shift under Conditions of Isotropic Averaging

2.2.1 The Xe Chemical Shift in Pure Xe Gas

The experimental temperature dependence of the density coefficient of the Xe chemical shift in Xe gas was established in 1970[1] after the pioneering work of Carr on the Xe resonance in the gas phase[2] showed how large the intermolecular effects on Xe chemical shifts in pure Xe could be,[2,3] more than 300 ppm over a range of phases (solid, liquid, gas) and temperature.[4] Using the formulation by Buckingham and Pople, the Xe chemical shift in the gas phase is expanded in a virial expansion in powers of density, just like the dielectric constant or other quantity for imperfect gases,[5]

$$\sigma(T,\ \rho) = \sigma_0(T) + \sigma_1(T)\rho + \sigma_2(T)\rho^2 + \sigma_3(T)\rho^3 + \cdots \tag{2.1}$$

so that the second virial coefficient, the linear density coefficient of the Xe shielding in the limit of zero density, could be expressed exactly in terms of the Xe shielding as a function of Xe–Xe distance $\sigma(R)$ and the probability of finding a Xe atom at this distance,[6]

$$\sigma_1(T) = 4\pi R^2 \int_0^\infty R^2 \mathrm{d}R\{\sigma(R) - \sigma(\infty)\}\mathrm{e}^{-V(R)/kT} \tag{2.2}$$

For Xe, σ_0 is the shielding for an isolated Xe atom which provides a convenient chemical shift reference, the limit of zero density. An accurate experimental determination of $\sigma_1(T)$ over a large enough temperature range could in principle permit the direct inversion of the data to yield the Xe–Xe intermolecular shielding function $\sigma(R)$, using an accurately known Xe–Xe intermolecular potential function, as we suggested in 1975,[7] but the limited temperature range could only result in an estimated form.

2.2.1.1 The Intermolecular Shielding as a Function of Distance and Angle in Xe_2 and in Xe_3

The characteristics of the intermolecular shielding function $[\sigma(R) - \sigma(\infty)]$ for Xe–Xe interaction, $\parallel$ and $\perp$ components, have been established.[8] Relative to the isolated Xe atom, the $\parallel$ component in Xe_2 is only a small shielding increment, whereas the $\perp$ component is a large deshielding response changing very steeply with close approach. The shape of the intermolecular shielding function $[\sigma(R) - \sigma(\infty)]$ was first estimated using a direct inversion of the experimental temperature-dependent density coefficient of shielding.[7] On this basis, the characteristic shape of the intermolecular shielding function was suggested in conference talks by the author in late 1970s, and was first calculated *ab initio* in 1992 for the Ar–Ar model at the RHF level.[9] Scaling these results provided the first *ab initio*-based calculations of $\sigma_1(T)$ for Xe-rare gas pairs and also the first exploration of the additivity of intermolecular shielding, using the Ar_3 cluster. The intermolecular shielding tensor calculations for Xe_2 dimer were later carried out at the RHF level, using 240 basis functions for Xe.[10] This basis set was originally used by Bishop to calculate the shielding response to an electric field and has become the standard one to use for Xe shielding calculations. Electron correlation contributions were later included, also for Xe–other rare gas systems using DFT-B3LYP.[8] Later refinements of electron correlation contributions by Vaara *et al.*[11] showed that CCSD theory can be regarded as a reliable and nearly converged electron correlation method for calculating the NMR shielding in Xe_2, at the non-relativistic level,[11] and after adding relativistic contributions (about 8%),[12] the experimental temperature dependence of the second virial coefficient of ^{129}Xe shielding is reproduced better than ever before.

The characteristics of the shielding tensor surfaces as a function of angle and R(Xe–Xe) in the Xe_3 cluster establish the limits of the pairwise additivity of Xe–other shieldings.[10] Subsequent non-relativistic RHF calculations by Vaara *et al.* also show that pairwise additivity of Xe shielding holds for most interatomic distances for Xe_n clusters ($n = 3$–12).[13] Further discussion of the pairwise additivity and its limits are in Section 2.3.1.1.

2.2.1.2 Beyond the Binary Interaction Limit. The Sign of Higher Order Terms

Since *ab initio* calculations show that the deviations from pairwise additivity of intermolecular Xe shielding become significant only at very short distances, then using pairwise additive shielding functions together with pairwise additive intermolecular potential energy functions can lead to semi-quantitative predictions of experimental Xe chemical shifts *except* at conditions of extremely high Xe densities. In eqn (2.1) the sign of $\sigma_2(T)\rho^2 + \sigma_3(T)\rho^3 + \cdots$ was found to be opposite to that of $\sigma_1(T)\rho$ in pure xenon gas for Xe number densities 100–250 times that of an ideal gas at standard conditions.[1] It has been found to be uniformly true for other nuclei, as well that the magnitude of the *effective* density coefficient at liquid densities:

$$\frac{[\sigma - \sigma_0(T)]}{\rho(T)} = \sigma_{1,\text{effective}}(T) \tag{2.3}$$

is smaller than that of the density coefficient in the limit of vanishing density in the gas.[14] For much higher densities, there are two quantities that are different from eqn (2.2): the shielding function itself is no longer strictly a pair function, that is, it depends on the cooperative shielding response to many atoms at a time and is a function of their configuration. Second, the probability of finding a neighbor atom is no longer given by the dilute gas limit form of $\exp[-U(R)/kT]$. The density dependence of the Xe chemical shift measured in supercritical xenon up to nearly 500 times the density of an ideal gas at standard conditions[15,16] is in complete agreement with this.

2.2.2 The Chemical Shift of the Single Xe Atom as a Probe of the Physical System

The Xe chemical shift has been found to have many applications in the characterization of materials, including biological systems. Understanding the chemical shifts helps us to make predictions in systems beyond those where measurements have been carried out. We introduce complexity in steps. In this section we consider examples of Xe chemical shifts as a probe of the physical system in the limit of no Xe–Xe contributions and under conditions of isotropic averaging. In Section 2.3.1 we consider the chemical shift tensor of a Xe atom in anisotropic spaces in the solid state and in 2.3.2 we consider probing physical systems with Xe–Xe contributions to the shift tensor.

2.2.2.1 The Xe Atom in a Homogeneous Electric Field

Electric field contributions have often been mentioned as a significant contribution to Xe chemical shifts in zeolites and other systems where charged species may be present. To be precise, the effects of electric fields on the Xe atom response to a magnetic field is actually small. For a homogeneous electric field E,

$$\sigma(E) = \sigma(\text{isolated, field-free Xe atom}) + BE^2 \qquad (2.4)$$

where the quadratic electric field coefficient of shielding, $B = (1/3)[(1/2)\sigma_{zzzz}{}^{(2)} + \sigma_{zzxx}{}^{(2)}]$.[17] *Ab initio* non-relativistic MP2 calculations yield $B = 4404$ ppm au[18] *vs.* 2415 ppm au from more recent 4-component relativistic calculations.[19] These values of B lead to very small chemical shifts for Xe. Effects of electric field gradients on Xe shielding are likewise small.[20] Therefore, electrostatic effects on Xe shielding from bare charges are almost insignificant. For example, when a Xe atom shielding is calculated in the presence of a lattice of point charges representing H and O atoms in crystalline clathrate hydrates with a Xe basis set constituted to provide quantitative electric field response, the Xe chemical shift is found to be of the order of only a few tenths of a ppm.[21] Differences in Xe chemical shifts commonly attributed to 'electric field effects' actually come from the response of the electrons of Xe to the changes in the electronic structure of the lattice atoms (typically O atoms) when a framework Si atom is replaced by an Al atom plus a charge-balancing positive ion, for example. Although the Xe shielding response is a local property in that it comes from Xe electrons experiencing overlap, exchange and correlation with electrons of an immediate neighbor, any changes in the electronic structure of the neighbors arising from long range effects will show up in the Xe shielding response. It is for this reason that Xe is such an exquisite probe of its environment.

2.2.2.2 The Xe Atom in a Gas Mixture

The Xe shielding tensor surfaces for Xe–Rg (Rg = Xe, Kr, Ar, Ne) provide models for the dependence of Xe intermolecular shielding on the electronic structure of the atom eliciting the Xe response.[8] Qualitatively the magnitude of the response is greater for Rg with greater polarizability.

Ab initio calculations of nuclear shielding surfaces $[\sigma(R,\Omega) - \sigma(\infty)]$ have been carried out for Xe interacting with molecular partners such as N_2, CO_2, CO,[22,23] O_2,[24] CH_4 and CF_4.[23] The shielding surfaces could be mathematically represented by sums over Xe–C and Xe–H contributions for Xe–CH_4, and by Xe–C and Xe–F contributions for Xe–CF_4 fitted to regenerate the large number of *ab initio* values calculated at a large number of configurations (*ca.* 100). Using this form of mathematical representation of the *ab initio* shielding values permits the Xe–C and Xe–H functions to be used later to estimate Xe shielding in liquid solvents, *e.g.*, Xe–alkane systems, and Xe–C and Xe–F functions to estimate Xe shielding in Xe-perfluoroalkane systems. For accurate calculations to reproduce the $\sigma_1(T)$ that result from experimental data obtained in the gas phase in the binary collision limit, it is very important to use accurate intermolecular potential functions that properly weight the calculated shielding functions, especially at short distances where the shielding changes very steeply. Furthermore, the shielding functions are highly θ-dependent, thus we need the correct θ dependence of r_0 of the intermolecular potential in order to obtain accurate density coefficients in the gas phase. Gas phase NMR data prove to be stringent tests of calculations, much more so than condensed phase. Pressure virial coefficients do not provide adequate tests for intermolecular potential functions. Piecewise functions parameterized to multiple experiments of high precision, including detailed scattering data from crossed molecular beam experiments, are found to be necessary for empirical-based potentials. On the other hand, *ab initio* surfaces calculated at the CCSD(T) level have been found to give results comparable to the best empirical-based potentials, see for example, V(Xe–Xe) calculated by Vaara *et al.*[11] Thermophysical properties which are used for empirical determinations of intermolecular potential functions are usually sensitive to the volume of the attractive bowl, but shielding averages need more accurate R dependence of the potential energy at short range. Classical MD simulations often use Lennard-Jones forms for non-bonded interactions; these L-J forms usually give inappropriate weighting of the shielding at close approaches. Thus, we recommend potential functions of the Maitland–Smith form, suitable for Monte Carlo simulations, and exp-6 form suitable for MD simulations.

