Quadrupolar Relaxation of ^{21}Ne, ^{83}Kr, and ^{131}Xe Dissolved in Acetonitrile. A Molecular Dynamics Study

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To increase the understanding of quadrupolar relaxation of noble gases in solution, molecular dynamics simulations are carried out for a series of noble gas atoms dissolved in acetonitrile. The quadrupolar relaxation of ^{21}Ne, ^{83}Kr, and ^{131}Xe in a highly polar solvent is studied for the effects of the solute size. Temperature effects are investigated and the activation energies are calculated for the key motions in the relaxation. Structure and dynamics of the solvation shell around the three noble gas atoms are studied, and their role in intermolecular quadrupolar relaxation is examined. The simulation results are discussed in relation to various theoretical models, frequently used by the experimentalists. An electrostatic treatment is found to be applicable, given that the size dependence is correctly taken into account. The overall agreement of the simulation results with experimental data is good.

I. Introduction

For nuclei with the nuclear spin quantum number $I \geq 1$, the coupling between the nuclear electric quadrupole moment and the fluctuating electric field gradient, originating from the neighboring molecular environment, is the most effective mechanism contributing to NMR relaxation.[1,2] In the extreme narrowing limit,[1] the longitudinal relaxation time T_1, can be written in terms of a time correlation function (TCF) for the electric field gradient (EFG) at the site of the studied quadrupolar nucleus:

$$1/T_1 = {}^3/_8 \frac{(2I+3)}{I^2(2I-1)}[eQ/\hbar]^2 \int_0^\infty \langle V_{ZZ,\mathrm{nuc}}(t) V_{ZZ,\mathrm{nuc}}(0)\rangle \, \mathrm{d}t \qquad (1)$$

The nuclear spin relaxation of monatomic ions or noble gas atoms depends on the structure and on the dynamic fluctuations of the surrounding solvent molecules.[3] This is particularly true for quadrupolar relaxation, which is highly sensitive to changes in solvation shell due to partially canceling molecular contributions to the EFG. Consequently, the relaxation measurements are rich sources of detailed information of solvation processes, provided that they can be properly interpreted from the spectral data.

The intermolecular relaxation of monatomic ions in solution has traditionally been a vital area of NMR investigations.[3] During the last decade, however, there has been an increasing interest also in NMR relaxation of noble gases in solution.[4] Experimental studies on xenon,[5,6] krypton,[5,7] and, to some extent, on neon[5,8] have been reported.[9] The objectives behind these studies have been to determine the relaxation mechanisms and, by using theoretical models, to gain information about the solution around the magnetic isotopes.

Monatomic ions, in contrast to noble gas atoms, interact strongly with the solvent molecules, creating well-structured solvation shells. This is particularly true for aqueous solutions, which have been studied extensively.[10] Solvation models, based on well-defined solvation structures, can be constructed and used to interpret the experimental data. For example, the so called "fully oriented solvent" (FOS) model has been used frequently[11] to rationalize the NMR results obtained in aqueous ionic solutions.

For the description of system with weak solvation other models are required. In the "nonoriented solvent" (NOS) model,[11] the solvent molecules around the solute is randomly oriented. In many experimental works on dissolved noble gases, the analysis is based on the "fully random distribution" (FRD) model,[12] in which uniform distributions of both the solvent molecules and their orientations around the solute are assumed. The FRD model has been fairly successful in reproducing the relaxation data for weakly interacting solutes, such as noble gases. Various solvation models have been compared by Versmold[13] in an analysis of the corresponding TCFs. Our own analysis of the simulated EFG-TCF results will in large follow the analytic treatment of Versmold, and we will examine his analogues of the FOS and NOS models, the "radially oriented solvent" model and the "randomly oriented solvent" model, respectively, in the following simply referred to as the FOS and NOS models.

For noble gases, although weakly interacting, the solvent may still become structured around the solute. This is typically the case in water solution, where the solvent is forced to create a clathrate-like structure due to hydrophobic hydration.[14] In nonaqueous solutions, the structure can critically depend on the balance between solute−solvent and solvent−solvent interactions. The present work introduces a particularly interesting case from the interaction point of view. The methyl groups in acetonitrile can be expected to readily solvate the nonpolar noble gas atoms in competition with solvent−solvent (dipole−dipole)

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interactions, strongly driving the acetonitrile molecules to mutually antiparallel orientations.

The EFG at the nucleus is caused by distortions from the spherical symmetry of the electron cloud due interactions with the solvent molecules. If the distortion is simply a polarization of the electron cloud by the electrostatic field of the solvent molecules, it is usually said to be of electrostatic origin. If on the other hand, the EFG is of other origin, *e.g.*, controlled by covalent interactions, it is ascribed to electronic interactions.

