Magnetic Field Dependent Xenon-131 Quadrupolar Splitting in Gas and Liquid Phase NMR

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At very high magnetic fields ($B_0 \geq 14$ T), the NMR spectrum of xenon-131 in the gas phase ($\sim$300 K, 400 kPa) shows a well resolved quadrupolar splitting. The experimental results suggest a dual nature of the observed splitting. One portion arises from exchange with xenon atoms adsorbed on the surface of the surrounding container wall. Another portion, previously unreported, is strongly field dependent and does not appear to originate from such surface interactions. This term indicates an electrical polarization of the xenon electron shell induced by the applied static magnetic field. [S0031-9007(98)06807-0]

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A nucleus with spin $S > \frac{1}{2}$ possesses a nonspherical charge distribution resulting in an electric nuclear quadrupolar moment. It can interact with the electric field gradient (EFG) that is generated by the surrounding electron shell. The coupling of the quadrupolar moment with the anisotropic part of the EFG may lead to a splitting of the NMR transition [1–3].

For a gas-phase NMR spectrum of the xenon-131 isotope ($S = \frac{3}{2}$) no quadrupolar coupling is expected since the spherical symmetry of the electron shell will not create any anisotropic EFG. Although this high symmetry may be disturbed by gas-phase collisions between xenon atoms, random rapid motion in the gas phase should lead to a zero average of all quadrupolar interactions created by such processes.

Nevertheless, it has been shown previously [4–9] that a quadrupolar splitting of the xenon-131 NMR transition can be observed in the gas phase. The splitting originates from adsorption of the xenon atoms on the surface of the surrounding container wall. This process reduces the symmetry of the electron shell, and the resulting quadrupolar couplings do not average to zero due to the fixed orientation of the surface with respect to the magnetic field. The phase information of the quadrupolar evolution on the surface is transferred by exchange into the gas phase, where it is detected.

In this Letter an additional contribution to the quadrupolar splitting is demonstrated which does not originate from exchange with the surface but depends strongly on the magnetic field strength. This effect [10] is shown in Figs. 1(a)–1(c) where the splitting of xenon-131 (gas contained in a plain NMR tube) increases with the field strength from $2\nu_Q = 0.6$ Hz at (flux density) $B_0 = 7.05$ T to a well separated triplet with $2\nu_Q = 3.9$ Hz at 16.92 T. The quadrupolar origin of this splitting is demonstrated in Fig. 2(a) using the spin-echo sequence:

$$90^\circ - \tau_e - 180^\circ - \tau_e - \text{acquisition}, \qquad (1)$$

where the 180° pulse cannot refocus evolution under the quadrupolar Hamiltonian. Using the irreducible tensor formalism [11–14], coherence of first rank and of first order is created after the initial 90° excitation pulse and the density matrix $\sigma(t)$ contains only the tensor elements $T_{1\pm1}$ for $t = 0$. Quadrupolar interaction will transform the initial coherence into second ($T_{2\pm1}$) and third ($T_{3\pm1}$) rank elements and one obtains from first order perturbation treatment [15,16]

$$\begin{aligned}\sigma(t) = {} & i\frac{1}{\sqrt{10}}[3\cos(\omega_Q t) + 2]\{T^{3/2}_{1,+1} + T^{3/2}_{1,-1}\} \\ & + \sqrt{\frac{3}{2}}\sin(\omega_Q t)\{T^{3/2}_{2,+1} - T^{3/2}_{2,-1}\} \\ & - i\sqrt{\frac{3}{5}}[\cos(\omega_Q t) - 1]\{T^{3/2}_{3,+1} + T^{3/2}_{3,-1}\}, \qquad (2)\end{aligned}$$