Xe chemical shifts in the presence of O_2 or other paramagnetic molecule requires not only the calculation of the usual magnetic shielding response but also the hyperfine tensor as a function of configuration.[24] For the density and temperature dependence of the Xe chemical shift in O_2 gas,[25] only the isotropic part of the hyperfine tensor, the Fermi contact part, can contribute since the traceless dipolar part averages isotropically to zero in the gas phase. On the other hand, the traceless dipolar part is responsible for the electron-spin-dipole–nuclear-spin-dipole mechanism for the relaxation of ^{129}Xe nuclear spin in the gas phase mixtures containing O_2, which we have also measured.[26]

2.2.2.3 The Xe Atom in Solution

The first observations of Xe chemical shifts in solution were made by Stengle and Williamson,[27–29] and they interpreted their results using reaction field theory. Experimental data are usually in the limit of Xe infinitely dilute in the liquid solvent, no Xe–Xe contributions. As we have seen above, dilute gas phase observations can be reproduced by direct integration of intermolecular shielding functions using the intermolecular potential function. For the Xe atom in a solvent, this type of averaging is no longer possible because of the many-body interactions in both the shielding response functions and in the potential energies associated with the system configurations. As a consequence, even in the limit of highly accurate *ab initio* calculations of the intermolecular shielding response in interacting molecular systems, the averaging can no longer be carried out to high accuracy. There are simply too many assumptions which can lead to error. Often by necessity, empirical "force fields" are used to define the nature of the liquid structure. With this caveat, we consider several methods of averaging Xe chemical shifts for Xe in liquid solvents such as to include temperature and dynamic effects.

First we consider general approaches to dynamic averaging of Xe shielding in condensed phases. Xe intermolecular shielding drops off with distance so that electronic structure of only those atoms within 6–10 Å of the Xe need to be accurate for Xe shielding hypersurface calculations. However, long range effects can contribute indirectly by affecting the electronic structure of the atoms nearest to Xe and also by affecting the distribution of those atoms in space, *i.e.*, the "free volume" in which the Xe atom executes its dynamics within the solvent cage, within an ionic liquid channel, in a protein pocket, or a transient pocket within a glassy polymer. Therefore, accurate description of the physical system, including theoretically difficult long range effects, is needed. As *quid pro quo*, it is precisely these effects that make Xe chemical shifts exquisitely sensitive to the environment; even when we are unable to describe the environments accurately quantum mechanically and classically, the distinct Xe chemical shifts in only slightly different environments serve as a sensitive and useful diagnostic property. The dependence of Xe chemical shifts on local geometry is revealed in variable temperature measurements. Any interpretation of Xe in condensed phase materials must be tested against the experimental temperature dependence of the Xe chemical shift since dynamic simulations at various temperatures require no change in the parameters of the shielding or potential energy surfaces. The dynamic averaging may be carried out in various ways, but, in general, one needs a means of generating configurations over which the averages are taken and a means of generating the shielding for a given configuration.

The means of generating configurations may be *via* a Monte Carlo (MC) process for canonical or grand canonical ensembles or *via* a (classical or quantum) molecular dynamics (MD) trajectory. Both methods of generating configurations have been used for dynamic averaging of Xe shielding. The usefulness of MD simulations is limited by their short duration. The shielding calculation converges quickly, but if the MD is to produce the correct long range structure of the physical system (which we need for accurate Xe intermolecular shielding for reasons discussed above), the pre-equilibration MD has to be done over a long enough trajectory or start from a configuration very close to the actual equilibrium configuration, or else various techniques such as simulated annealing have to be employed to let the system get over barriers in the potential energy hypersurface. In classical MD, the interaction potentials between the particles are functions of the inter-particle coordinates and may include pairwise, three-body, and higher order terms, whose functional forms are related to the nature of interactions and bonding in the system under study. These parameterized functional forms have been obtained by fitting the parameters to a set of experimental or theoretically calculated data. Many widely used combinations of potentials (or force fields) specifically developed for biological systems (AMBER, CHARMM, GROMOS, *etc.*) or systems consisting of organic molecules (OPLS) have been used extensively in dynamic averaging of shielding of various nuclei in solutions. Beyond classical MD are quantum MD methods which have been used for shielding calculations for other nuclei[30] but not for Xe shielding. The biggest weakness in using classical MC or MD simulations arises from the intermolecular potential functions used in the simulations. It is therefore important that these be tested independently by reproducing other physical quantities such as adsorption isotherms or solubility, or else quantum MD such as CPMD, which calculates all interactions quantum mechanically, should be used.

There are various means of generating the Xe shielding for a given configuration. Obviously, this is based ultimately on quantum mechanical calculations of Xe shielding. For the purpose of dynamic averaging, shielding may be calculated using Periodic Boundary Condition (PBC) methods for a completely QM description of the entire system as represented by a supercell.[30] In principle PBC methods could be applied to Xe shielding in a crystalline or amorphous polymer, or to a Xe shielding in a protein pocket. In an alternative approach, only a finite number of molecules are included in a cluster, the molecule in question plus some number of neighbours. The cluster method has been used for a rare gas atom in a zeolite cage[31] or an organic cage,[32–35] or a pair of molecules at various distances and orientations.[8,23,24] The number of molecules in the cluster could be two or more; for example, calculations of the shielding for Xe in benzene have included 9–10 benzene molecules in the cluster,[36] and the calculations for Xe in clathrate hydrates included 40–48 explicit water molecules.[21] An improvement is afforded by an embedded cluster approach. The cluster may be placed in a reaction field, or the cluster may be embedded in a collection of self-consistently determined point charges while doing the quantum calculation,[21] using embedded ion EIM[37] or enhanced embedded ion EEIM[38] methods to determine the charge field that describes the periodic lattice.

Finally, the procedure for doing the averaging of the intermolecular shielding is, in general, (a) to select a series of configurations from MD or MC simulations, do quantum calculations of shielding for those snapshots and take the equally weighted average, or (b) to use pre-calculated shielding hypersurfaces and evaluate the average during the process of generating the configurations in an MD or MC simulation. We cite some examples in the following.

2.2.2.3.1 Quantum Calculations of Shielding from MD or MC Snapshots. This is a commonly applied method of averaging in condensed phase. In this method, the snapshots are first generated and then the shielding calculation is done for each snapshot. For Xe in benzene solution, the highly anisotropic nature of the interaction between Xe and the benzene molecule makes it difficult to precisely express the set of calculated shielding values for Xe at various positions relative to a benzene molecule into a suitable analytic mathematical form of the Xe shielding hypersurface. Instead, Standara *et al.*[36] carried out classical MD simulations of one Xe atom in a periodic box of benzene molecules and selected snapshots from the classical MD trajectory. A cluster including a Xe atom with its first solvation shell of 9–10 benzenes was carved out of each selected snapshot. This cluster was used for the quantum mechanical calculation of the isotropic ^{129}Xe shielding using non-relativistic density functional theory as well as relativistic Breit–Pauli perturbation corrections. Thus, the correlation and relativistic effects as well as the temperature and dynamics effects could be included in the calculations.[36] Most of the experimentally observed isotropic ^{129}Xe shift was recovered in the nonrelativistic dynamical region, while the relativistic effects explain about 8% of the total ^{129}Xe chemical shift. Theoretical results are found to agree with the experimental value at room temperature. This was a rather fortunate result, since the Xe–benzene potentials used were approximate, taken from mixing rules and Xe L-J potentials ($r_0 = 3.975$ Å, $\varepsilon/k = 214.7$ K) and not previously tested against the equilibrium structure and optical spectra of Xe–benzene van der Waals complex, for example, or other appropriate experimental data.

2.2.2.3.2 Use of Pre-calculated Shielding Hypersurfaces in MD or MC Himulations. For Xe in liquid water, *ab initio* calculations of Xe shielding surfaces were carried out (as a function of position within the cage) in the rigid experimental geometry of various clathrate hydrates of known neutron diffraction structure with disorder in the proton positions constrained to follow the ice rules, including the effects of the extended lattice in the *ab initio* calculations; then the *ab initio* shielding tensors were mathematically expressed in terms of pairwise Xe–O and Xe–H terms, which are functions of distance. Monte Carlo simulations of Xe chemical shift tensors in the various clathrates had been used to verify the Xe–H and Xe–O shielding functions against Xe@clathrate spectral lineshapes. The pre-calculated isotropic Xe–H, Xe–O shielding functions in rigid solvent cages in the extended lattice system were used as the shielding functions for Xe in liquid water, calculating the Xe shielding contributions on the fly during the MD trajectories in simulations of Xe solution in liquid water.[39] A well-established liquid water potential and the same Xe–H and Xe–O interaction energy functions used for Xe in the clathrate hydrates were used to calculate the Xe–H and Xe–O interactions. Results are in excellent agreement with experimental Xe chemical shift in liquid water, not surprising since the shielding functions had been tested against the solid state experiments in clathrate hydrates, reproducing not only the isotropic shieldings but the anisotropic line shapes as well.