The electronic theory of Deverell[15] has met some serious criticism for not showing any correlation between the relaxation rate and the chemical shift of xenon.[6] Several electrostatic theories have been suggested in literature[11−13,16−18] and used with varying success. The theories proposed by Hertz and Valiev[11,12,16,17] agree better with experiments than other theories, based on either electronic[15,19] or electrostatic models.[6,7] Hertz theory was originally developed for ions in aqueous solution, thus making use of the well-structured hydration shells. It uses dipoles to represent the solvent molecules. The success of Hertz theory, however, is diminished by difficulties in determining the numerous parameters prior to applying the theory. Some authors have suggested that the electric dipole approximation would be valid even for nonpolar (or slightly polar) solvents, such as CCl_4 or $CHCl_3$. This is based on the property of multipole expansions of the molecular charge distribution to break down at close distances, so that the solute at close distances experiences only the local dipoles of the closest solvent molecules. In fact, a similar behavior has been observed previously in molecular dynamics (MD) simulations, where the electric multipoles have been shown to break down into individual charges at short distances in benzene solutions[20] and methanol solution.[21] There has also been experimental indications of limitations to the multipole description.[22−24]

MD simulations have shown that the quadrupolar relaxation of xenon can be accounted for in an electrostatic description,[20,21,25] whereas for the relaxation of certain ions also electronic contributions come into play.[26−28] In the present work, we limit the treatment of EFG mechanisms to electrostatic terms,[29] as has been done earlier to study xenon in different solutions.[20,21,25,30,31] The Sternheimer approximation is employed, in which the EFG at the nucleus is related to the field external to the atom via the Sternheimer factor $(1 - \gamma_\infty)$,[29] which accounts for the amplifying effect of the polarizability.

Numerically, the "external field" has been written simply as a sum of molecular contributions. These can be derived from a special EFG property surface[26−28] or simpler from the partial charges of the solvent potential model. Either way it is possible to decompose the EFG-TCF into molecular self correlation terms and cross correlation terms which can be analyzed separately to gain physical insights on the significance of cross correlations in the EFG-TCF.

$$\langle V_{ZZ}(t)V_{ZZ}(0)\rangle = \sum_m (\langle V_{ZZ,m}(t)V_{ZZ,m}(0)\rangle + \sum_n \langle V_{ZZ,m}(t)V_{ZZ,n}(0)\rangle) \quad (2)$$

Quite recently, Jokisaari and co-workers[5] have questioned the applicability of the purely electrostatic description of the EFG tensor by investigating possible electronic contributions for quadrupolar relaxation of noble gases in solution. They have compared their relaxation data to *ab initio* results by calculating the EFG at the noble gas in an energy optimized configuration of an isolated noble gas−solvent molecule pair. After deriving the amplitude of the EFG-TCF from the "one-molecule" EFG, they are able to calculate the corresponding correlation times from the measured relaxation times. Vaara *et al.*[5] find the correlation times unreasonably short, and they draw the conclusion that the electrostatic description is insufficient for explaining the quadrupolar relaxation of noble gases in solution. They also compare the binding energy, obtained in the *ab initio* calculations, with the corresponding activation energy for the relaxation rate and find support for the theory of a collision induced EFG.[15]

In this paper we limit our comparison between the EFG-TCF and molecular processes to the self correlation term. The reason for this choice is to perform the comparison on properties with very good statistics. For a model to be physically relevant, it at least has to describe the self-EFG-TCF correctly. Only when these criteria are fulfilled, the modeling of more cumbersome cross terms must be considered. (Note that this reasoning only applies to models which are naturally analyzed in terms of self and cross correlations!)

Since the fluctuation in the EFG is caused by the relative motions of the noble gas and the closest solvent molecules, the EFG is complicated to describe. There are several different processes that may affect the dynamical behavior of the EFG. For example, it has been shown that both reorientation and translation contributes to the relaxation.[21,25] By choosing a single relaxation process, for example, the reorientation of the solvent molecule, the quadrupolar relaxation can be used to give "indirect" information about the behavior of the solvent in the close neighborhood of the quadrupolar nucleus. In aqueous solution, there is a retardation of the water molecules observed near the noble gas atoms.[8] It should be borne in mind, however, that the results from these studies rely on assumptions about the relaxation processes. Because of the correlation between the solvent molecules themselves,[12,21,25,26] it is not even likely that the quadrupolar relaxation would be possible to describe in terms of single solvent molecule properties. It has been experimentally shown that the relaxation of ^{131}Xe in acetonitrile cannot be entirely due to solvent reorientation, since the corresponding activation energy of the relaxation rate (2.9 kJ mol^{-1}) is much smaller than that for the rotation (8.4 kJ mol^{-1}).[6] Other experiments on ^{21}Ne, ^{87}Kr, and ^{131}Xe give activation energies between 3.5 and 5.5 kJ mol^{-1}.[32]

The temperature dependence of the relaxation rate, which can be assumed to be exponential in small intervals, can be used to calculate the activation energy for the processes behind the relaxation. One should be cautious, however, when comparing the obtained activation energy to those obtained for simple molecular processes in solution. Nevertheless, it is interesting to observe that the relaxation is connected to an activation energy which is remarkably low and rather different from that of the solvent reorientation.[6,32]

Xenon has been a popular target in several quadrupolar relaxation studies in the past,[5,6] whereas both krypton and neon have received attention only quite recently.[5,8] A general picture has been suggested, in which the activation energies, $E_a(1/T_1)$ would increase with the size of the solute.[32] The E_a has also been analyzed in terms of some macroscopic properties, such as viscosity.[5,32] However, it has been difficult to translate this information to a molecular level. Also, a connection to the self diffusion of the molecules has been proposed,[32] although it has not been pointed out as the only source of relaxation. Relaxation measurements, made on the solvent nuclei, have been used as a probe to determine whether the solvent reorientation is significantly affected by the presence of the solute or not. These studies have, however, a limited value due to the low solubility of noble gases in polar solvents and the conclusions mainly vary with the solvent in question. Measurements of ^{2}H relaxation in a $C_6H_6-C_6D_6$ mixture as a solvent show that benzene

