

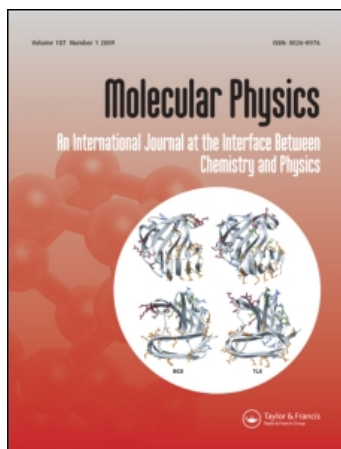
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J. Vaara ^a; J. Jokisaari ^a; T. T. Rantala ^a; J. Lounila ^a

^a Department of Physics, University of Oulu, Oulu, Finland

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Computational and experimental study of NMR relaxation of quadrupolar noble gas nuclei in organic solvents

By J. VAARA, J. JOKISAARI, T. T. RANTALA and J. LOUNILA
Department of Physics, University of Oulu, FIN-90570 Oulu, Finland

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The spin-lattice relaxation times T_1 of the quadrupolar noble gas nuclei ^{21}Ne , ^{83}Kr and ^{131}Xe were measured in various solutions by applying the inversion-recovery method. The relaxation activation energies were determined from the temperature dependence of T_1 . *Ab initio* calculations were carried out in order to gain insight into the origin of the fluctuating electric field gradient (EFG) interacting with the nuclear electric quadrupole moment and (dominantly) causing the relaxation. The calculations, together with the experimental findings, clearly indicate the insufficiency of the electrostatic model, according to which the EFG arises from the charge distribution of the solvent molecules. Additional contributions to the EFG due to the deformation of the electron cloud of the solute atom have to be taken into account.

1. Introduction

During the 1980s, several studies on ^{129}Xe (spin 1/2) nuclear magnetic resonance (NMR) were published, mostly dealing with xenon gas adsorbed in zeolites, dissolved in isotropic liquids or trapped in clathrates. The purpose of these studies was to use xenon as a probe for deriving information on its surroundings. The choice of the ^{129}Xe nucleus is obvious for many reasons. Besides other benefits, its NMR receptivity is relatively high (32 times that of ^{13}C) and its chemical shift is extremely sensitive to the structure of its environment. The latter property, in particular, has been applied to study the dimensions of pores and channels in zeolites (see [1]). Other applications are, for example, detection of phase transitions [2] and determination of the temperature dependence of order parameters [3] in liquid crystals. A disadvantage of ^{129}Xe is the long spin-lattice relaxation time [4, 5].

In addition to ^{129}Xe , the noble gases ^3He (spin 1/2), ^{21}Ne (spin 3/2), ^{83}Kr (spin 9/2) and ^{131}Xe (spin 3/2) dissolved in isotropic and anisotropic liquids, have recently drawn increasing attention (for example, [6-8]). This is due to the fact that neither the basic reasons for the shielding effects, nor those for the electric field gradient (EFG) causing the relaxation of quadrupolar nuclei are known. The situation until the beginning of 1993 has been reviewed by one of the present authors [9].

The relaxation of the quadrupolar noble gas nuclei is predominantly due to the interaction between the nuclear electric quadrupole moment and the fluctuating EFG at the nuclear site. It is, however, still an open question as to what the origins are of the EFG. Various models have been developed. They can be classified into (a) electrostatic [10-12], and (b) electronic [13] models. The electrostatic models assume the EFG to be caused by the solvent molecules represented by point charges, point dipoles or quadrupoles, or a dielectric continuum. In the electronic approach, the

EFG is considered to be a consequence of the deformation of the spherical electron distribution of the noble gas atom resulting from collisions between this atom and solvent molecules and/or from the formation and breakage of bonds between the two species.

Independently of whether the electrostatic or electronic approach is applied, the spin–lattice relaxation rate (due to the quadrupolar interaction) can be approximated in the extreme narrowing condition as [14]

$$R_1 = \frac{1}{T_1} = \alpha_S \langle F_{\parallel}^2 \rangle \tau_c, \quad (1)$$

where

$$\alpha_S = \frac{3}{8} \frac{2I + 3}{I^2(2I - 1)} \left(\frac{eQ_n}{\hbar} \right)^2 (1 - \gamma_{\infty})^2. \quad (2)$$

In equations (1) and (2), I is the nuclear spin quantum number, eQ_n is the nuclear electric quadrupole moment, $\hbar$ is Planck's constant divided by 2π , γ_{∞} is the Sternheimer antishielding factor [15], $(1 - \gamma_{\infty})^2 \langle F_{\parallel}^2 \rangle$ is the time average of the square of the EFG component along the external magnetic field at the solute nucleus, and τ_c is the correlation time of the autocorrelation function of the EFG, taken to be exponentially decaying. The electron cloud of the atom modifies the EFG caused by the surroundings of the atom, and leads to an enhancement of the EFG experienced by the nucleus. This is taken into account by using the large positive multiplication factor $(1 - \gamma_{\infty})$ with the EFG. The values of the parameters for ^{21}Ne , ^{83}Kr and ^{131}Xe are tabulated in [16].

In this study, we report experimental results for the spin–lattice relaxation rates of ^{21}Ne , ^{83}Kr and ^{131}Xe dissolved in liquid acetonitrile (krypton and xenon in CD_3CN , neon in CH_3CN), benzene (krypton and xenon in C_6D_6 , neon in C_6H_6), 1,3,5-trifluorobenzene, hexafluorobenzene and carbon tetrachloride, which have quite different electrostatic properties. Moreover, in order to gain insight into the origin of the EFG, *ab initio* calculations to model the solute–solvent interactions were carried out.