There are data for Xe in liquid N_2,[40] and Xe in liquid CO_2 and liquid NNO.[41] Although the shielding functions have been calculated for these Xe-linear molecule pairs using DFT methods, these shielding calculations and/or the established intermolecular interaction potentials were not accurate enough when tested against the gas phase density coefficients of Xe chemical shift as a function of temperature; only semiquantitative agreement with experiment was found.[23] Nevertheless the methods are now well known and *ab initio* calculations using CCSD(T) with perturbative relativistic corrections for Xe shielding at various (R,Ω) configurations can be carried out. With large enough basis sets, *ab initio* CCSD(T) calculations of the Xe-linear molecule intermolecular interaction potentials could yield as good a quality as was found for the best empirical Xe–Xe potentials.[12] The isotropic Xe chemical shift as a function of temperature for Xe in liquid N_2, and supercritical CO_2 and NNO can then be calculated.

There exists a large amount of data for Xe chemical shifts in liquid alkanes in various homologous series.[42–45] In that literature, the global interpretation of the Xe chemical shifts in terms of constitutive contributions of CH_3 and CH_2 groups and corrections for cyclic *vs.* normal chains had been incorrect and counter-intuitive, primarily because of making comparisons of Xe chemical shifts in liquids at the same temperature, as opposed to comparing them in liquids at the same thermodynamic state. Another empirical assignment of group contributions had been attempted.[46] A rational comparison of Xe chemical shifts in different solvents in a homologous series can be made if the solvents are in the same thermodynamic state. This was brought to the attention of the Xenon NMR community by E. J. M. Felipe and R. Bonifacio at the first XeMAT conference in 2000. They suggested using liquids at the same reduced temperature (T/T_c) or reduced density (ρ/ρ_c).[47]

They have since carried out simulations of Xe in the various liquid solvents illustrating this concept.[48] We carried out atomistic MD simulations of Xe in normal alkanes and cyclo-alkanes using pre-calculated Xe shielding hypersurface for Xe–CH_4, fitted to pairwise sum of Xe–C and Xe–H functions and tested against the temperature dependent density coefficient of Xe chemical shift in CH_4 gas. These functions are used to calculate Xe shielding on the fly during the MD trajectory; using a cutoff distance and periodic boundary conditions permits simulations to be carried out for the entire solution. Since the additive chemical shift contributions from the CH_3 and CH_2 groups are obtained separately in the simulation, we determine these constitutive contributions to the Xe chemical shift for each temperature in each solvent and find that per CH_3 contributions are greater than per CH_2 contributions for each case, a ratio of around 1.5. One of the possible physical insights to be drawn from the above comparisons is the effect of the accessibility of the functional group in the solvent molecule on its contribution to $\sigma_{1,\mathrm{effective}}$(Xe–solvent) in eqn (2.3). For example, end groups have a distinct advantage in contributing to the Xe chemical shift because of the site effect. This means that the CH_3 group contribution to the effective second virial coefficient of the Xe chemical shift in the solvent should be larger than CH_2, not only because there are more atoms contributing to the sum of Xe responses, but also because of the site effect. At the same reduced temperature, $(T/T_c) = 0.5$, the CH_3 (and the CH_2) contributions to $\sigma_{1,\mathrm{effective}}$(Xe–solvent) are nearly constant and therefore can be considered transferable from one alkane to another. This permits the prediction of the Xe chemical shift in higher alkanes ($n = 9$–16) from their experimental density, using the CH_3 and CH_2 contributions from MD in alkanes ($n = 4$–8).[49] The values of $\sigma_{1,\mathrm{effective}}$ (Xe–CH_2), the per CH_2 contribution at $(T/T_c) = 0.5$ are found to be very similar for the $n = 5, 6, 8$ cyclo-alkanes (~ 2.69 ppm mol^{-1} L^{-1} per CH_2) found in MD simulations but smaller than the corresponding values (~ 3.14 ppm mol^{-1} L^{-1} per CH_2) found in the linear alkanes.[50] The site effect, the CH_2 in linear alkanes are more accessible to Xe than the CH_2 in cyclo-alkanes, is obvious here. The additive nature of Xe intermolecular shielding lends itself to sensible constitutive contributions for Xe chemical shifts in homologous series of solvents.

A particularly interesting Xe chemical shift is that for Xe in the blood substitute PFOB (perfluorooctylbromide).[51] Using the same MD method, the Xe chemical shifts for Xe dissolved in water (as described above) and Xe dissolved in PFOB were individually accurately predicted,[39] respectively 105 ± 5 and 195 ± 5 ppm relative to the isolated Xe atom, to be compared with the experimental 106 and 196 ppm. The Xe in PFOB was calculated by MD simulations carried out using the additive Xe–C, Xe–F and Xe–Br shielding functions. The Xe–C and Xe–F shielding functions were taken from the *ab initio* calculations in the Xe–CF_4 dimer system at various configurations, represented by fitting to pairwise Xe–C and Xe–F shielding functions of distance only, tested against the experimental Xe chemical shift in CF_4 density coefficient as a function of temperature in the gas phase.[23]

The Xe–Br shielding function was obtained from the Xe–F shielding function by well-established shielding scaling factors for atoms in the same family in the Periodic Table.[9] These studies of Xe in liquids lead to the following general conclusions: the Xe chemical shift in liquid solutions depend on the local contributions to the Xe shielding by atoms or groups of atoms. Therefore, the Xe chemical shift in a solution is determined by the chemical constitution of the solvent molecule and the accessibility of the Xe to the various atomic groups in the solvent cage, the same quantities which determine Xe shifts for xenon in gas mixtures and xenon trapped in solid structures. Changes in temperature affect the distribution of the atoms or groups of atoms of the solvent relative to the Xe position. In dilute gases, this is governed by $\exp[-V(R,\Omega)/kT]$. In solutions, the structure of the liquid changes with the thermodynamic state, the density typically decreasing with increasing temperature, leading to smaller Xe chemical shifts. What can be compared from one liquid solvent to another are the density coefficients at the same reduced temperature, the Xe-group contributions to the density coefficients being about the same as long as their accessibility to Xe is about the same.

Ionic liquids (IL) have more local structure than ordinary liquids.[52] One of the most important features of ionic liquid structure is charge ordering, the need to maintain a lattice-like arrangement of cations and anions to minimize the Coulombic energy of the liquid.[53] It has been estimated that the size of local structures is several tens of nanometres.[54] This is consistent with the fact that some ionic liquids experience unusually long equilibration times.[55] A typical ionic liquid is 1-alkyl-3-methylimidazolium cation and a selected anion. The crystal structure of 1-butyl-3-methylimidazolium chloride shows channels in which the Cl^- anions are accommodated as chains.[56] The close contact (2.5–2.7 Å) between three H atoms of the cation and the Cl^- ion indicate hydrogen bonding and the out-of-plane all-*trans* configuration of the *n*-butyl group is probably the reason for the large separation distance between the two imidazolium rings. There is spectroscopic evidence (Raman) that the local structure in the liquid is very similar to that in the crystal. Xe chemical shifts of xenon dissolved in 1-alkyl-3-methylimidazolium ionic liquids are large, ranging from a low of 161.1 ppm for the bulky anion bis(trifluoromethanesulfonyl)imide to 215.5, 228.5, 253.5 ppm for Cl^-, Br^-, and I^-, respectively, relative to the low density gas.[57] These measured shifts appear to have negligible Xe–Xe contributions. These results and an additional set of ^{129}Xe chemical shift measurements of Xe dissolved in four IL homologous series based on 1-alkyl-3-methyl-imidazolium cations, $[C_n\text{mim}]^+$, $n = 2$–12, combined with different anions, (altogether 30 distinct ionic liquids) were interpreted by Filipe *et al.* using MD simulations.[58] Comparing these various ionic liquids at the same thermodynamic state is easier than with alkanes; at room temperature all are at approximately the same reduced temperature $T/T_c \sim 0.25$. The MD simulations provide the $g(r)$ Xe–A radial pair distribution functions, where A = imidazolium ring, or anion, or various carbons of the alkyl side chain. To obtain the Xe–A contribution to the chemical shift, it would be necessary to integrate the Xe–A shielding function of R(Xe–A) weighted by the $g(r)$ for $r \sim 0.75r_0$ to $r =$ cut-off, which in this case was 16 Å. It would have been interesting to see the one-body distribution function for Xe in the ionic liquids, which could easily have been collected during the MD. The one-body distribution function would give a better picture of where the Xe spends most of its time. With progressively longer alkyl chains, the Xe tends to "disappear" from the vicinity of the imidazolium ring and have a greater probability of being found near the terminal group (CH_3) of the alkyl chain.[58] This would counter the speculations in the previous work by Castiglione *et al.*[57] which explained the observed Xe chemical shifts for ILs with different anions by guessing the volume of the "cavity" where Xe might reside.