TABLE 1: Some Selected Data from the Simulated Electric Field Gradient Time Correlation Functions[a]

system	Ne (298 K)	Kr (283 K)	Kr (298 K)	Xe (283 K)	Xe (298 K)	Xe (313 K)
$\langle V_{ZZ}^2\rangle_{\mathrm{self}}$ (10^{38} V^2 m^{-4})	6.40	3.25	3.30	2.51	2.57	2.63
$\tau_{\mathrm{EFG,self}}$ (ps)	0.53	0.95	0.90	1.08	1.09	1.04
$\langle V_{ZZ}^2\rangle$ (10^{38} V^2 m^{-4})	4.04 ± 0.19	1.48 ± 0.04	1.59 ± 0.03	1.06 ± 0.05	1.09 ± 0.05	1.06 ± 0.05
τ_{EFG} (ps)	0.23 ± 0.03	0.37 ± 0.04	0.30 ± 0.04	0.32 ± 0.06	0.33 ± 0.08	0.37 ± 0.07
p^2	0.63	0.46	0.48	0.42	0.42	0.40
$\tau_{\mathrm{EFG}}/\tau_{\mathrm{EFG,self}}$	0.43	0.39	0.33	0.30	0.30	0.36
$1/T_1^{\mathrm{MD}}$ (s^{-1})	1.14	10.7	9.32	109	115	126
$1/T_1^{\mathrm{exp}}$ (s^{-1})	1.2[b]		13.7[c]		149[d]	

[a] For more details, see the text. [b] Reference 9. [c] Reference 11. [d] Reference 28.

molecules reorient only slightly faster upon the increasing concentration of xenon and krypton.[8,32] No difference, however, could be found between the bulk benzene and the benzene molecules in the solvation sphere around xenon in the MD simulations.[20] Furthermore, Stengle *et al.*[6] performed relaxation measurements on ^{17}O and ^{14}N in xenon solutions of acetone and acetonitrile, respectively. They concluded that the influence of xenon on the reorientation of the solvent molecules was smaller than the experimental error. In other relaxation measurements, made on the solvent molecules in the presence of ^{83}Kr,[7] an increased mobility of the solvent molecules around the solute was observed.

In aqueous solution of xenon, the reorientation of the water molecules is experimentally determined to be slower in the solvation shell than in the bulk.[33,34] Furthermore, there exists a weak experimental indication that the reorientation of the water molecules around xenon is slightly faster than around the neon atoms.[8]

It has been observed in previous MD simulations that in *polar* solvents the EFG fluctuations are mainly caused by collective motions of the solvent molecules, whereas for example for xenon in an *apolar* solvent the fluctuations can be directly related to the motions of individual solvent molecules, relative to the quadrupolar nucleus.

In this work, we have applied the electrostatic model, which has been shown to be successful in the past and able to reproduce the experimental results.[20,21,25] The electronic description, suggested to be more adequate for the treatment of quadrupolar relaxation in the noble gas solutions,[5] should be put to a thorough investigation.

II. Computational Details

MD simulations are carried out for “infinitely”diluted solutions of quadrupolar isotopes: ^{21}Ne, ^{83}Kr and ^{131}Xe, respectively, by placing one single noble gas and 255 acetonitrile molecules in a cubic box. The concentration of all the simulated solutions is 0.07 mol L^{-1}, slightly lower than used in a recent experiment by Holz et al.[32] A series of simulations (three for xenon, two for krypton, and one for neon) was carried out at temperatures close to room temperature. The density was kept the same as for the pure solvent at the actual temperatures.[35] A six-site (all-atom) model by Böhm *et al.*[36,37] was used for acetonitrile, while the noble gas atoms are described using Lennard-Jones type of potentials by Clifford *et al.*[38] All nondiagonal atom−atom interactions were constructed using the standard Lorentz−Berthelot combination rules.

The calculations were carried out using a modified version of the *McMoldyn* simulation package[39] on an IBM RISC 6000/590 workstation. The Ewald summation was used to treat the long-range coulomb interactions[40] and the Nosé−Hoover NVT algorithm was applied to maintain the temperature.[41,42] Time step was 1.0 s, and the length of all the six simulations was 250 ps each, of which an initial period of 50 ps was considered as an equilibration phase and was not included in the sampling. All the three noble gas systems were started from an equilibrated pure solvent by replacing one solvent molecule with a noble gas. All the simulations of the same noble gas followed each other. The trajectories were saved at each 10 fs for a later structural and dynamical analysis. The EFGs from the solvent molecules was derived from the partial charges of the solvent potential model.

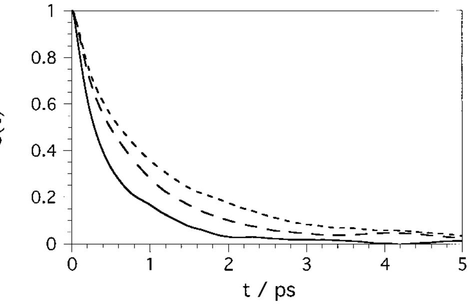

Figure 1. The TCFs of the molecular (self) auto-correlation terms of the EFG. Neon (solid), krypton (dashed), and xenon (dotted).