2. Experimental

Commercially available solvents, mentioned above, were used without further purification. The liquids were put into heavy wall (thickness 1 mm) glass tubes of outer diameter 10 mm. All the liquids were degassed in a vacuum line prior to transferring the noble gas into the tube. Liquid helium (for neon) and nitrogen (for krypton and xenon) were used to condense the noble gas and thus achieve a reasonable concentration in the sample; the gas pressure was about 1 atm for neon, 2 atm for krypton and 5 atm for xenon (1 atm = 101 325 Pa). Experiments have shown that the relaxation rate is independent of pressure at least when working below 10 atm [17]. Since the relative NMR receptivities of ^{21}Ne (3.26×10^{-3} with respect to ^{13}C) and ^{83}Kr (1.24) are low, enriched gases (supplied by Isotech, Miamisburg, USA) were used in order to shorten the experiment time; the degrees of enrichment were 94 at% and 74 at% for ^{21}Ne and ^{83}Kr , respectively.

All the measurements were carried out on a JNM-GX400 FT NMR spectrometer operating at 31.577 MHz for ^{21}Ne , 15.391 MHz for ^{83}Kr and 32.798 MHz for ^{131}Xe .

The spin-lattice relaxation time T_1 was determined by applying the inversion-recovery method (pulse sequence 180° - τ - 90° -free induction decay (FID)) in each case. The 90° pulses were 32, 53 and 31 μ s for ^{21}Ne , ^{83}Kr and ^{131}Xe , respectively. Due to the fact that the ^{21}Ne measurements are very time consuming, only eight values of τ were used. For ^{83}Kr and ^{131}Xe the number of τ values was 18. The T_1 value was resolved by a nonlinear least-squares fit (to the peak intensities) with three variables. The program, which estimates also the errors of the parameters, was run on a PC with a 486 processor. The average relative statistical errors of the T_1 values (one standard deviation) are estimated to be: 5% for ^{21}Ne and 2% for both ^{83}Kr and ^{131}Xe .

3. Calculations

Information on the relative importance of the two mechanisms as the origin of the EFG at the solute noble gas nucleus can be obtained by calculating properties of the electrostatic field caused by the solvent liquid and the deformations of the electron cloud of the solute. The external EFG, due to the electric multipole moments of the solvent molecules, should be compared with the experimental relaxation rates and the information that is available on the solute deformations. The present solute-solvent systems are very different, as they consist of ^{21}Ne , ^{83}Kr and ^{131}Xe noble gas atoms (differing in size and polarizability) dissolved in electrostatically different liquids. While acetonitrile has a strong electric dipole moment, benzene and hexafluorobenzene are non-polar but have strong quadrupole moments. Trifluorobenzene has a small quadrupole moment and carbon tetrachloride has neither a dipole nor a quadrupole moment but is octopolar. Idealized approaches in extracting information about problems of the present kind include, e.g., the evaluation of the relaxation rate due to solvation shells of the liquid molecules with different degrees of radial orientation around the solute atom [11] and estimation of the average EFG based on integration over a simple form of the solute-solvent pair distribution function [18]. The computational means cover molecular dynamics simulations and *ab initio* calculations. Classical molecular dynamics methods provide detailed information on this inherently dynamic problem. However, they rely on parametrizations of the intermolecular interactions, which are obtained from various sources that are not necessarily directly connected with the research interest at hand. Therefore, to obtain a consistent high-level description of all the present systems, we resort to *ab initio* electronic structure calculations of static complexes consisting of the noble gas solute and a single solvent molecule.

In performing the *ab initio* calculations, we utilized the commercial program DMol (Version 2.2) [19–21] which is based on the local density approximation (LDA) of density functional theory, as parametrized by von Barth and Hedin [22]. The molecular wavefunction was expanded as a linear combination of numerical atomic orbitals (LCAO). The system was allowed to find its ground state geometry within the LDA framework and the resulting charge density was subjected to a distributed multipole analysis (DMA). The molecular deformation charge density, i.e., the difference between the molecular charge density and the promolecule density (unrelaxed sum of the atomic densities), was partitioned among the atoms of the molecule [23]. Point electric multipoles, charge q_i , dipole moment μ_i and quadrupole moment Q_i were evaluated as the expectation values of the corresponding operators over the molecular deformation charge distribution, with the weight of each

Table 1. The basis sets used in the *ab initio* calculations. In addition to the atomic orbitals occupied in the ground state of a free atom, extra basis functions are utilized. The additional functions come from three sources. Those denoted by * have been calculated for the corresponding ion of charge +2, the notation ** is used for hydrogenic orbitals with the nuclear charge $Z = 5$ (1.3 for H itself), and the notation *** denotes a result of an excited state calculation. The last member of the basis set is the polarization function in each case.

Element	Basis
H	1s 1s** 2p**
C	1s 2s 2s* 2p 2p* 3d**
N	1s 2s 2s* 2p 2p* 3d**
F	1s 2s 2s* 2p 2p* 3d**
Ne	1s 2s 2s* 2p 2p* 3d**
Cl	[Ne] 3s 3s* 3p 3p* 3d*
Kr	[Ne] 3s 3p 3d 4s 4s* 4p 4p* 4d***
Xe	[Kr] 4d 5s 5s* 5p 5p* 5d***

expansion centre (nucleus i) equal to the contribution of the corresponding atom in the promolecule charge density.

The basis set used is given in table 1. The geometry of the solvent molecule was optimized before the addition of the solute atom. The energy of the solute-solvent system was minimized by optimizing the location of the solute with respect to the solvent molecule. The binding energy E_b of the resulting complex was evaluated as the difference of the electronic energy of the complex when the solute atom is in its minimum energy location and when the solute is infinitely far from the solvent molecule. The present *ab initio* method lacks the possibility of gaining dynamical information and, as such, is related to *ab initio* molecular dynamics methods similarly to the way in which molecular mechanics relates to classical molecular dynamics. The calculated minimum energy geometry of the solute-solvent complex can be regarded either as representing a typical geometry or as a true complex between the two species.