Xe is such a sensitive probe of liquid structure that it can detect the presence of ions in solution[59] or changes in hydrogen bonding structure of the liquid due to deuteration.[60]

2.2.2.4 Xe Atom in a Cage in Solution

We have seen that Xe shielding response is steeply changing at short distances and that the Xe chemical shifts in solution depend on the average internal volume of the solvent cage, the "free volume" in the liquid solvent which changes with temperature. A stringent test of this idea is the Xe shielding in a semi-rigid cage of known structure, *e.g.*, C_{60}. The fullerence C_{60} has been synthesized such as to encapsulate a Xe atom. The Xe chemical shift has been measured, 182.35 ppm when expressed relative to Xe atom.[61] It is to be expected that RHF calculations cannot fully describe the shielding response provided by C_{60} which itself requires electron correlation to reproduce its equilibrium geometry. DFT-B3LYP-optimized geometry was very close to experimental geometry, and DFT calculations using B3LYP functional could provide a Xe chemical shift in reasonable agreement with experiment. It was found in this study that the Xe shielding is very sensitive to the geometry of the cage as defined by the C–C bond lengths.[32] Single point calculation of Xe shielding at the center of the cage provides a chemical shift of $[\sigma(\text{Xe atom}) - \sigma(\text{Xe@C}_{60})] = 181.6$ ppm, fortuitously close to experiment; indeed the B3LYP functional has been found to overestimate Xe chemical shifts in general. Because of the tight fit of Xe in this cage, the dynamic average over various Xe positions within a rigid cage is expected to be small and was later found to be no more than 0.5 ppm.[62] More recent calculations using the BH and HLYP functional and molecular mechanics geometry for the cage found the non-relativistic value for Xe@C_{60} at rest in vacuum is only 132.1 ppm.[33] Relativistic corrections using Breit–Pauli perturbation theory for this condition is 14.2 ppm. The dynamic effects from thermal averaging of the C_{60} geometry, and the effect of benzene solvent, which had been thought to be small, was later found to be of the order of 14.1 and 12.3 ppm.[33] Unfortunately, there are no measurements of the temperature dependence studies of the Xe chemical shift in this system to check these estimates, and the MD of the C_{60} cage in benzene solvent used empirical potentials which could lead to a C_{60} cage which is too flexible.

There is no exchange of Xe between the inside and outside in this case; the C_{60} has to be chemically opened to permit this. A series of cages which do permit a slow exchange of Xe, slow enough for measurement of Xe chemical shift inside the cage, is the cryptophane series which have two cyclotribenzylene caps joined by three linkers, where the linkers are $–O–(CH_2)_n–O–$.[63] Cryptophanes are the best molecular hosts for Xe when the linkers are relatively short. Xe has been trapped in cryptophane A (222), where each of the three linkers are $–O–(CH_2)_2–O–$,[64] and in cryptophane 223 and 233,[65] in cryptophane 333,[66] and in cryptophane 111.[67] We mapped out the Xe shielding in various locations within the cryptophane A (222) cage[34] by doing DFT-B3LYP and RHF calculations; RHF results were insufficiently deshielding, while B3LYP-DFT results were too deshielding. This is a rather general result for Xe shielding calculations using DFT. We fitted the shielding values to pairwise additive Xe–A shielding contributions, each a function of distance, where site A differentiates between three types of carbons: ring, CH_2 in the cap, C–O in the OCH_2CH_2O linkers or the OCH_3, and each oxygen atom is represented by a site at the oxygen center and a site representing the centroid of the lone pairs 1.2 Å from the oxygen center. Using these Xe-site shielding functions, the quantum mechanical values of the Xe shielding at various Xe positions in the cage could be reconstituted. All the Xe–A functions were monotonically deshielding with decreasing distance except for $Xe–C_{ring}$. *Ab initio* values were positive in a small region where ring currents would predict shielding rather than deshielding. These findings would lead to predictions of unusually small Xe chemical shifts in cryptophane 111, where the linkers are short, thereby forcing the Xe to spend more time in those positive regions in comparison with the cryptophane 222, or 223 or 233. Indeed it is found experimentally that in 111, the volume inside the cage may be smaller, yet the average Xe chemical shift is not greater than in 222.[67]

The general trends of Xe chemical shifts with cage size, when comparing similarly constituted cavities, arise from the universal shape of the Xe shielding response function proposed by us in 1982 and verified by *ab initio* calculations on Ar and later on Xe.[8,9] The dependence of the Xe chemical shift on cage size follows from the fact that a smaller cage provides the Xe atom with many more atoms at short distances to evoke a large quantum mechanical shielding response. More polarizable atoms evoke a larger Xe shielding response. Care should be exercised when the constitution of the cage is such that some chemical groups are sampled more than others, or in the case of highly anisotropic groups. In liquid benzene, Xe samples all positions in plane and out of plane, above the ring and so on. In a cryptophane cage, Xe can only sample the benzylene groups above the plane and only in certain regions relative to the ring, thus the averaging is very different, weighing only some regions and not others because of Xe confinement in the cage. A more subtle example of dependence on cage size is the differential Xe chemical shifts upon successive deuteration of the cage.[68] Our interpretation is that the heavier deuterium mass does not permit the larger vibrational excursions of the lighter proton, leading to small incremental shifts with each D replacement. Simply making the r_0 of the Xe–D potential function 0.07 Å shorter than that for Xe–H, while keeping all other quantities the same, is sufficient to provide the observed differential shifts upon D substitution at the linker and the methoxy groups. The per-D isotope effect being smaller for the methoxy than the linker is reproduced, showing that our MD simulations of Xe atom in the cage predicts the correct relative accessibility of linker *vs.* methoxy groups.

Derivatives of cryptophane A (CryA) have been synthesized for the purpose of using the Xe in the cage as a biosensor, by attaching a biological ligand. The initial publication on xenon biosensors by the Pines group suggested the possibility of multiplexing, that is, using several cage types or derivatives with different biological ligands to detect several targets at the same time.[66] This concept is based on the Xe chemical shifts being tuned to different points on the Xe chemical shift range by choice of substituents or using more than one cage architecture. The mechanism of the sensing action, *i.e.*, a different Xe chemical shift for the free sensor molecule than the sensor molecule attached to the target, has been established to be due to the dynamic average for the Xe in cage in the free sensor molecule being different than when the sensor is attached to the target.[34] The cage undergoes different molecular dynamics in the attached sensor because contact of the cage with the protein surface leads to greater deformations of the cage than for the free-floating sensor. From the calculations it was predicted that the shorter the tether, the larger is the Xe chemical shift difference between the attached and free sensor. This trend was later observed when biosensors with varying tether lengths were synthesized.[69] The cryptophane cage itself is handed and is commonly synthesized as a racemic mixture. When an attached ligand is achiral, the NMR signal of the Xe atom in the functionalized cage in solution is a single isotropic peak, since the Xe shielding tensor components in the **R** and **L** cages differ by no more than the signs of the off-diagonal elements. Chiral substituents can split the cage-encapsulated Xe NMR signal into one or more sets of doublets, depending on the number of asymmetric centers in the substituent. The Xe chemical shift discriminates between diastereomers, leading to splitting of signals.[35] The dynamic interactions between the tether and the cage are different for the various handed tethers: In a sense, the left handed tether arranges itself around the left-handed cage differently than on the right-handed cage. The electronic structure of the cage can detect this difference and, in turn, the Xe can detect the difference in the cage shielding response. A combination of *ab initio* calculations and molecular dynamics simulations have permitted us to assign the observed split peaks to the **Rl** and **Ll** diastereomers. Where the substituent itself possesses two chiral centers, calculations permit the prediction of the Xe spectrum of diastereomeric systems in solutions containing **Ll***r*, **Rl***r*, **Ll***l*, and **Rl***l* systems.[35]

Other groups have synthesized variants of the Xe@CryA biosensor. When the substitution is for the CH_3 group in one of the $–O–CH_3$ moities in CryA, Xe in the functionalized cage is more shielded (smaller chemical shift relative to Xe atom) in the original Pines *et al.* biosensor[66] than in the parent cage, as our calculations predicted,[34] and this too has been found to be the case in other variants.[70] The sensing mechanism for the new protein sensors[71,72] appears to be the same as we proposed earlier, deformation of the cage upon binding of the sensor to the protein, leading to higher Xe chemical shift in the bound than the unbound sensor. On the other hand, the sensing mechanism for detecting a specific DNA target, which has the Xe in a cryptophane A covalently attached to a spacer attached to a single strand of the complementary nucleotides, is different; association between sensor and target toward the formation of the double stranded DNA causes the encapsulated Xe to move to 1 ppm lower chemical shift.[73] The criteria required for an efficient biosensor have been reviewed comprehensively.[74]

2.3 The Intermolecular Xe Chemical Shift Tensor of Confined Xe

2.3.1 One Xe Atom as a Probe of Anisotropic Spaces in the Solid State

Clathrate hydrates of Xe are crystalline and have distinct cages formed by water molecules. Depending on the conditions, various types of hydrates have been prepared: Structure I, Structure II, H, bromine hydrate. There are altogether 12 distinct cage types in these particular hydrates and Xe in each one has a characteristic average shielding tensor which has the characteristic number of distinct components determined by the nuclear site symmetry at the center of the cage,[75] based on the analysis by Buckingham and Malm.[76] Ripmeester *et al.* provided these earliest experimental examples of Xe chemical shift anisotropy for a single Xe atom in cages.[77,78]