where $\omega_Q = 2\pi\nu_Q$. The $T_{2\pm1}$ and $T_{3\pm1}$ tensor elements can be isolated by double quantum filter (DQF) and triple quantum filter (TQF) experiments [9,15–17]. The $T_{2\pm1}$ evolution was chosen to be monitored due to its faster initial buildup and its sign inversion which provides a more accurate determination of the coupling constant in cases where relaxation damps out the evolution rapidly. In addition, the $T_{2\pm1}$ term is less likely to be generated by incoherent processes which may disturb the accuracy of the measurement [9,15–17]. The $T_{2\pm1}$ term can be isolated by a modified double quantum filter experiment as introduced by Navon and co-workers [18,19]:

$$[90^\circ - \tau - 180^\circ - \tau - 54.7^\circ]_\phi - \Delta - 54.7^\circ - \text{acquisition}. \qquad (3)$$

The transmitter phase ϕ for the DQF experiment is stepped through $\{0^\circ, 90^\circ, 180^\circ, 270^\circ\}$ while the receiver phase is alternated by 180° for each increment of ϕ. An interval Δ of 25 ms is needed for the transmitter phase to be shifted. A conventional DQF measurement using two 90° pulses instead of the 54.7° pulses would allow both ($T_{2\pm1}$) and ($T_{3\pm1}$) rank elements to pass the filter.

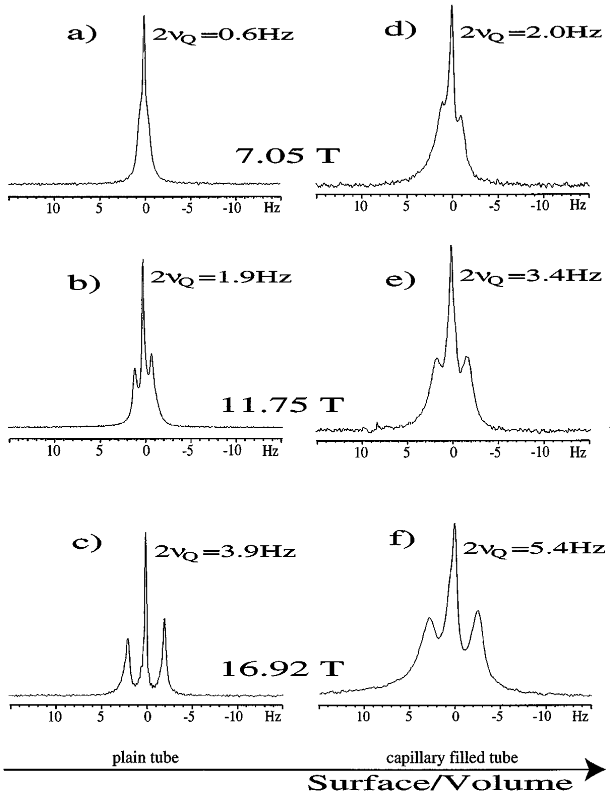


FIG. 1. NMR gas phase spectra of natural abundance xenon-131 (21.2%) contained in a cylindrical tube (symmetry axis aligned with the magnetic field) at 400 kPa and 305 K for various field strengths [(a),(d) 7.05 T corresponding to 300 MHz proton frequency or 24.7 MHz ^{131}Xe frequency; (b),(e) 11.75 T, 500 MHz, 41.2 MHz; (c),(f) 16.92 T, 720 MHz, 59.4 MHz]. The gas for the experiments in (a)–(c) was contained in a plain 6 mm inner diameter (i.d.) tube of 22 cm length, whereas an increase of the surface to volume ratio by a factor of about 4.5 was achieved by filling the tube with glass capillaries [(d)–(f)]. The spectral lines in (d)–(f) are broadened due to magnetic susceptibility of the glass capillaries. Gas pressures above 400 kPa will lead to further broadening of the line shape.