The electrostatic potential caused by the solvent charge distribution, as determined from the DMA procedure for the solvent molecule alone, can be expressed as

$$V(\mathbf{r}) = k_0 \sum_i \left(\frac{q_i}{r_i} + \frac{\boldsymbol{\mu}_i \cdot \mathbf{r}_i}{r_i^3} + \frac{\mathbf{r}_i^T \cdot \mathbf{Q}_i \cdot \mathbf{r}_i}{r_i^5} + \dots \right) \approx \sum_i (V_{qi} + V_{\mu i} + V_{Qi}), \quad (3)$$

where $k_0 = 1/(4\pi\epsilon_0)$ and $\mathbf{r}_i = \mathbf{r} - \mathbf{R}_i$ is the vector from the i th nucleus ($\mathbf{R}_i$) to the observation point $\mathbf{r}$ outside the charge distribution of the molecule, or outside the van der Waals radii of the constituent atoms. As compared with placing the total molecular dipole and quadrupole moments at the centre of mass location, the present distributed multipoles allow the observation point to reside much closer to the molecule [23]. The electric field, obtained from equation (3), is

$$\mathbf{E}(\mathbf{r}) = -\nabla V(\mathbf{r}) \approx \sum_i (\mathbf{E}_{qi} + \mathbf{E}_{\mu i} + \mathbf{E}_{Qi}), \quad (4)$$

where the components of the terms arising from the contributions of the charges,

dipoles and quadrupoles are

$$(\mathbf{E}_{qi})_{\alpha_i} = \frac{k_0 q_i \alpha_i}{r_i^3}, \quad (5)$$

$$(\mathbf{E}_{\mu i})_{\alpha_i} = \frac{k_0}{r_i^3} \left[3(\boldsymbol{\mu}_i \cdot \mathbf{r}_i) \frac{\alpha_i}{r_i^2} - (\boldsymbol{\mu}_i)_{\alpha_i} \right] \quad (6)$$

and

$$(\mathbf{E}_{Qi})_{\alpha_i} = \frac{k_0}{r_i^5} \left[5(\mathbf{r}_i^T \cdot \mathbf{Q}_i \cdot \mathbf{r}_i) \frac{\alpha_i}{r_i^2} - 2 \sum_{\beta_i} (\mathbf{Q}_i)_{\alpha_i \beta_i} \beta_i \right] \quad (7)$$

respectively. α_i , β_i and (later) γ_i are used to denote any of the Cartesian coordinates x_i , y_i or z_i of $\mathbf{r}_i$. The EFG is a second rank tensor

$$\mathbf{F}(\mathbf{r}) = \nabla \mathbf{E}(\mathbf{r}) \approx \sum_i (\mathbf{F}_{qi} + \mathbf{F}_{\mu i} + \mathbf{F}_{Qi}), \quad (8)$$

where

$$(\mathbf{F}_{qi})_{\alpha_i \beta_i} = \frac{k_0 q_i}{r_i^3} \left(\delta_{\alpha_i \beta_i} - 3 \frac{\alpha_i \beta_i}{r_i^2} \right), \quad (9)$$

$$(\mathbf{F}_{\mu i})_{\alpha_i \beta_i} = \frac{3k_0}{r_i^5} \left[\alpha_i (\boldsymbol{\mu}_i)_{\beta_i} + \beta_i (\boldsymbol{\mu}_i)_{\alpha_i} + (\boldsymbol{\mu}_i \cdot \mathbf{r}_i) \left(\delta_{\alpha_i \beta_i} - 5 \frac{\alpha_i \beta_i}{r_i^2} \right) \right] \quad (10)$$

and

$$\begin{aligned} (\mathbf{F}_{Qi})_{\alpha_i \beta_i} = \frac{k_0}{r_i^5} \left\{ \frac{10}{r_i^2} \left[\alpha_i \sum_{\gamma_i} \gamma_i (\mathbf{Q}_i)_{\gamma_i \beta_i} + \beta_i \sum_{\gamma_i} (\mathbf{Q}_i)_{\alpha_i \gamma_i} \gamma_i \right] \right. \\ \left. + 5 \frac{\mathbf{r}_i^T \cdot \mathbf{Q}_i \cdot \mathbf{r}_i}{r_i^2} \left(\delta_{\alpha_i \beta_i} - 7 \frac{\alpha_i \beta_i}{r_i^2} \right) - 2 (\mathbf{Q}_i)_{\alpha_i \beta_i} \right\}. \end{aligned} \quad (11)$$

The EFG caused by the bare solvent molecule was evaluated at the minimum energy location of the solute atom. We took the approach of approximating $\langle F_{\parallel}^2 \rangle$ with the largest component of the diagonal EFG tensor, F_{cc}^2 (the subscript refers to the principal axis system of $\mathbf{F}$). F_{cc}^2 is to be compared with the experimental relaxation rate normalized with the appropriate prefactor α_s from equations (1) and (2).

The deformation of the solute was addressed by calculating its dipole and quadrupole moments, $\boldsymbol{\mu}_s$ and $\mathbf{Q}_s$, respectively, induced by all the interactions with the solvent. This was achieved by performing a similar DMA as described above, now for the full solute-solvent complex. The deformation was compared with the results of the external electric field and EFG calculation to find out if other (e.g., repulsion-induced) contributions to the EFG are important.

4. Results of NMR experiments

The T_1 values were measured for the nuclei ^{21}Ne , ^{83}Kr and ^{131}Xe dissolved in the present solvents at variable temperatures by the inversion-recovery method. They were resolved by applying a three parameter (B_0 , B_1 , and T_1) fit of the peak intensities to the function

$$A(\tau) = B_0 - B_1 \exp\left(-\frac{\tau}{T_1}\right), \quad (12)$$

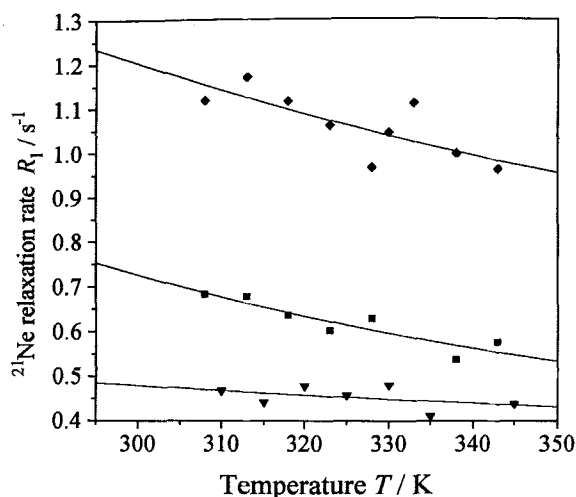


Figure 1. The measured spin-lattice relaxation rate of ^{21}Ne versus temperature in various solvents. The solvents are denoted as follows: CH_3CN ($\blacklozenge$), C_6H_6 ($\blacksquare$) and CCl_4 ($\blacktriangledown$).