2.3.1.1 *Predictions from Pairwise Additivity Model*

The shielding tensor of Xe calculated for Xe–Rg pairs and larger collections of rare gas atoms at various Xe–Rg distances, such as Xe_3,[10] Xe in the center of 6 and 8 Ne atoms,[10] and Xe in a helix of 7, 8 and 15 Ne atoms,[79] provide the basis for the idea that shielding tensor components as well as the isotropic shielding can be duplicated by sums of pairwise shielding tensors over a wide range of distances, although deviations from additivity become significant at very short distances. The first time the concept of additivity of intermolecular shielding was used was for Ar shielding in Ar_3,[9] but the formal presentation of the ‘‘additive dimer tensor model’’ was made in ref. 80. Other calculations also support the additivity of the isotropic Xe intermolecular shielding in Xe_n clusters.[13]

The shielding tensor of a single Xe atom located at a specific position (x_J, y_J, z_J), within a cage, helix, or channel constituted of Ne atoms is approximated by a sum of Xe–Ne contributions. In the additive dimer tensor model, the intermolecular Xe shielding is considered to arise from contributions from each atom of the channel by considering each Xe-atom contribution at a time. In other words, it is assumed that the Xe shielding of the *J*th Xe atom at position (x_J, y_J, z_J), can be calculated by using a summation over the contributions of Xe–Ne dimers, using the *ab initio* XeNe dimer shielding function (for example, the function $\sigma_\perp$ and $\sigma_\parallel$ from ref. 8) in each case. For example, the contribution to the Xe shielding due to *i*th Ne atom located at (x_i, y_i, z_i) is given by the *ab initio* tensor component, the function $(\sigma_\perp, \sigma_\perp, \sigma_\parallel)_{\mathrm{XeNe}}$ (evaluated at r_{XeNe}). The derived expressions turn out to be very simple geometric factors coupled with $\sigma_\perp$ (evaluated at r_{XeNe}) and $\sigma_\parallel$ (evaluated at r_{XeNe}). For example,

$$\sigma_{XX} = \left[\frac{(x_i - x_J)}{r_{iJ}}\right]^2 \sigma_\parallel + \left\{\left[\frac{(y_i - y_J)}{r_{iJ}}\right]^2 + \left[\frac{(z_i - z_J)}{r_{iJ}}\right]^2\right\}\sigma_\perp \tag{2.5}$$

$$\frac{1}{2}[\sigma_{XY} + \sigma_{YX}] = \left[\frac{x_i - x_J}{r_{iJ}}\right]\left[\frac{y_i - y_J}{r_{iJ}}\right](\sigma_\parallel - \sigma_\perp) \tag{2.6}$$

Terms like these are summed to include all the atoms in the channel. The $\sigma_\perp$ and $\sigma_\parallel$ are functions of distance. We have used a sum of inverse even powers of r to fit the *ab initio* values of Xe–Rg shielding components but some other functional forms, such as sums of exponentials, may be used as well. Then the Xe shielding response in an external magnetic field (B_0) along a particular chosen direction (θ, ϕ) with respect to the crystal frame can be calculated as follows:[81,82]

$$\begin{aligned}\sigma_{B_0}(\theta,\varphi) = {} & \sigma_{XX}\sin^2\theta\cos^2\varphi + \sigma_{YY}\sin^2\theta\sin^2\varphi + \sigma_{ZZ}\cos^2\theta \\ & + \frac{1}{2}[\sigma_{XY} + \sigma_{YX}]\sin^2\theta\sin 2\varphi + \frac{1}{2}[\sigma_{XZ} + \sigma_{ZX}]\sin 2\theta\cos\varphi \\ & + \frac{1}{2}[\sigma_{YZ} + \sigma_{ZY}]\sin 2\theta\sin\varphi\end{aligned} \tag{2.7}$$

When the cage enclosing the Xe is a cage of water molecules, as in the clathrate hydrates, the *ab initio* calculations in the best representation of the Xe environment (cage, plus all waters hydrogen bonded to the waters of this cage, plus a self-consistent set of partial charges representing the remainder of the clathrate crystal) are included in the quantum mechanical calculation of Xe shielding in various positions within the cage and yield an overdetermined number of data points such as to fit $\sigma_\perp$ and $\sigma_\parallel$ to functions of Xe–O and Xe–H distances. In this case, the additive dimer tensor formulas mathematically reconstitute the *ab initio* results that have been precalculated for various Xe positions within the cage in the clathrate crystallite. The canonical Monte Carlo averaging using the additive dimer tensor model does not involve additional approximations about the shielding response when used to generate Xe NMR spectra for the same clathrate structures. The generality of the shielding response is assumed when the exact same Xe–O and Xe–H shielding functions and potential functions are used to generate Xe NMR spectra for Xe in *other* structure types of clathrate hydrates.

In another example, additive sums of Xe–C and Xe–H shielding functions used to regenerate the *ab initio* values of the Xe shielding in a large number of configurations for Xe–CH_4 may be used with the best available Xe–CH_4 potential function fitted to Xe–C + Xe–H terms to predict the temperature dependent density coefficient of Xe chemical shift in CH_4 gas. Comparison with experimental values in Xe–CH_4 mixtures over a wide temperature range provides a test for both the shielding surface and the potential functions. Additional approximations are involved when the exact same Xe–C and Xe–H shielding functions and potential functions are used in a GCMC simulation to approximate the shielding response from the atoms of a cage or channel in which CH_3 groups form the inner surface,[83] or CH_2CH_2 groups[84] or when the exact same functions are used to represent in MD simulations the Xe shielding response in solutions of Xe in liquid alkanes.[49] While keeping in mind the nature of the additional approximations involved, the additive dimer tensor model serves as a very useful means of predicting average Xe NMR chemical shift tensors for Xe in nanocavities and nanochannels in solid materials. For example, the progression of line shape changes with increasing Xe loading such as those observed for Xe in ALPO4-11 by Ripmeester *et al.*[85] were reproduced.[80] These are the first anisotropic line shape calculations which explicitly took into account the dynamic averaging of Xe shielding response within an atomistic representation of the channels in a crystalline material.

The nature of the functions calculated for the $\parallel$ and $\perp$ components of the Xe–Rg shielding and the assumption of pairwise additivity have formed the basis in our work for general predictions of the qualitative behavior of Xe chemical shifts and its anisotropy as a function of temperature and Xe loading in a wide variety of environments, even before carrying out any simulations, in flat disks, in narrow medium and wider bore pipes, and in pipes with elliptical cross sections.[10] The atoms constituting the channel structure represented by a single type of atom, even a rare gas atom, could provide predictions of line shapes as a function of Xe loading and temperature[80] which reproduce anisotropic line shapes obtained in experiment under various conditions. Quantitative line shape predictions for various clathrate hydrate structures,[21] channel structures such as $ALPO_4$-11,[80] zeolites SSZ-24 and silicalite,[86] and crystalline dipeptide nanochannels[83] could be obtained for the first time by using the additive dimer tensor model in GCMC simulations.

2.3.1.2 Example: A Xe Atom in Clathrate Hydrate Cage

The model used in the *ab initio* calculations of Xe shielding comes from the neutron diffraction data on Structure I Xe clathrate hydrate, and the hydrogen positions reflecting the remaining proton disorder were determined such as to follow Pauling's ice rules. The quantum mechanical calculations included the Xe atom, the water molecules that constitute the cage and all the water molecules that are required in order to provide the hydrogen bonding partners of every water molecule in the cage (a total of 40 or 48 water molecules) and the remaining water molecules in the crystal fragment are represented by point charges. Monte Carlo simulations used supercells with $n \times n \times n$ unit cells as the propagating unit to create a periodic lattice. ($n = 4$ for Structure I clathrate and $n = 2$ for Structure II was sufficient to produce a statistically valid result). The 73 Xe shielding values are fitted to universal pairwise additive Xe–O and Xe–H shielding functions, and the Monte Carlo simulations to generate the Xe NMR line shapes appropriate to the microcrystalline sample of the experiments used these shielding functions. Pairwise additive potentials of the Maitland–Smith form were used. The line shapes calculated for Xe in the 12 types of cages in clathrate hydrate structures I, II, H, and bromine hydrate, using *the same* shielding functions and *the same* potential functions, are in excellent agreement, in terms of the existence of anisotropy, the sign of the anisotropy, and the magnitude of the anisotropy, with the line shapes observed experimentally by Ripmeester and co-workers in Xe type I hydrate, in Xe–propane type II hydrate, in Xe type H hydrate, and in bromine hydrate.[77,78,87,88] We have assigned the individual average tensor components to specific axes of the cages or the crystal. While the agreement with the experimental values that can be deduced from the Xe spectra is not excellent in every case, we believe the assignments of relative magnitudes of the components to the specific principal directions are reliable. Such assignments cannot be unequivocally determined from the experimental spectra in many cases. We have established that *the* average Xe shielding tensor of a single Xe atom in a cage reflects the symmetry of the cage itself, as canceling contributions of equal magnitude, and opposite signs, are uniformly included in the averaging process through built-in proper statistical sampling. Thus, the Xe NMR line shapes directly provide information about the symmetry of the cage, in the number of unique components, and in the relative magnitudes of the components parallel and perpendicular to the symmetry axis of the cage itself. The basic ideas about Xe intermolecular shielding in confined spaces derived in ref. 10 are in fact sufficient to make the assignments of relative magnitudes and directions of tensor components for each of the 12 types of cages found by canonical Monte Carlo averaging of quantum mechanical shielding hypersurfaces in the clathrate hydrates. It would be wrong to compare magnitudes of shielding anisotropies in cages with different chemical compositions, however.