In addition to the fluctuations of the EFG tensors, we also studied the dynamics of the solvent molecules in the first solvation shell around the noble gases. This was done in order to allow us to analyze the various assumptions made in the theoretical models.[13] In order to limit the analysis to the first shell, switching functions were used. These functions were assigned a value 1 for molecules inside the solvation shell, otherwise 0. The switching was made at the first minimum of the solute-solvent RDF, and thus it differs with the solute. We calculated TCFs for solvent molecules in the solvation shell in two different ways. 1. A solvent molecule was included in the average for $\langle A(t)A(t+\tau)\rangle$, if it was within the solvation shell at time t. 2. A solvent molecule was only included in the average, if it was within the solvation shell both at time t and time $t+\tau$, and each point of the resulting TCF had to be normalized with the TCF constructed from the corresponding switching functions in order to obtain the wanted TCF.

Both ways of calculating the TCFs gave the same results. Thus there is no cross correlation between the switching and the properties studies.

III. Results

A. Nuclear Relaxation. The most essential information from the EFG-TCF results is gathered in Table 1, containing amplitudes and correlation times for both self and total correlation terms.[21,25] In Figure 1 the molecular self EFG-TCFs are shown for the three noble gases at 298 K. All these curves decay roughly exponentially after an initial gaussian decay. Only the *zz*-component of the EFG tensor is needed to give the isotropic value for the field gradients.[3] The statistical accuracy can be improved, however, by treating the whole tensor. The time correlation functions are therefore calculated as tensor

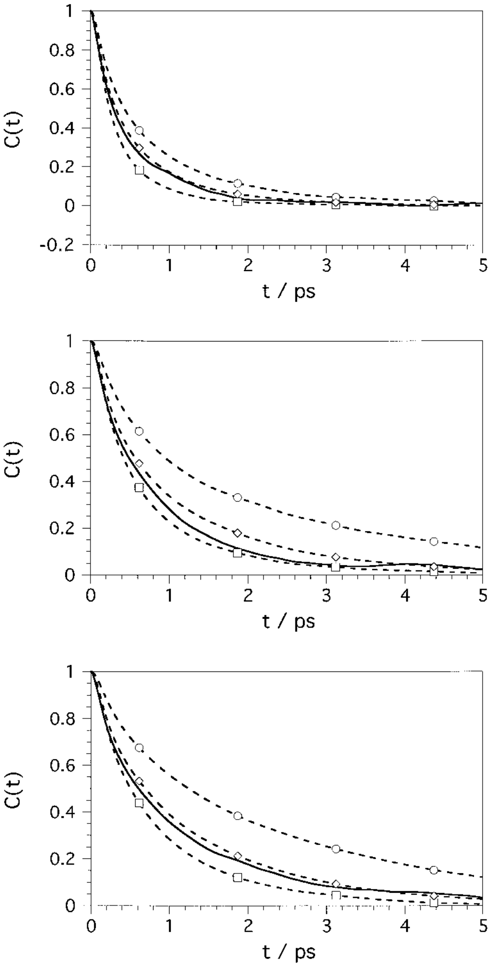

Figure 2. Comparison between the simulated molecular self EFG-TCF and some different theoretical models: MD (solid), models (dashed), NOS (square), FOS (ring) and our *ad hoc* model (diamond). (a) neon, (b) krypton and (c) xenon.

scalar products. Since the various tonsorial components of the corresponding spherical tensor are equal in an isotropic system, the amplitude of the whole tensor is

$$\langle V^2(0)\rangle = {}^{15}/_{2}\langle V_{ZZ}^2(0)\rangle \qquad (3)$$

The correlation times of the TCFs are calculated by integration. In the case of the self TCFs, the long-time tail is calculated from a single-exponential fit.

The size of the solute has an impact on the electrostatic interactions at the site of the noble gas atoms in the series from neon to xenon. The electrostatic interaction is found to be largest for the smallest atom in the series, neon, for which also the amplitude of the self-EFG-TCF is largest. Because of the strong influence of the molecular cross-interactions in polar fluids,[21,25] it is difficult to reliably predict the corresponding amplitude for the total EFG-TCF from the strength of the electrostatic interactions.

The cross correlation in the different molecular contributions to the EFG affects the relation between the total EFG-TCF and the molecular self-EFG-TCF in two ways. Firstly, there is an instantaneous canceling of the individual molecular contributions to the amplitude of the EFG, resulting in a static quenching in the EFG. Secondly, there is a dynamic quenching of the correlation time due the correlation in motions of the solvent molecules in the solvation shell.

In analytic treatments, the difficulties with the cross correlations are avoided by assuming they are proportional to the self-correlations with a factor, $(1 - P^2)$. The so-called polarization factor[16] P^2 can be used as a measure of the degree of cross correlations. In many experimental works this quantity is assumed to be the same for all the noble gas atoms in order to make comparisons possible between different noble gases. By comparing the amplitudes of the total and the self EFG-TCFs, we can derive the static quenching contribution to the polarization factor. (The polarization factor can be considered to account also for differences in correlation time.) It decreases with the size of the noble gas (see Table 1). This could be expected since the solvent molecules naturally become less correlated, while spread out to form a larger solvation sphere. Also the correlation time for the molecular cross EFG-TCF increases upon increasing the size of the atom while going from neon to xenon, which can be deduced from the values in Table 1.