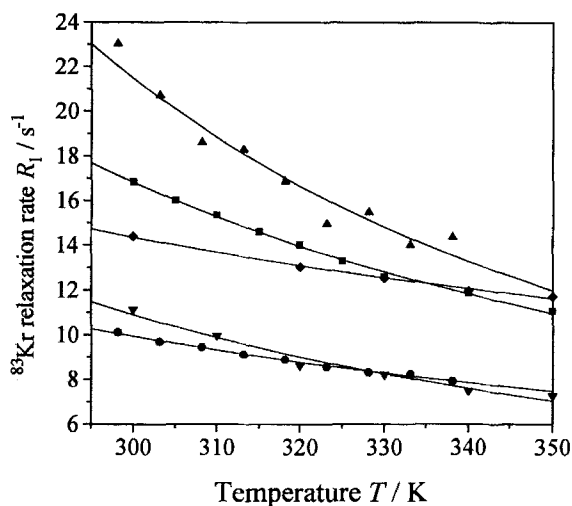


Figure 2. The measured spin-lattice relaxation rate of ^{83}Kr versus temperature in various solvents. The solvents are denoted as follows: CD_3CN ($\blacklozenge$), C_6D_6 ($\blacksquare$), C_6F_6 ($\blacktriangle$), $\text{C}_6\text{H}_3\text{F}_3$ ($\bullet$) and CCl_4 ($\blacktriangledown$).

where τ is the delay between the 180° and 90° pulses. The results are shown in figures 1–3. The T_1 values of ^{21}Ne are less accurate than those of ^{83}Kr and ^{131}Xe (this is seen, for example, in figure 1 as a larger scatter of experimental points from the fitted curve than in the cases of ^{83}Kr and ^{131}Xe , figures 2 and 3). There are two (partly interrelated) reasons for this: (a) Only eight τ values in the ^{21}Ne measurements were used because of long experiment times due to the low concentration and the relatively long T_1 of ^{21}Ne . (b) The signal-to-noise ratio in the ^{21}Ne spectra is lower than in the ^{83}Kr and ^{131}Xe spectra.

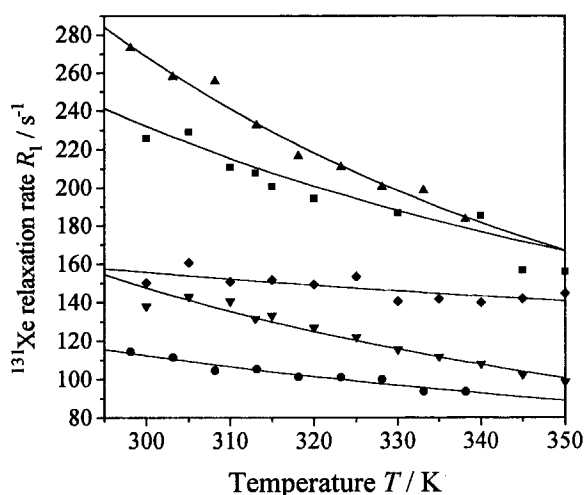


Figure 3. The measured spin-lattice relaxation rate of ^{131}Xe versus temperature in various solvents. The solvents are denoted as in figure 2.

The relaxation activation energies E_a , collected in table 3, were obtained by linear least-squares fits to the logarithmic form of the decaying exponential

$$R_1 = R_0 \exp\left(\frac{E_a}{RT}\right), \quad (13)$$

where T is the absolute temperature and R is the universal gas constant.

The present ^{83}Kr relaxation rates and activation energies are in excellent agreement with the results reported by Mazitov *et al.* [24] for the ^{83}Kr nucleus in benzene, hexafluorobenzene, carbon tetrachloride and acetonitrile. On the other hand, the activation energy of 0.044 ± 0.004 eV (4.2 ± 0.4 kJ mol $^{-1}$) determined by Stengle *et al.* [25] for ^{131}Xe in acetonitrile is about twice as high as our 0.018 eV (1.77 kJ mol $^{-1}$). The only ^{21}Ne T_1 study published until now deals with solvents different from ours and, furthermore, only one fixed temperature was used [26]. Consequently, no direct comparison concerning the ^{21}Ne results can be made. However, the T_1 values measured in the solvents of the present study are of the same magnitude as the ones obtained by Mazitov *et al.* [26] in water, alcohols and n -alkanes.

5. Calculated results and discussion

As a check of the quality of the present LDA calculations, we present in table 2 the molecular dipole moments M_z and the quadrupole moments Θ_{zz} calculated from the DMA procedure for acetonitrile and the benzenes. A comparison with some literature values (tabulated in [27]) is also made in the table. The molecular dipole and quadrupole moments $\mathbf{M}$ and $\mathbf{\Theta}$, respectively, were obtained from the calculated point multipoles as

$$\mathbf{M} = \sum_i (q_i \mathbf{R}_i + \boldsymbol{\mu}_i) \quad (14)$$

Table 2. The molecular electric dipole and quadrupole moments of the solvent molecules calculated from the distributed multipole analysis. The quadrupole moment of the dipolar acetonitrile has been calculated with respect to the centre of mass location. The geometries are as illustrated in figure 4. For reference, some literature values [27] are also shown.