2.3.2 Xe–Xe Interactions as a Probe of Anisotropic Spaces in the Solid State

Anisotropy of the inner spaces probed by Xe becomes more obvious when Xe NMR is observed as a function of Xe loading in crystalline pores. This arises from the Xe shielding response from other Xe atoms being quantitatively more deshielding than most atoms constituting the inner surface of a pore. The average Xe shielding anisotropy at full loading becomes very pronounced. For any given architecture of the atoms constituting the pore, at a fixed temperature, the magnitudes of the components of the average shielding tensor change with Xe loading in a *predictable* way under certain conditions.[10] The general predictions from our analysis of the Xe tensor components and line shapes that result from considering the anisotropic Xe shielding response from Xe–wall and Xe–Xe interactions have been applied to observations of Xe in various real systems with channels of symmetrical and also elliptical cross-sections, for example aluminophosphate molecular sieves ($AlPO_4$-5, -31, -11, and -41) and their corresponding silicoaluminophosphate (SAPO) variants,[89] rhombus-, and square-shaped cross-section channels formed by metal organic frameworks,[90–92] channels in organic crystals like tris(*o*-phenylenedioxy)cyclotriphosphazene,[93–96] channels in crystalline inorganic complexes such as $Co(en)_3Cl_3$,[84] large ellipsoidal pores connected by elliptical windows in crystalline Zn hexacyanocobaltate,[97] monitoring the growth of one type of aluminophosphate crystal structure from another,[98] channels in various crystalline dipeptides[99,100] and channels formed by *para*-acylcalix[*n*]arenes assemblies.[101]

2.3.2.1 Xenon in a 1-Dimensional Narrow Bore Channel

For 1-dimensional channels, we considered the model of an idealized smooth pipe of uniform circular cross-section (which we have designated as a narrow bore relative to the van der Waals diameter of the Xe atom, such that the low energy position for the Xe is along the pipe axis). In such a channel, no two Xe atoms can occupy the same plane perpendicular to the channel axis; that is, the Xe atoms cannot pass each other within the channel. We predicted the number and relative magnitudes of the tensor components as follows. The only electrons which can provide contributions to the Xe shielding response are those electrons in the plane passing through the Xe nucleus and perpendicular to the direction of the B_0. At zero loading, $\delta_{\parallel} > \delta_{\perp}$ since the ring of atoms in the plane passing through the Xe nucleus and perpendicular to the channel axis are greater in number and closer, giving rise to a greater deshielding (larger chemical shift $\delta_{\parallel}$) while channel atoms in the plane containing the Xe nucleus and passing through the channel axis are fewer and farther away. At full loading we predicted $\delta_{\perp} > \delta_{\parallel}$; with increasing Xe loading at constant temperature, the $\delta_{\parallel}$ remains unchanged, while the $\delta_{\perp}$ progresses smoothly and monotonically from the value at the zero-loading limit to the value at the full loading limit. The Xe shielding response from the electrons of Xe atoms in the channel above and below the Xe nucleus becomes more pronounced with increasing probability of finding Xe in those regions. The Xe shielding tensor component along the direction of the channel axis arises entirely from the electrons of the ring of atoms of the channel in the plane of the Xe nucleus. For a pipe of uniform diameter, this component remains unchanged, irrespective of how many other Xe atoms are in single file motion in the channel. In at least some cases, the single-file diffusion of Xe atoms have been well characterized by a combination of techniques.[94,102–104] See also the chapter by Bowers on single file diffusion in this book.

There are several well-known examples, although the molecular crystal channels are by no means smooth: crystalline dipeptides L-Ala–L-Val and its retro analog L-Val–L-Ala, several other binary dipeptides, and the organic molecular crystal tris(*o*-phenylenedioxy)cyclotriphosphazene (TPP). Experimental observations of Xe line shapes as a function of Xe loading in these channels do indeed show the behavior described above for dipeptides Ala–Val and Val–Ala,[83] in other binary dipeptides,[99,100] and in TPP.[93] Grand canonical Monte Carlo simulations using quantum mechanical shielding surfaces reproduce the respective behaviors found experimentally as a function of Xe loading for dipeptides L-Ala–L-Val and L-ValLL-Ala,[83] other binary dipeptides L-ValLL-iLeu, L-iLeuLL-Val, L-iLeuLL-Ala, L-LeuLL-Ser, L-ValLL-Val, L-AlaLL-iLeu,[105] and in TPP,[106] and also in the channels of the ionic crystal (±)-$[Co(en)_3]Cl_3$.[84] Among zeotypes, $ALPO_4$-31 has channels with nearly circular cross-section in which Xe chemical shift as a function of loading and temperature behaves as predicted.[89]

Deviation from the predictions of the idealized smooth narrow bore pipes can be expected, especially when the channel consists of cells connected by narrowed regions. At low temperatures, the Xe tend to stay in the low potential energy cells and traverse across the barriers of the narrowed regions at higher temperatures. The narrowed regions will be sampled more often at high temperatures leading to a temperature dependence of the chemical shift tensor component along the channel axis $\delta_{\parallel}$, whereas no temperature or loading dependence would have been expected for $\delta_{\parallel}$ in the idealized smooth narrow bore pipe. Of course in the narrowed regions the Xe gets closer to the wall atoms leading to a higher $\delta_{\parallel}$ at higher temperatures. This is indeed observed for Xe in a single crystal of TPP oriented such that the channel axis is along B_0.[95] In this case, the narrowed regions also have more pronounced quantum mechanical shielding values, leading to a pronounced temperature dependence of $\delta_{\parallel}$. Unlike sealed samples of known Xe concentration (inside, outside and over-all), where the loading and the temperature of the sample can be decoupled, that is, it is possible to observe the loading dependence under constant temperature conditions, in a continuous flow of Xe (as is typical of hyperpolarized Xe experiments) increased loading necessitates lowering the temperature, thus $\delta_{\perp}$ increases with decreasing temperature because of increasing Xe loading.

2.3.2.2 Xenon in Structured 1-Dimensional Channels

Most molecular channels in which Xe has been observed are not smooth narrow-bore pipes. Depending on the anisotropy of the cross-section, Xe chemical shift tensor at near-zero-loading may have two or three distinct chemical shift tensor components. Any ellipticity in the channel cross-section leads to distinguishable $\delta_{\perp}$ and $\delta_{\perp}{}'$ averages, as seen in

$ALPO_4$-11[80,85] and $ALPO_4$-41,[89] with respectively 4.0×6.5 and 4.3×7.0 Å openings. As found also in the rhombus-channels of the metal–organic framework MIL-53[90] at near-zero loading, the tensor component $\delta_\perp$, which is the greater chemical shift, is that along the major axis of the cross-section, with the lesser $\delta_\perp{}'$ being that along the minor axis, just as predicted earlier for elongated cross-sections.[10] Other examples of elliptical medium bore channels in MOFs exhibit the same relative order of tensor components perpendicular to the channel axis.[91]

When the channel architecture does not permit two Xe to pass each other, then the individual average tensor components as well as the isotropic Xe chemical shift change *linearly* with increasing Xe loading, as was found experimentally and in simulations in the case of Xe in the elliptical channels of $ALPO_4$-11.[80,85] and also experimentally in the rhombus channels of MIL-53.[90] Shielding tensor calculations for the central Xe in the trimer Xe_3 at various Xe–Xe–Xe angles[10] already suggest that when the channel diameter is large enough to permit the Xe nucleus to have a shielding response from the electrons coming from Xe atoms in the same plane or just below/above, then $\delta_\parallel$ could change with loading, increasing only slightly up to not quite half-full and increasing much more pronouncedly between half and full occupancy. Even when the isotropic Xe chemical shift increases perfectly linearly with loading, the individual average tensor components behavior with Xe loading can reveal the pea-pod type structure of the channel, as in the case of Xe in ZSM-12 zeolite.[107] Using the same parameters as used for Xe in $ALPO_4$-11, GCMC simulations for Xe in a ZSM-12 structure leads to the curved behavior of three distinct components with increasing loading individually very similar to experiment, although more accurate potentials would be needed to get the cross-over points to match experimental line shapes.[108]

In our earlier work,[10] some of our predictions for *symmetrical near-circular* wide-bore channels were inaccurate because we had not considered averaging of the two perpendicular components $\delta_\perp$ and $\delta_\perp{}'$. We have later shown that GCMC averaging leads to only one distinct perpendicular component in the near-circular wide bore case,[86] for example in SSZ-24. With the same structure but different chemical composition, $ALPO_4$-5 exhibits also two distinct Xe tensor components like SSZ-24.[89] Both components $\delta_\parallel$ and $\delta_\perp$ change with temperature as predicted, since the Xe no longer stays at the center of the channel but is more spread out. As in the narrow bore case, $\delta_\perp$ increases with increasing loading. When the channels are extra large pores as in the gallophosphate cloverite (30 Å diameter)[109] then the Xe may be in fast exchange with the gas phase so that the observed chemical shift does not necessarily reflect the internal environment in the channel.