The EFG at the solute nucleus arises almost entirely from the electric field of the closest solvent molecules. This makes it possible to develop models for the relaxation based on the solvation shell only. In order to analyze the origin of the fluctuations in the EFG, we may compare our self-EFG-TCF results with those of the expressions by Versmold,[13] based on the interaction induced quadrupolar relaxation model. The different TCFs of the models are computed from the simulation, which gives the comparison an internal consistency. In Figure 2a−c, the simulated results at 298 K are displayed together with the “fully oriented” and “nonoriented” solvent models, in which the solvent molecules are represented as idealized electric dipoles. (The models are based on three geometrical properties. The distance between the quadrupolar nucleus and the solvent dipole $r_{is'}$, the intermolecular angle describing reorientation of the nucleus−solvent vector ($\theta_{sis'}$, and the angle describing reorientation of the solvent dipole, $\phi_{ss'}$. The (′) is signifying the time dependence.) The TCF based on the FOS model consists of two parts:

$$\langle r_{is}^{-4}(0) r_{is}^{-4}(t) P_2[\theta_{sis'}(t)]\rangle$$

one with a radial dependence and the other which depends on the reorientation of the vector between solute and solvent molecule. The corresponding TCF, based on the NOS model, has an additional dependence on the solvent−dipole reorientation:

$$\langle r_{is}^{-4}(0) r_{is}^{-4}(t) P_3[\theta_{sis'}(t)] P_1[\phi_{ss'}(t)]\rangle$$

In Figures 2, we also included an *ad hoc* model:

$$\langle r_{is}^{-4}(0) r_{is}^{-4}(t) P_2[\theta_{sis'}(t)] P_1[\phi_{ss'}(t)]\rangle$$

which lacks a direct molecular interpretation, but has been shown earlier to agree well with the simulated TCF results.[21,25,43] In fact, we can see that our *ad hoc* model is in best agreement with the simulated TCFs in all cases.

Although the dynamics of the EFG cannot be precisely accurately modeled, it is possible to exclude the FOS model quite definitely. The *ad hoc* model and the NOS model both contain three physically different functions, which all can be studied as separate TCFs. As can be observed, there is no correlation between the different functions and the total TCF of the NOS model is separable into three contributions. Analogously for the *ad hoc* model we obtain

$$\langle r_{is}^{-4}(0) r_{is}^{-4}(t)\rangle\langle P_2[\theta_{sis'}(t)]\rangle\langle P_1[\phi_{ss'}(t)]\rangle$$

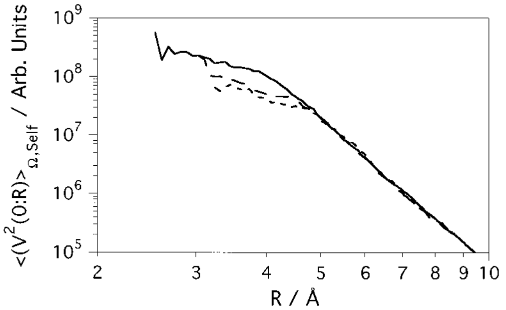

Figure 3. The radial dependence of contributions to the molecular self term of the EFG, $\langle V^2(0{:}R)_{\Omega,\mathrm{self}}\rangle$, at the noble gases. Neon (solid), krypton (dashed), and xenon (dotted).

The first, distance dependent TCF is very slowly decaying, thus the reorientational part will totally control the relaxation. In the NOS model, the third Legendre polynomial is found to be totally dominating, while in the *ad hoc* model the both reorientational terms contribute about equally much.

The corresponding activation energy for the distance dependent

$$\langle r_{\mathrm{is}}^{-4}(0) r_{\mathrm{is}}^{-4}(t)\rangle$$

is much smaller than for the orientational TCFs. This is expected since the interaction energy between the solvent and the noble gas atom is low, and there are no forces creating a stable solvation shell. Again, the solvation sphere of neon shows a very much different behavior compared to the two other noble gases studied in this work. The

$$\langle r_{\mathrm{is}}^{-4}(0) r_{\mathrm{is}}^{-4}(t)\rangle$$

and

$$\langle P_2[\theta_{\mathrm{sis}'}(t)]\rangle$$

TCFs decay substantially faster for neon than for krypton or xenon.

By studying the radial dependence of the various contributions to the EFG, a special function,

$$\langle V^2(0{:}r)\rangle_{\Omega,\mathrm{self}}$$

can be constructed to analyze the solvent.[21,31]

It is implicitly defined by

$$\langle V^2(0{:}R)\rangle_{\mathrm{self}} = 4\pi\rho \int_0^R r^2 g(r) \langle V^2(0{:}r)\rangle_{\Omega,\mathrm{self}}\, \mathrm{d}r \qquad (4)$$

($\langle V^2(0{:}R)\rangle_{\mathrm{self}}$ is the cumulative radial distribution function of the molecular self contributions for the EFG, which at $R = \infty$ equals the amplitude of the self-EFG-TCF.) If the solute experiences the solvent molecules as idealized electric dipoles and the dipoles orient themselves uniformly over all possible angles, this function will decay proportionally to R^{-8}. In Figure 3, we can see that this is true for long distances for which the power can be fitted to give -8.3: ± 0.1. At short distances, corresponding to the radius of the solvation sphere, the power is much smaller: -2.6 (Ne), -4.8 (Kr), and -3.5 (Xe). This would suggest that either the dipole approximation or the approximation of a uniform distribution of molecular orientations breaks down—or a combination of both. It appears that the acetonitrile solutions, studied in the present work, do not behave in a simple way, as was found previously for some other systems, when studied using the same method.[21,31] Since the dipoles of the solvent molecules are able to come closer to the noble gas when they are oriented perpendicular to the dipole–solute vector, than when they are parallel to it, the distribution of angles is not uniform at short separations.