Molecule	Calculated dipole moment $M_z/10^{-30}$ C m	Calculated quadrupole moment $\Theta_{zz}/10^{-40}$ C m ²	Literature values $M_z/10^{-30}$ C m $\Theta_{zz}/10^{-40}$ C m ²	Method ^a
C ₆ H ₆	0.00	-30.0	Θ_{zz} : -33.3 ... -28.4	IB, QM, MA + SE
C ₆ F ₃ H ₃	0.00	-4.25	Θ_{zz} : 3.14	IB
C ₆ F ₆	0.00	19.6	Θ_{zz} : 31.7	IB
CH ₃ CN	-13.6	-6.00	M_z : -13.98 ... -13.05 Θ_{zz} : -6.0, -15.3	QM MA, QM

^a Abbreviations are used for the methods utilized in obtaining the cited values as follows: IB, induced birefringence; MA, magnetizability anisotropy; QM, quantum mechanical calculation; and SE, semi-empirical calculation.

and

$$\Theta_{\alpha\beta} = \frac{1}{2} \sum_i \{ 3[q_i(\mathbf{R}_i)_\alpha(\mathbf{R}_i)_\beta + (\mathbf{R}_i)_\alpha(\boldsymbol{\mu}_i)_\beta + (\mathbf{R}_i)_\beta(\boldsymbol{\mu}_i)_\alpha] + 2(\mathbf{Q}_i)_{\alpha\beta} - \delta_{\alpha\beta}[q_i R_i^2 + 2(\mathbf{R}_i \cdot \boldsymbol{\mu}_i)] \}. \quad (15)$$

The calculated values for acetonitrile and benzene show good agreement with the values reported in the literature. The quadrupole moment of C₆F₆ is positive, as expected from the opposite polarity of the C—F bonds of the molecule as compared with the C—H bonds of benzene (Θ_{zz} is negative for C₆H₆). The present value is, however, smaller than the experimental one. For C₆F₃H₃ we find a small Θ_{zz} , in agreement with the experimental one. Our results for the benzenes satisfy quite well the intuitive vision of the properties of trifluorobenzene as being averages of the properties of benzene and hexafluorobenzene. That would give, applying the rule to our calculated results, $\Theta_{zz}(\text{C}_6\text{F}_3\text{H}_3) \approx \frac{1}{2}[\Theta_{zz}(\text{C}_6\text{H}_6) + \Theta_{zz}(\text{C}_6\text{F}_6)] = -5.2 \times 10^{-40}$ C m², which is close to the LDA value actually calculated here, -4.25×10^{-40} C m². Also the calculated molecular geometries (indicated in figure 4) are in good agreement with the literature values. These facts give us confidence of success in finding realistic ground states and consistent distributed multipoles for the molecules of interest.

The minimum energy geometries for the solute atom–single solvent molecule systems are illustrated in figure 4. The energy minima of the solutes are located at the axis of highest symmetry of each of the benzenes, with practically no dependence of the solute–solvent distance on the fluorine content of the solvent. In all the present solvents the minimum energy distances from the solute atom to the solvent molecule increase with increasing solute size, as expected by considering the atoms as being hard spheres with the proper van der Waals radii. ⁸³Kr and ¹³¹Xe minima are always relatively close to each other with all solvents. Note that, when drawn with the actual van der Waals radii, the solutes practically touch the solvent molecule.

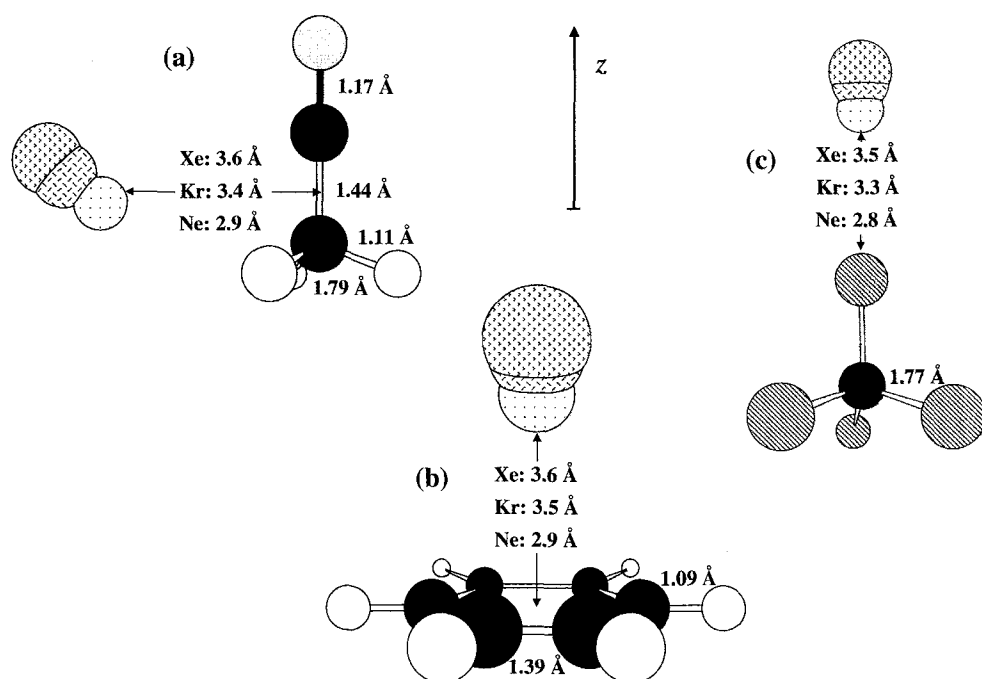


Figure 4. The calculated minimum energy geometries for noble gas solutes in (a) acetonitrile, (b) benzene and (c) carbon tetrachloride. The indicated distances are from the nucleus of the solute atom to the C-C bond in (a), centre of symmetry in (b) and the nucleus of the nearest atom in (c). For the fluorobenzenes C_6F_6 and $C_6F_3H_3$, the distances indicated in (b) apply to the displayed accuracy. The calculated bond lengths of the solvent molecules are indicated. The C-C bond lengths for C_6F_6 and $C_6F_3H_3$ are 1.39 Å and 1.38 Å, respectively. The C-F bond lengths equal 1.34 Å for both the fluorobenzenes and the C-H bond length of $C_6F_3H_3$ is 1.10 Å. In (b) and (c) the solutes reside on the symmetry axis and in (a) the noble gases are located in the plane halving the HCH bond angle. With respect to the C atom of the CN group the z coordinates of the solutes are as follows: ^{21}Ne , -0.92 Å; ^{83}Kr , -0.54 Å; and ^{131}Xe , -0.32 Å.