2.3.2.3 Xenon in 2-Dimensional Spaces

In a set of elegant studies Xe explores 2-dimensional space on the surface of a single crystal in a high-vacuum chamber.[110–112] These challenging experiments by Jänsch and his group are described more fully in a chapter in this book. With the normal to the crystal surface along the B_0, the Xe chemical shift ($\delta_{\parallel}$) comes entirely from Xe–Xe interactions, whereas with the plane of the surface along B_0, the Xe chemical shift ($\delta_{\perp}$) component comes entirely from Xe interaction with the surface atoms of the crystal, in this case the O atoms of the –CO or the $-CH_3$ groups of the ethylidyne $>CH-CH_3$ that are chemically bound to the metal surface. GCMC simulations of Xe on a –CO passivated Ir(111) surface and an ethylidyne covered surface provide rotation patterns and Xe tensors which reproduce the experiments.[113] When the surface is a bare metal surface such as Ir(111), there is the additional Knight shift,[111] which we will not consider here. Thus, for a Xe monolayer or less, $\delta_{\perp}$ is independent of coverage. On the other hand, ($\delta_{\parallel}$) coming entirely from Xe–Xe interactions increases with increasing coverage.

Hectorite forms silicate layers; the open gallery between layers is intercalated by pillars which are bulky counterions. The gallery is a two-dimensional space punctuated by counterions here and there maintaining the separation between layers at 5–7 Å, depending on the counterion. When Xe can enter this space at very low loading, there are only interactions with the occasional counterions that contribute to the Xe chemical shift component along the normal to the layers ($\delta_{\parallel}$). The $\delta_{\parallel}$ increases with increasing Xe loading as contributions from Xe–Xe interactions set in. On the other hand, the components in the plane of the layers ($\delta_{\perp}$) arise from interactions between Xe and the silicate layer above and below which does not change with Xe loading, provided the pillars which determine the layer separation restrict the movement of the Xe atoms to in-plane. Both tensor components are expected to change with temperature. Two studies using hyperpolarized Xe in hectorite with different cations do indeed find that the $\delta_{\parallel}$ increases markedly with increasing Xe loading.[114,115] As with other continuous flow hyperpolarized Xe measurements, the temperature and loading effects are conflated with one another; lower temperatures are necessarily accompanied by increased loading. This behavior of Xe chemical shift in 2-dimensional spaces was predicted earlier by considering Xe trapped between idealized parallel plates.[10]

2.3.2.4 Xenon in Intersecting Channels

The chemical shift tensors of Xe in one-dimensional channels are relatively easy to understand because the Xe atoms explore only one channel at a time when the crystallites are not too small. However, many interesting systems for which Xe serves as a probe of internal space have intersecting channels. In some cases large cavities interconnected by shared small windows or smaller cavities constitute the 3-dimensional space in which Xe atoms move. In some cases, one type of channel intersects an altogether different type of channel, as in silicalite. When extensive averaging through all accessible channel types and intersection regions occurs throughout the crystallite, is it still possible to observe Xe chemical shift tensor information? The answer is yes, of course, even in a microcrystalline sample, provided the crystallites are large enough so that Xe predominately reports from inside surfaces. An archetypal example of intersecting channels is silicalite (the all-Si form of zeolite ZSM-5), where one set of channels is straight and the other is sinusoidal. By synthesizing larger crystals we were able to observe the 3 components of the average Xe chemical shift tensor at high loading.[116] A millimetre-sized single crystal of silicalite with HP Xe at room temperature rotated in a goniometer in the magnetic field traces out the shielding response as a function of angle as given in eqn (2.7),[117] providing the highest quality experimental data for comparison with calculations. The experimental crystal rotation patterns are reproduced by our GCMC simulations,[86] and simulation provides the three tensor components and their directions at near-zero loading in silicalite.

Some internal spaces are highly symmetrical, for example, the large cavities called supercages in faujasite silicates (synthetic 13Y, for example) are each connected to 4 others and the Linde Type A zeolites with cavities each connected to 6 others, forming 3-dimensional networks. Xe chemical shifts in these crystals would have little anisotropy except for the symmetry breaking effects of different degrees of Al/Si substitution requiring the presence of counterions. In these structures, the Xe line shape therefore exhibits no clear singularities, rather some broadening is sometimes observed due to the minor asymmetry caused by the Al/Si substitution. The observed temperature dependence of the Xe chemical shift in 13Y[118] has been reproduced by GCMC simulations.[119]

2.4 The Chemical Shifts of Xe_n in a Cage Reveal Distributions in Porous Materials

The Xe chemical shift that is observed is an average over all the regions explored by the Xe atoms. The greater the extent of averaging the more limited the accuracy of the interpretation of what is observed. For example, under fast exchange between Xe in the gas phase and the adsorbed Xe, we may not be able to directly determine the Xe chemical shift ''inside''. When the Xe is in symmetrical cages, there are no observed tensor components that could be used as a check on the interpretation, and one can associate only an isotropic shift with an overall Xe loading. At any given loading, there are actually fluctuations in the distribution of Xe among the pores or cavities, that is, an overall loading of 5 Xe per cage does not mean that every cage has 5 Xe atoms. In order to find out what fraction of cages have 5, what fraction has 4 or 6 or 1 Xe, it would help to be able to see separately the signal from only those Xe atoms in cages containing 4 (or 6 or 1) xenon. For a given overall loading, how does the distribution of occupancies change with temperature? How are those 4 Xe atoms distributed within a cage and how does that distribution change with increasing temperature? When another gas competes with Xe for adsorption, what is the distribution of the two types of molecules among the cages for a given overall mole fraction? The chemical shift of Xe inside the pores of zeolite 5*A*, say, at a given overhead pressure of Xe at room temperature is a result of the answers to the above fundamental questions in adsorption into porous materials, but any interpretations we make from this one measurement are untestable. Fortunately we have model systems in which such details can be observed directly. In *A* zeolites Na*A*, K*A*, and Ag*A*, the framework atoms Al/Si = 1 and the cations required for charge balance are respectively Na^+, K^+, and Ag^+. Six of the cations sit in the windows that are shared by adjacent cages, at positions such as to keep the Xe from freely exchanging between cages. The long residence times permit each Xe_n to be separately observed quantitatively in terms of intensity and chemical shift at various temperatures and overhead Xe pressures, thus providing an incredible amount of detailed information which can be used to test any interpretations. Furthermore, fundamental ideas that are revealed for Xe can be generalized to other adsorbed molecules; only the fine details will differ. This fundamental investigation of distributions in adsorption is made possible by the very large chemical shift range of Xe atom itself in a range of environments, spread out over several hundred ppm. Other molecules, *e.g.*, CH_4, can enter the same size pores as Xe but neither ^{13}C nor ^{1}H intermolecular shifts can fan out the separate signals like Xe can.

2.4.1 Xe_n in Zeolite Na*A*, K*A* and Ag*A*

Upon observation of 5 well-resolved Xe peaks in the spectrum of xenon in zeolite Na*A*, Samant *et al.* assigned the lowest chemical shift to one Xe in an alpha cage, and so on to 5 Xe in a cage.[120] Later observations by Chmelka *et al.* revealed as many as 7 Xe in a cage.[121] We reported the first observation of 8 Xe per cage, and the equilibrium distribution of occupancies of Xatoms in the cages at 300 and at 360 K for low, medium, and high xenon loading. It was found that the experimental distributions differ from the strictly statistical distributions of hard sphere atoms in mutually exclusive specific lattice sites (hypergeometric distribution), or the statistical distribution of freely moving hard spheres in alpha cages with no specific sites. We also reported the temperature dependence of the chemical shift for each of the Xe_n 'clusters'.[122] The wealth of detailed experimental information in addition to the adsorption isotherm for Xe in Na*A* permitted the testing of GCMC simulations for reproducing the experimental distributions as a function of temperature, as well as the temperature dependence of the individual Xe_n chemical shifts. In turn, the ability to reproduce all the details lent confidence to the information available from the simulations, such as one-body distributions of Xe in the cages (how is the Xe distributed within the cage?). Without altering the set of parameters describing the *ab initio*-based shielding functions for Xe and the framework atoms[31] and the set describing the adsorption-isotherm-based potential functions, all data at various overhead gas densities and sample temperatures could be reproduced, without making assumptions of a distribution model.[123] The same experimental and simulation methods were applied to zeolite K*A*.[124] Observations of similar distributions and Xe_n chemical shifts in zeolite Ag*A*[125] could also be reproduced by using the same simulation methods.[126] The Xe–Na^+, K^+, and Ag^+ shielding functions were taken from *ab initio* calculations. When Na*A* zeolite has been altered by ion-exchange, *i.e.*, Na^+ ions were replaced successively by Ca^{2+} ions, Xe_n chemical shifts discriminate between those cages which have no Ca^{2+} ion *versus* those that have one Ca^{2+} ion and those that have two Ca^{2+} ions, as revealed when magic angle spinning narrowed the lines so as to completely resolve these fine differences for each of the Xe_n.[127] Further Ca^{2+} substitution of course leads to all-Ca^{2+} zeolite *A* (so-called Ca*A* or Linde 5*A*), where Xe can move freely from cage to cage because the Na^+ ions guarding the windows of the cage have been completely removed and replaced by Ca^{2+} sitting within the cage walls. The single Xe peak that results from the extensive averaging in 5*A* is typically what one could observe in larger pore zeolites at various overhead Xe densities and temperatures.[128] The distributions of Xe among the cages of 5*A* will be very similar to those found experimentally in Na*A*; the only difference is that they are experimentally observable in Na*A*, but are hidden in the average shift in 5*A*.