Of course, it should be kept in mind that this analysis concerns only the molecular self-EFG-TCF results, rather than the total EFG-TCFs, to which measured activation energies should be compared.

From the results in Table 1, the relaxation times for the quadrupolar noble gas nuclei can be calculated. The isotopes ^{21}Ne, ^{83}Kr, and ^{133}Xe have nuclear spin quantum numbers $I = {}^3/_2$, $^9/_2$, and $^3/_2$, respectively. We have used the Sternheimer anti-shielding factors: $(\gamma_\infty)_{\mathrm{Ne}} = -9.145$,[44] $(\gamma_\infty)_{\mathrm{Kr}} = -68$,[44] and $(\gamma_\infty)_{\mathrm{Xe}} = -138$.[45] Some slightly different values for Kr and Xe can be found in literature.[44] The nuclear quadrupole moments can be determined more accurately. We have used $Q_{\mathrm{Ne}} = 0.101\,55 \times 10^{-28}\ m^2$, $Q_{\mathrm{Kr}} = 0.253 \times 10^{-28}\ m^2$ and $Q_{\mathrm{Xe}} = -0.12 \times 10^{-28}\ m^2$. These values are taken from the recent compilation by Pyykkö.[46] The relaxation rates, calculated from the MD simulation data, are in good agreement with the experimental values, being somewhat lower than the experimental ones for krypton and xenon.

B. Relaxation in Relation to Solvation Structure and Dynamics. By comparing the reorientation of the solvent molecules in the solvation shell around the noble gas atoms to the reorientation of those solvent molecules found in the bulk, it is possible to study how the presence of inert solutes affects the dynamics of highly polar molecules as acetonitrile. For the sake of convenience, this is done by comparing the reorientational correlation times for the solvent molecules, found in the solvation shell, with the corresponding correlation times averaged over all the solvent molecules. No difference was found between the two sets of correlation times in krypton and xenon solution, both giving $\tau_1 = 2.95 \pm 0.01$ ps and $\tau_2 = 0.98 \pm 0.01$ ps at 298 K. The corresponding activation energies were 6.9 and 6.3 kJ mol^{-1}, respectively. The correlation time τ_2, calculated from experimental relaxation time at 295 K, is reported between 0.9 and 1.3 ps, depending on the choice of liquid state quadrupolar coupling constant[37] and the simulation of pure acetonitrile using the same six-site model gives 0.95 ps (from integral) and 1.15 ps (from slope) at 291 K.[37] Somewhat surprisingly, the reorientation of the solvent is slowed down in the solvation shell around neon: $\tau_1 = 3.60 \pm 0.01$ and $\tau_2 = 1.13 \pm 0.01$ ps, whereas when averaged over all the solvent molecules in neon solution, the same results are obtained as in krypton and xenon solutions.

It is of some interest to study the behavior of the residence (switching) time correlation function for the occupancy of the solvent molecules in the solvation shell. It is found to change a great deal with the noble gas solutes. In krypton and xenon solution, the correlation times at 298 K are $\tau_c = 6.76$ ps for krypton and $\tau_c = 7.16$ ps for xenon, with the corresponding activation energies of 2.8 kJ/mol and 1.9 kJ/mol, respectively. The residence correlation time for solvent in the solvation shell around neon is considerably shorter, $\tau_c = 3.65$ ps. How the short correlation time in neon solution is related to the longer reorientational correlation times in comparison with krypton and xenon solution is not clear.

The static solvation structure can be studied conveniently using radial distribution functions (RDF). (Note: the numbering of the atoms in acetonitrile is N–C2–C1–H$_3$. In our previous paper,[21] the two carbon atoms were accidentally interchanged in the analysis of the RDF results.) The RDFs are calculated between the solute noble gases and the centre-of-mass of the solvent molecules in order to determine the thickness of the spherical solvation shell in each case. All the three curves,

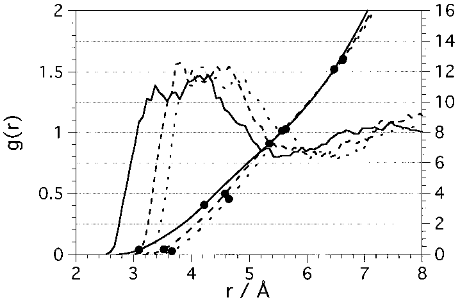

Figure 4. The radial distribution functions $g(r)$ of the noble gases and the solvent centre-of-masses. The right axis refers to the running coordination numbers $n(r)$, for which the curves are displayed with dots. Neon (solid), krypton (dashed), and xenon (dotted).

calculated from 298 K trajectories, are shown in Figure 4. All these RDFs have a same shape but shifted in accordance to the size of the solute atom. From the RDFs, the coordination numbers can be calculated by integrating to the first minima. These are found: 8, 11, and 12 for neon, krypton, and xenon solutions, respectively. These numbers are approximated to the closest integers since the accuracy is poor due to the broad minima.