The calculated binding energies E_b of the solute atom-solvent molecule systems are given in table 3, together with the viscosity activation energies E_η of the solvent liquids. The difference between E_b and the experimental activation energy of NMR relaxation E_a is indicative of the importance of other contributions (besides the solute-single solvent molecule interactions) to the thermal deactivation of the relaxation. One such contribution may be due to the viscosity η of the liquid. The relaxation rate is proportional to τ_c which, in turn, is proportional to η . The order of magnitude of the calculated binding energies is in reasonable mutual agreement with both E_η and E_a . The roles of E_η and E_b are similar: η decreases with increasing temperature with the slope proportional to E_η , while the mobility of the solute increases as there are increasing amounts of thermal energy available for jumping out of the potential well of depth E_b . If the contributions to the relaxation rate due to complex binding effects and viscosity are additive, the process with the higher activation energy dominates at higher temperatures. According to the calculations,

Table 3. Viscosity-activation energies [28], measured NMR relaxation activation energies and calculated binding energies for solute atom–solvent molecule systems. E_η for mono-fluorobenzene ($\text{C}_6\text{H}_5\text{F}$) equals 0.091 eV [28]. kT equals 0.026 eV at room temperature and the energies in kJ mol^{-1} can be obtained as $E (\text{kJ mol}^{-1}) \approx 96.485 \times E(\text{eV})$.

Solvent	Viscosity activation energy E_η/eV	Solute	Relaxation activation energy E_a/eV	Binding energy E_b/eV
C_6D_6	0.106 ^a	$^{21}\text{Ne}^a$	0.056	0.058
		^{83}Kr	0.077	0.096
		^{131}Xe	0.060	0.108
$\text{C}_6\text{F}_3\text{H}_3$	—	^{21}Ne	—	0.054
		^{83}Kr	0.052	0.090
		^{131}Xe	0.042	0.102
C_6F_6	—	^{21}Ne	—	0.056
		^{83}Kr	0.106	0.090
		^{131}Xe	0.086	0.102
CCl_4	0.108	^{21}Ne	0.019	0.038
		^{83}Kr	0.079	0.063
		^{131}Xe	0.070 ^a	0.071
CD_3CN	0.070 ^a	$^{21}\text{Ne}^a$	0.041	0.042
		^{83}Kr	0.038	0.068
		^{131}Xe	0.018	0.076

^a Measurements for undeuterated species.

increasing solute size causes the binding energy to increase towards the viscosity activation energy of the corresponding solvent in all the cases studied, as is readily understood from the larger polarizability of the heavier species. It appears that the strongly bound heavier solutes ^{83}Kr and ^{131}Xe are more associated to the solvent liquid molecules than the light ^{21}Ne is. This implies that, in the case of the heavy solutes, the EFG fluctuations and other time-dependent features of the solute–solvent interactions are reflecting the movement of the solvent molecules more than the motion of the solute atom itself relative to the solvent molecules. A similar conclusion was also drawn by Engström *et al.* [29] for the heavy Cl^- solute compared with Li^+ in water. For CCl_4 , E_b seems to be a lot smaller than E_η for all solutes. It is noteworthy that the benzenes exhibit practically identical binding energies for a given solute. E_η is seen to be approximately twice as big as E_a , as also noted by Mazitov *et al.* [24]. The energetics of the thermal deactivation of R_1 cannot be attributed solely to the effect of the viscosity of the solvent. Other effects, e.g., those associated to complex formation, must contribute as well.

Brupbacher *et al.* [30] used many-body perturbation theory for the neon–benzene complex and found the minimum energy distance of Ne from the plane of the benzene molecule to be 3.39 Å with a binding energy of 0.019 eV. According to our present calculations, the complex is a tighter bound one; the respective parameter values are 2.90 Å and 0.058 eV. A possible explanation of the differences may be in the smaller basis set superposition errors [21, 30] in the present numerical LCAO approach, as compared with using Gaussian atomic orbitals. In [30], the binding energy increased by over 50% even in the last refinement of the basis set. This implies that their E_b value had not converged to a final value. Weber *et al.* [31] performed an experimental study utilizing resonance-enhanced two-photon ionization and found an average separation of 3.46 Å of Ne from the plane of the benzene. Hobza *et al.* [32]

calculated the properties of the argon–benzene complex and found the binding energy to be 0.053 eV, closer to the range of our present LDA results for the other noble gases. That work also showed a lack of convergence of E_b , since the better of the two basis sets used gave a 22% larger energy than did the simpler one. It must be noted, however, that despite the possible tendency of the present LDA method to overestimate binding effects, the different systems of interest here are treated equivalently and, thus, a comparison between them is possible.

The solvent dependence of R_1 is not the same for all the noble gases studied here. While the dipolar CH_3CN is a faster relaxing environment than the quadrupolar C_6H_6 in the ^{21}Ne case, for the heavier solutes the order is reversed: at low temperatures benzene causes faster relaxation. The transition to the neon-like order occurs at $T = 335\text{ K}$ for ^{83}Kr and, as determined from the slopes of the experimental curves, would occur above the present measurement range for ^{131}Xe . The order reversing behaviour is reflected in the solute–solvent binding energies that increase in the order ^{21}Ne , ^{83}Kr , ^{131}Xe . Acetonitrile has also the lowest E_η and, correspondingly, the smallest slope of the viscosity versus temperature curve among the present solvents (the viscosity of monofluorobenzene is nearly the same as that of benzene in the temperature range of the present study [28], therefore we also expect $\text{C}_6\text{F}_3\text{H}_3$ and C_6F_6 to have qualitatively similar data). A similar tendency to change order is noted also in the $\text{CCl}_4/\text{C}_6\text{F}_3\text{H}_3$ and $\text{C}_6\text{F}_6/\text{C}_6\text{H}_6$ data of ^{83}Kr and ^{131}Xe . The results indicate that the contributions of the deformations of the electron cloud are significant for the heavier solutes at low temperatures. The viscosity of carbon tetrachloride is by far the highest among the liquids studied here. While the high η implies a long correlation time for the translational motion of the solvent molecules, the relevance of η for the different rotational degrees of freedom of the near-spherical CCl_4 is not obvious. CCl_4 and $\text{C}_6\text{F}_3\text{H}_3$ display expectedly small experimental R_1 values, since their lowest-order non-vanishing electric multipoles are octopole and weak quadrupole moments, respectively.