2.4.2 Xe in Competitive Physical Adsorption in Zeolite Na*A*

Nearly all applications of porous solids in separations and catalysis involve competitive adsorption and diffusion. Since gases are not ideal, mixture adsorption isotherms are difficult to understand and predict. A fundamental view of competitive adsorption should be able to answer the question: for a given mole fraction of A and B in the overhead gas, what is the probability of having m molecules of type B also present in the same pore where there are n molecules of type A, for any m, n combination? The Xe chemical shifts permit us to answer these types of fundamental questions about competitive adsorption. In an unusually fortunate case, it was indeed possible to see the separate peaks for Xe_nKr_m in zeolite Na*A*.[129] The relative intensities provide the distributions of occupancies, and the Xe chemical shifts from individual Xe_nKr_m signals permit detailed tests of the GCMC simulations that reproduce these distributions and chemical shifts.[130] Here, the Kr atoms are large enough to have long residence times within a cage. However, even when the co-adsorbate (Ar, CH_4, CO_2, N_2 or CO) can freely move from cage to cage while the Xe_n stay put, it is still possible to find the same type of distribution information as could be obtained in the case of Xe–Kr adsorption. The chemical shift increment between the Xe_n observed in pure Xe adsorption and the $Xe_nAr_{\langle m\rangle}$ peak observed in the Xe–Ar adsorption provides the value of $\langle m\rangle$ for every Xe_n, where $\langle m\rangle$ is the average instantaneous number of Ar atoms visiting a cage containing n Xe atoms.[131] This can be obtained by a combination of the same type of Xe experiments as in pure Xe adsorption and GCMC simulations to verify the interpretations. Added in are the *ab initio* shielding functions and potential functions for Xe–Ar (or Xe–CH_4, Xe–CO_2, Xe–N_2, or Xe–CO) which are used and verified *via* comparison with Xe chemical shift data in these gas phase mixtures.[23,132] Thus, the Xe chemical shifts provide as detailed a picture of competitive adsorption as has ever been obtained. Comparison of GCMC results against a highly used model, such as Ideal Adsorption Theory, permits quantitative exploration of the limitations of this model for competitive adsorption, and the conditions under which it works well enough. A binary mixture version of the hypergeometric distribution has been proposed which provides useful insight into cases where the co-adsorbed species are quite similar in size, and the conditions under which its limitations become evident have been explored by comparison with GCMC simulation results.[131]

Again, the fundamental molecular level observations about distributions of co-adsorbed molecules among the pores of a solid material made possible by Xe chemical shift measurements can be generally applied to competitive adsorption of other binary mixtures. The relative sizes and shapes of the co-adsorbed species must play a part, but some generally applicable conclusions about the detailed nature of competitive adsorption have been found that could be applied to other systems.[133]

2.4.3 Xe in Exchange among Multiple Environments

Nearly all applications of Xe in porous solids involve two or more environments for the Xe atom, even when the solid sample is chemically uniform and crystalline. In general, there are at least the following: reservoir I: Xe in the overhead gas, reservoir II: Xe between the crystallites (some Xe may be adsorbed on the outside surface of the zeolite), reservoir III: Xe inside the crystallites that are within an exchangeable layer near the outside, and reservoir IV: Xe deep inside the crystallites (incapable of exchanging with the Xe outside, within the NMR time scale). The relative volumes of these reservoirs depend on morphology and size of crystallites, crystallite packing, overhead Xe gas pressure. In addition to exchanges within each reservoir, mass transport in zeolites include the following exchanges: I ↔ II ↔ III ↔ IV. *Only the Xe chemical shift and line shape in reservoir IV is characteristic of the pore or channel*. Therefore, it is best to work with large crystals. How fast the exchange is between Xe atoms inside the crystallite and Xe atoms outside the crystallite depends on the size of the crystallites, the crystallite packing, the overhead Xe pressure, and the temperature. When there are intercrystalline regions with pores or channels of size comparable to the inside channels or pores, then there are several consequences: The intercrystallite pore-like regions can compete with the channels for Xe population. The Xe chemical shift gives the wrong occupancy number (Xe atoms per cavity); apparent Xe occupancy is greater than that actually present inside because significant numbers of Xe are in reservoir II (between the crystallites). A significant number of Xe in reservoir II means that the exchange I ↔ II gives a I/II weighted ‘‘gas peak’’ chemical shift. The ratio of populations III/IV is not negligibly small; the weighting factor for Xe in reservoir IV do not dominate, so the ‘‘adsorbed peak’’ is not characteristic of the pores or channels. In this case, the peaks observed in the Xe spectrum are due to exchange averaging and do not provide true chemical shifts; the weighting factors are the numbers of Xe atoms in those reservoirs which are exchanging. At extremely low Xe density, there will still be exchange with the gas, but the number of Xe atoms in the gas is nil; the weighting factor for the gas is nearly zero so the observed Xe chemical shift is that of Xe atom in those pores where it has the lowest potential energy. Lowering the temperature slows down all exchanges, but also leads to greater adsorption which can correspond to multiple Xe occupied pores.

In a mixture of porous materials where each constituent consists of cystals large enough that there are only reservoirs I (outside) and reservoirs IVa, IVb, IVc, ... (inside) the Xe chemical shift will report on each constituent independently, as if the other constituents were not present; that is, the chemical potential of the Xe in I will be equal to the chemical potential of Xe in IVa, and also the Xe in IVb, the Xe in IVc, *etc*. In other words, the Xe chemical shift tensor in IVa will reflect only the $\langle N_{\mathrm{Xe}} \rangle_{\mathrm{a}}$ in the channels in that constituent, for example, and the relative overall area under the peak will reflect the total numbers of Xe in that constituent. GCMC simulations of Xe in each constituent at the same chemical potential as for the gas can be carried out independently to obtain $\langle N_{\mathrm{Xe}} \rangle_{\mathrm{a}}$, $\langle N_{\mathrm{Xe}} \rangle_{\mathrm{b}}$, *etc*. The relative areas depend on the relative amounts of constitutents multiplied by these occupancies. Note that the relative areas are not direct measures of the composition of the mixture since the chemical potential of Xe within each type of crystalline pore or channel depends on the atomic structure of the latter. The reaction progress from an amorphous phase to $AlPO_4$-5 and its subsequent conversion to $AlPO_4$-18 was quantitatively monitored by Xe spectroscopy and GCMC calculations of both Xe chemical shift tensors in just this way.[98]

2.5 Conclusions

The Xe chemical shift and its chemical shift anisotropy have been found to be exquisitely sensitive to the environment in which the Xe atom finds itself. We have seen that encoded in the intrinsic shielding response surface is the electronic structure of the system (a supermolecule or a crystal fragment) as a function of nuclear configuration in the immediate vicinity of the Xe. The dynamic averaging encodes further information about the Xe nuclear environment into the observed chemical shift, such as the architecture of the channel, the diameter of the channel, the aspect ratio of the cross section of the channel, the average size of the cage, the average symmetry of the cage, the number of Xe and other molecules in the cage, the electronic structure of the atoms constituting the cavity walls, the Xe coverage on a single crystal surface, the heterogeneity of the sample, and much more. In the solid, the point group symmetry at the center of the cage in which a single Xe atom is trapped determines the number of non-vanishing tensor components and the number of distinct components of the shielding tensor observed.

The dimensions of the cage determine the magnitudes of these non-vanishing components, their relative magnitudes depending on whether the cage is elongated or squat. Dynamic averaging of the Xe inside a semi-rigid cage does not change the relative order of the components. Similarly, Xe line shape signatures in diamagnetic nanochannels reveal many attributes of the channels. The number of unique components at near-zero loading and at high Xe loading provide information about the aspect ratio of the channel cross section (2 nearly circular, 3 if elliptical). One constant tensor component with changing loading means that the channel diameter does not permit two Xe to pass each other. A linear behavior of each component with Xe loading suggests that an orderly arrangement of Xe atoms in the channel is possible, *i.e.*, Xe can sit in register with low potential energy sites along the walls; Xe is unable to do this when the low energy sites are too close together. A non-linear behavior of tensor components with Xe loading suggests a non-uniform channel cross section. The component parallel to the channel axis does not change with Xe loading or with temperature, if the cross section is of uniform small diameter throughout. On the other hand, some constrictions in the channel can cause a strong temperature dependence of this component. In solid porous materials, the Xe chemical shift can provide information about the distribution of Xe atoms among the pores and also the distribution of other molecules sharing the same pores. As we have seen, there is much that Xe intermolecular chemical shift and shift anisotropy can tell us about materials. This sensitivity of Xe intermolecular shifts to the structure and dynamics of its environment is based on the intrinsic sensitivity of Xe shielding arising from the large $\langle a_0{}^3/r^3\rangle$ for Xe atoms in the first place, and secondly, to the very steep deshielding behavior with close approach of another atom. Although the CH_4 molecule has roughly the same size as Xe atom and can explore the same cavities, neither ^{13}C nor ^{1}H possesses these two advantages of Xe atom. Hydrogen can get closer to neighbor atoms, but does not have the large number of electrons in p and d orbitals that can provide a strong intermolecular shielding response at the nucleus.

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