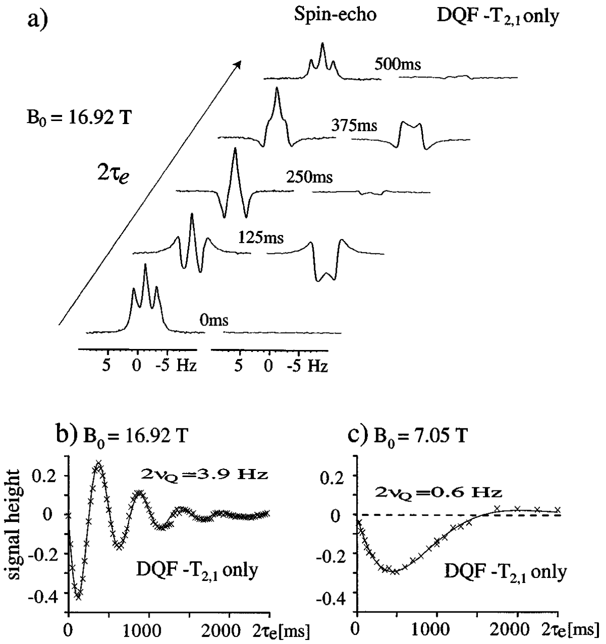


FIG. 2. The pulse sequences [Eqs. (1) and (3)] applied on xenon-131 at 16.92 T results in the spin echo and DQF signals depicted in (a) for various echo times $2\tau_e$. The envelope of the DQF experiment (crosses) and the fitting of the data (line) to three parameters are shown in (b) (16.92 T) and (c) (7.05 T). The adjustable parameters were $2\nu_Q$ (sinusoidal evolution), relaxation T_2 (exponential decay), and the initial intensity I_0 of the $T_{2,1}$ term. The reference intensity (set to 1.0) is taken from the signal height of a single 90° pulse experiment under otherwise identical experimental conditions. Since the DQF line shape at 16.92 T is somewhat more complicated due its resolved splitting [see (a)], the DQF signal intensity has been defined by the averaged height of its two peaks.

The experimental results using this pulse sequence [Eq. (3)] are shown in Fig. 2(a). For an evolution time $2\tau_e = 0$ the only coherence present is $T_{1\pm1}$, which cannot pass the double quantum filter and therefore results in zero signal intensity. At $2\tau_e = 1/(2\nu_Q)$ (closest point in the measurement at $2\tau_e = 125$ ms) the $T_{2\pm1}$ term is largest causing maximum signal intensity, whereas at $2\tau_e = 1/\nu_Q$ (measurement at $2\tau_e = 250$ ms) the amount of $T_{2\pm1}$ coherence is again zero while $T_{1\pm1}$ and $T_{3\pm1}$ are present. Note that a $T_{3\pm1}$ measurement in a TQF experiment (not depicted) yielded maximum intensity at this point. For larger evolution times the $T_{2\pm1}$ coherence builds up again, however with opposite sign. The envelope of the measurements is displayed in Fig. 2(b) (i.e., the signal intensity as a function of the evolution time $2\tau_e$). Fitting of the envelope determines a quadrupolar coupling of 3.9 Hz which is in total agreement with the splitting in Fig. 1(c). The DQF envelope of xenon at 7.05 T in Fig. 2(c) suggests a 0.6 Hz coupling that is difficult to obtain from the 1D spectrum [Fig. 1(a)].

The increase in quadrupolar splitting from the lower to the larger surface/volume sample is only little affected by the field strength. This can be seen by comparing Figs. 1(a)–1(c) with the spectra at corresponding fields depicted in Figs. 1(d)–1(f) where a sample with ca. 4.5 times larger surface to volume ratio had been used. At 7.05 T the difference is $\Delta 2\nu_Q = 1.4$ Hz, at 11.75 T it is 1.5 Hz and yields to $\Delta 2\nu_Q = 1.5$ Hz at 16.92 T. This indicates that the splitting due to surface interactions is largely field independent; whence, an additional second phenomenon that causes the field dependence and is independent from surface interactions should be considered. Both phenomena seem to be additive and result in the overall splitting of the observed triplet.