The largest components of the EFG tensors caused by the different solvent molecules at the minimum energy sites of the solutes are illustrated in figure 5 and tabulated in table 4. The bars of figure 5 indicate squared EFGs which contribute to R_1 . The values are compared with the normalized relaxation rates R_1/α_s , where R_1 is the experimental relaxation rate at $T = 320\text{ K}$ and α_s includes the Sternheimer factor. For the benzenes and carbon tetrachloride, $\mathbf{F}$ is a diagonal tensor with cylindrical symmetry (vanishing asymmetry parameter). In these cases the zz component (in the coordinate system of figure 4) is displayed ($F_{cc} = F_{zz} = -2F_{xx} = -2F_{yy}$). The other of the two largest components (of almost identical absolute values and opposite signs) of the diagonalized EFG tensor of CH_3CN is shown in figure 5.

The EFGs are very different for different solutes in the same solvent, as can be seen, e.g., in the cases of benzene and carbon tetrachloride. The values decrease expectedly with the solute–solvent distance, except for C_6F_6 with which ^{21}Ne experiences a smaller EFG than do the other solutes. This is due to a cancellation effect between the different contributions to the EFG, felt only sufficiently close to the molecule. Although the quadrupole and lower moments of CCl_4 are vanishing, the solutes experience significant EFGs at their minimum energy sites, since their close proximity to the solvent molecule allows the contributions of the distributed multipoles to survive as opposite to the case where the observation point resides far from the molecule. Due to thermal motion, the atom samples also regions of space other than the minimum energy location. The true quantity $\langle F_{\parallel}^2 \rangle$ is, therefore, smaller

Table 4. The calculated external electric fields and squared external electric field gradients^a at the minimum energy sites of the solute nuclei along with the induced dipole and quadrupole moments^b of the solute, μ_s and Q_s , respectively, for several solute-solvent systems.

Solvent	Solute	$E_c/10^9 \text{ V m}^{-1}$	$F_{cc}^2/10^{38} \text{ V}^2 \text{ m}^{-4}$	$\mu_s/10^{-31} \text{ C m}$	$Q_s/10^{-41} \text{ C m}^2$
C_6H_6	^{21}Ne	-3.685	9.193	-2.93	0.86
	^{83}Kr	-2.346	3.213	-8.79	3.81
	^{131}Xe	-2.053	2.355	-12.4	6.20
$\text{C}_6\text{F}_3\text{H}_3$	^{21}Ne	-0.880	1.302	-2.36	0.65
	^{83}Kr	-0.458	0.234	-6.47	3.97
	^{131}Xe	-0.375	0.138	-8.61	6.62
C_6F_6	^{21}Ne	1.753	0.348	-1.83	0.48
	^{83}Kr	1.334	0.572	-4.19	4.14
	^{131}Xe	1.198	0.507	-5.21	6.97
CCl_4	^{21}Ne	2.215	9.135	-0.88	1.38
	^{83}Kr	1.236	2.138	-0.71	4.67
	^{131}Xe	1.026	1.347	-0.53	6.25
CH_3CN	^{21}Ne	2.908	3.846	3.26	4.81
	^{83}Kr	2.212	2.218	7.79	8.78
	^{131}Xe	1.937	1.707	9.80	12.9

^a The subscripts *c* and *cc* in the electric field and EFG refer to the principal axis system of the solvent molecule. For the field, the *c* axis is almost or exactly parallel with the *z* axis of the molecule (for CH_3CN and other solvents, respectively). For EFG, *cc* stands for the *zz* component in all solvents apart from CH_3CN . In that solvent, there are two components of opposite signs and almost equal magnitude. The two components correspond to orthogonal eigenvectors located roughly symmetrically with respect to the direction of the *z* axis in the plane containing the solute and the symmetry axis of CH_3CN .

^b The tabulated μ_s and Q_s values are *z* and *zz* components, except in the case of CH_3CN , where an absolute value is tabulated for the former and the largest diagonalized component for the latter. In CH_3CN , the μ_s are along the *y* axis, which is approximately the direction of the vector separating the solute and the nearest carbon atom of the solvent molecule. *y* is also the principal axis of Q_s .

than our present approximation. A general qualitative feature of the results is that, while the experimental R_1/α_s decreases with increasing solute size, its changes are far less dramatic than the corresponding changes in EFG. As examples of the apparent discrepancies of the results, the experimental R_1/α_s values for ^{83}Kr and ^{131}Xe in C_6F_6 are higher than those measured in C_6H_6 , contrary to what would be expected from the calculated EFGs. A similar situation can be seen between $\text{C}_6\text{F}_3\text{H}_3$ and CCl_4 , in which ^{83}Kr nuclei relax with practically equal rates although the calculated EFGs are far higher for the latter solvent.