Also some selected atom−atom RDFs can be calculated in order to study the structure of the solvation shell in some more details. In Figures 5a−d, are the corresponding curves $g(r_{\mathrm{ng-N}})$, $g(r_{\mathrm{ng-C2}})$, $g(r_{\mathrm{ng-C1}})$ and $g(r - \mathrm{ng} - H)$, where *ng* denotes noble gas. In pure liquid acetonitrile, the molecules are assumed to orient themselves mutually in an antiparallel fashion.[36] This is favored due to the strong dipole-dipole interactions between the very dipolar acetonitrile molecules. In fact, the same structure can be seen even in the solvation shell. This can be concluded since both the nitrite nitrogen and the methyl hydrogens come to a close contact with the solute. The both carbons C1 and C2 are found at a only slightly longer distance from the solute than nitrogen or hydrogens. This means that, at short intermolecular distances, the solvent molecules are oriented perpendicular to the solute−solvent vector, *i.e.*, the angular distribution is not uniform in the solvation shell. It is also apparent that the configuration with methyl contacts is more stable than nitrite contacts. This can be seen from the narrower peaks for ng − C1 pairs in comparison with ng − C2 peaks. It is also possible to see that in the methyl contacts, the acetonitrile molecules are not directed straight outward from the solute, because two distinct peaks can be observed for ng − H pairs. The first peak comes apparently from two of the hydrogens and the second peak from the remaining third hydrogen.

Besides the static solvation structure and the rotational motion of the solvent molecules, the linear translational motion is significant for intermolecular relaxation processes. Using simulation data, obtained at different temperatures, we are able to obtain an estimate to the activation energies for krypton, xenon, and the average value for solvent acetonitrile as 9.6, 7.7, and 5.4 kJ mol^{-1}, respectively.

Many models for intermolecular NMR relaxation contain diffusion as a parameter. In Table 2 are the calculated translational diffusion coefficients quoted. These are calculated by integrating the translational velocity autocorrelation functions (VACF). The noble gas atoms are diffusing considerably faster than the solvent molecules. In acetone the diffusion coefficient of noble gases have been experimentally observed to increase with decreasing solute size[47] and in water the diffusion of neon is much faster than for xenon.[48] Diffusion measurements in acetonitrile are lacking in the literature, but our calculated values are in good agreement with the experimental diffusion data for acetone,[8] which is also a polar liquid with nearly the same viscosity. The error in the diffusion coefficients for the noble gases is estimated to 20%.

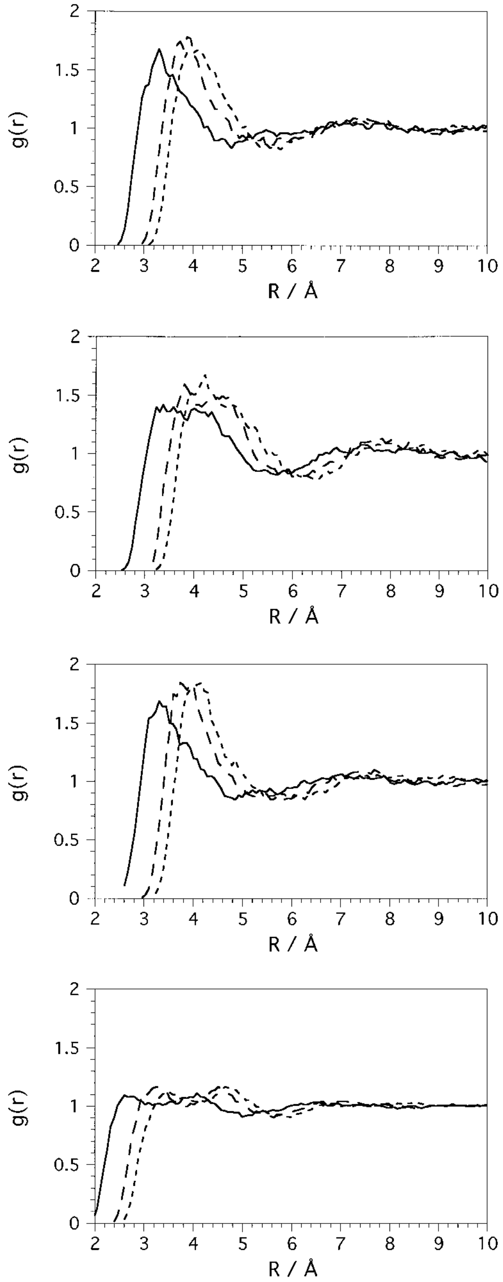

Figure 5. The radial distribution functions $g(r)$, of the noble gases and the various solvent atoms. Neon (solid), krypton (dashed), and xenon (dotted): (a) noble gas−nitrile nitrogen, (b) noble gas−nitrile carbon, (c) noble gas−methyl carbon, (d) noble gas−methyl hydrogen.

IV. Conclusions

The description based on only electrostatic (as opposed to electronic) contributions to the EFG has once more proved to be able to explain the quadrupolar relaxation data obtained for noble gases in solution. These simulations clearly show that the static quenching, *i.e.*, the strength of the molecular cross correlations decreases with the size of the weakly interacting solute. The dynamic quenching, however, appears to vary in a slightly irregular fashion.[21,30] The correlation time of the molecular cross correlation decreases with the increasing size of the solute, whereas the total correlation time increases.

There has been experimental attempts to determine the order of the solvent multipole experienced by the quadrupolar nucleus of noble gases in different solvents.[22,23] These make use of

TABLE 2: Translational Diffusion Coefficients. Calculated from the Integrals over the Velocity Autocorrelation Functions

system	Ne (298 K)	Kr (283 K)	Kr (298 K)	Xe (283 K)	Xe (298 K)	Xe (313 K)
D_V (solute) 10^{-9} m^2 s^{-1}	20	7	8	5	7	7
D_V (acetonitrile) 10^{-9} m^2 s^{-1}	5.21	4.73	4.95	4.36	4.65	5.76

the difference in size between neon, krypton, and xenon. Under the assumptions of equal static quenching P^2 and equal correlation times τ_{EFG} for the different noble gases, the relaxation rates should follow a power law, $R^{-\alpha}$, dependence on the solvent−solute distance in the first solvation shell. (The relaxation rates of different noble gases have to be normalized to account for differences in spin quantum numbers, nuclear quadrupole moments, and Sternheimer factors.) The electric multipole causing the relaxation can then be derived for a particular model of solvation. The similarities in the RDFs support this form of analysis, since the surroundings of the noble gases only seem to differ in size of the solvent shell. Furthermore, the radii of the solvation shells change linearly with the atomic radii of the noble gases. A cancelation of the trends in the static quenching and the correlation time may justify the assumptions, of equal polarization factor and correlation time, employed in the analysis of experimental data. Especially if their mutual dependence on the size of the solute is kept in mind.

Under these assumptions and by applying the FRD model, it has been found that in water $\alpha = 5$, corresponding to dipoles, whereas in lower hydrocarbons or $\alpha = 3$, corresponding to monopoles.[22,23] (In higher hydrocarbons with more > 8 carbons in the chain $\alpha = 5$.) By comparing the relaxation rates for different noble gas atoms in acetonitrile, a dependence corresponding to electric quadrupoles has been found $\alpha = 7$.[22,23] A possible interpretation of this is that the strong tendency for acetonitrile molecules to align antiparallel to each other results in an effective electric quadrupole. However, we see in the RDFs that the angular distributions are not uniform, which is one of the assumptions in the FRD model.

It is anyhow worth while to use our calculated data for similar analysis, since we can not only compare relaxation rate, but we can also directly compare the amplitudes, $\langle V^2(0)\rangle$, which does not depend on the assumption of equal correlation times, and the amplitude of the self-EFG-TCF, which only depends on the assumptions in the FRD model. Since our relaxation rates compare well with experiment and we get $\alpha = 6 - 7$. When the assumption of equal correlation times is released the value of α increases to ~9, whereas when also the assumption of equal polarization factors is released α remains 6−7. The cancelation of these effects may justify the assumptions of equal polarization factor and correlation time.

The non uniform angular distribution also could also explain the discrepancy between the analysis of the self-EFG-TCF ($\langle V^2(0{:}r)\rangle_{\Omega,\mathrm{self}}$) and radial dependence of the relaxation rates.

A word of warning should be placed of not to use too simple models for the fluctuations causing quadrupolar relaxation while interpreting the experimental data. There are some essential features in the fluctuations of the EFG, those being the static and dynamic quenching in polar solvents,[21,30] the rhombicity of the EFG tensor,[31] and finally not forgetting the multitude of processes causing the EFG fluctuations and this even within the electrostatic treatments. Finally, the assumptions about the structure of the solvent is very crucial for the interpretation, as we have seen in the analysis of the FRD model.

Because of the great complexity of the problem, it would be of great value to evaluate the electrostatic and electronic theories based on *ab initio* calculations, and to some extent computer simulations, rather than making direct comparisons between *ab initio* calculations and relaxation rates. For example, the validity of the Sternheimer approximation can easily be controlled by *ab initio* calculations alone.

The collective nature of the relaxation mechanism suggests that a treatment based on cage variables[49−51] may be adequate for describing the fluctuating EFG. Particularly for light nuclei, like neon, in polar solvents. It might be more suitable for handling the problem than theories, based on single molecule properties.[12,15.17]

Due to the narrow temperature interval and the very limited number of temperatures, it was not possible to determine the activation energy of the quadrupolar relaxation. In the experimental studies,[6,32] the activation energy of the relaxation process was observed to be significantly smaller than that of the solvent reorientation. In the molecular dynamics, we have seen that the reorientational motion is only slightly perturbed near the solute. We have also determined the activation energy for the solvent reorientation, which compares well with experiment. Furthermore, we have seen that the residence correlation time, measured from the TCF of the switching function, has a very low activation energy. From the activation energies, we propose a model for the quadrupolar relaxation, in which the fluctuations in the EFG are mainly caused by the exchange of solvent molecules around the quadrupolar nucleus. Notice that when we say that exchange in the solvation shell is the main process causing the relaxation, it does not imply that the exchange will have the same correlation time as the relaxation process, because of the collective character of the EFG.

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