While the present EFGs are static quantities, we believe that they are indicative of the amplitude of the EFG fluctuations that really cause the relaxation. This is corroborated by the molecular dynamics calculations of Luhmer *et al.* [33], who found that the amplitudes of the EFG correlation functions felt by a ^{131}Xe solute in C_6H_6 are in the range $2.38\text{--}3.54 \times 10^{38} \text{ V}^2 \text{ m}^{-4}$, which is in good agreement with our squared static EFG for that system, $2.355 \times 10^{38} \text{ V}^2 \text{ m}^{-4}$. The present results are in strong contrast to a study by Dejaegere *et al.* [18], who used partial charges only to adjust to the experimental quadrupole moments of the benzenes studied here. With their partial charges roughly three times larger than the ones found in the present work, they calculated practically equal average EFGs from both C_6H_6 and

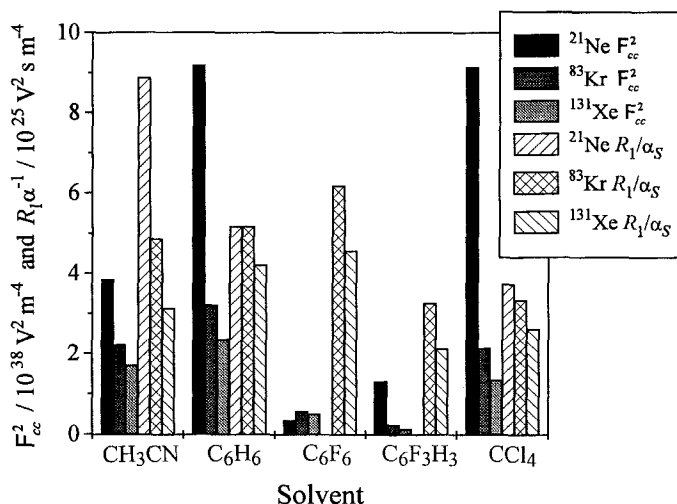


Figure 5. The calculated squared electric field gradients caused by the solvent molecules at the minimum energy positions of the solute noble gas atoms for several solute–solvent systems. The experimental NMR relaxation rates (measured at $T = 320 \text{ K}$) with normalization by the prefactors α_S (see equations (1) and (2) in the text), are also shown for the systems.

C_6F_6 , by integrating over their specified form of the solute–solvent pair distribution function. In doing that, they disregarded the electrostatic contributions to the energy of the solute–solvent systems, however.

It appears that, within the present approach, the multipoles of the solvent cannot solely explain the relaxation data. However, the EFGs and the normalized relaxation rates cannot be compared directly since, according to equation (1), R_1/α_S equals the product $\langle F_{\parallel}^2 \rangle \tau_c$. Let us make the assumption that the EFG at the solute nucleus (and therefore also the NMR relaxation) is caused by the multipoles of the solvent alone. Figure 6 shows the resulting correlation times τ_c ; the values have been obtained by dividing the experimental R_1/α_S values (figure 5) by the corresponding calculated F_{cc}^2 values. In all the cases the energetically and geometrically similar ^{83}Kr and ^{131}Xe solutes exhibit similar correlation times. A marked feature is that the correlation times of benzene are far shorter than those of the fluorobenzenes, despite the relatively similar solute–solvent complexes (binding energy, minimum energy separation) formed by all of them with a given solute. The viscosity is presumably very similar for all the benzenes studied here, ruling out different nature of the translational motion of the solvent molecules as a possible cause for the different τ_c values of these solvents. It was argued in [33] that the principal origin for the EFG fluctuations in the ^{131}Xe –benzene system is the rotation of the solvent molecules around their twofold axes. The shorter τ_c of C_6H_6 could then be thought to be a consequence of its smaller moment of inertia in comparison with the heavier fluorobenzenes. The τ_c of the heavier of the latter solvents (C_6F_6) is, however, clearly shorter than that of $\text{C}_6\text{F}_3\text{H}_3$, indicating that the inertia effect does not explain the figure. Thus, we draw a conclusion that the data in figure 6 do not match the actual correlation times and there has to be an additional mechanism for the existence of the EFG at the solute nucleus—a result also deduced recently by some of the present authors from the

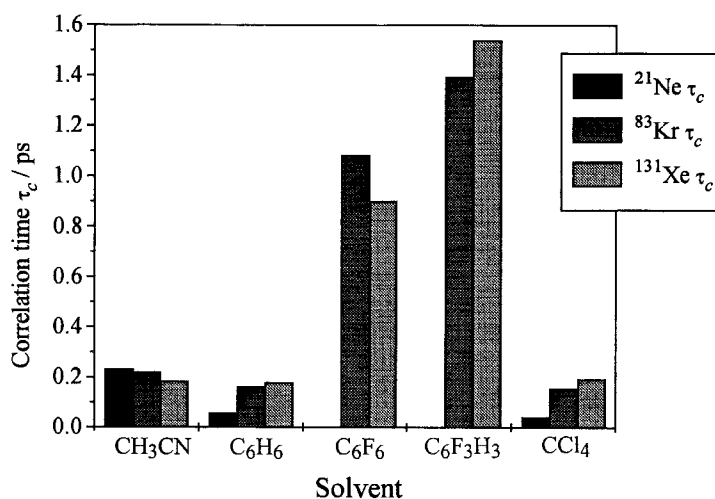


Figure 6. The correlation times of the electric field gradient fluctuations of the present solute-solvent systems. The figure has been drawn using the approximation that the true EFG at the solute nucleus is caused by the charge distribution of the solvent molecule alone. The solute atom is taken to be in its minimum energy location with respect to the solvent molecule.

temperature dependence of the quadrupolar couplings of the present solutes in liquid crystal environments [16]. Also, Engström and Jönsson came to the same conclusion regarding Li^+ ions dissolved in water [34].

The calculated induced dipole moments μ_s and quadrupole moments Q_s of the solute atoms, along with the electric fields E_c experienced by the solutes, are presented in table 4. The deformations are seen to increase with increasing solute size. They do not show even a qualitative correlation with the external electric field or EFG. Instead, it appears that the interaction-induced multipole moments of the solutes are relatively similar, despite the different electric fields from the solvents. This points to the importance of other mechanisms, such as collision-induced dynamic deformation, in causing the deformation, and also the EFG at the solute nuclei. Since the solute deformations are high for the heavy solutes for which the external EFGs are low, the present data support the intuitive picture that the importance of the electronic deformation mechanism grows with the size of the solute.

6. Conclusion

Electrostatic theory, according to which the EFG at the nuclei of solute noble gas atoms is caused solely by the charge distribution of the solvent molecules, is not capable of explaining the present experimental results. This indicates that there is an additional contribution to the EFG, which arises from the deformation of the electron cloud of the solute atom.

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