In order to prove the assumption, the contribution from surface interactions could be eliminated if the xenon was contained in a very large vessel with a surface to volume ratio close to zero. Because of spatial limitations of NMR magnets, the decrease of the surface to volume ratio has been utilized by condensing xenon to the liquid phase. Although relaxation of condensed xenon-131 occurs at a much faster rate than in the gas phase, it slows down with increasing temperature. Just below the critical point at 289 K and 5.8 MPa, the spin-lattice relaxation time T_1 is approximately 110 ms which is about one-tenth of the corresponding gas-phase relaxation. A large-volume, high pressure NMR tube for this kind of experiment was set up following the procedure of Roe [20]. A few modifications have been made to facilitate the transfer of bulk material (i.e., glass capillaries) into the single crystal sapphire tube of 9 mm inner diameter. The obtained spectra exhibit a half height linewidth of around 8–10 Hz due to relaxation and magnetic susceptibility effects. As a result, the splittings are obscured even at highest available fields. However, DQF experiments reveal the quadrupolar coupling as shown in Fig. 3. The exchange with the surface will have a minor effect due to a larger fraction of "bulk" (i.e., liquid) xenon compared to surface adsorbed xenon. This is best demonstrated in Fig. 3(a) where the outcome of the DQF experiment shows only minor differences between the plain and the capillary filled tube [compare to Figs. 1(a) and 1(d)]. At 16.92 T [Fig. 3(c)], an inversion of the DQF signal for evolution delays $2\tau_e >$ 300 ms can be recorded, while at all other field strengths the sensitivity was not sufficient to obtain corresponding signals, thus leading to much less precise values for the coupling constants.

The coupling constants from the liquid xenon DQF measurements are summarized in Fig. 4. They are reduced by about $\Delta 2\nu_Q = 0.4$ Hz compared to the gas-phase splitting [plain tubes, Figs. 1(a)–1(c)] indicating that this difference is caused by surface interactions. The coupling of $2\nu_Q = 0$ for zero field strength was taken from Mehring and co-workers [7] who demonstrated by optical pumping experiments that the quadrupolar couplings of the xenon-131 at low magnetic fields ($<10^{-6}$ T) are entirely due to surface interactions [21].

Having excluded surface exchange as a plausible cause, the observed anisotropy can be provided only by the magnetic field itself. Quadrupolar splittings in deuterons of gaseous benzene have been previously reported as a magnetic alignment effect [22]. This effect is proportional to B_0^2 and requires an anisotropy of the magnetic susceptibility not present in xenon atoms. Short lived xenon van der Waals complexes may possess such an anisotropy but the observed splitting should strongly depend on the concentration of the xenon. However, spectra of diluted xenon show only minor alterations which are presumably surface effects: Neither dropping the xenon pressure from 400 to 20 kPa, nor subsequent dilution by 400 kPa of CO_2 alters the $2\nu_Q = 3.9$ Hz splitting at 16.9 T by more than 0.1 Hz.

Even in the absence of an alignment effect, the magnetic field may contribute to an electrical anisotropy with nonzero average. The applied static magnetic field induces an electrical current in the electron shell which in turn causes a local magnetic field thus generating the well known chemical shift in NMR spectroscopy [23]. Recently, it has been predicted that this induction may also lead to an electrical polarization of the electron shell, thus altering the EFG at the nucleus [24]. The dependence upon the magnetic field is assumed to be quadratic [24–26], since the xenon atom should obey time-reversal symmetry which seems to exclude linear or other odd order external field effects. Nevertheless, taking into account the magnetic moment of the nucleus, a linear effect may exist as shown in calculations presently being performed by Salsbury and Harris [27] which also substantiate the order of magnitude of the observed splitting. A first glance at the nature of the field dependence can be taken in Fig. 4, but more reliable data are expected from

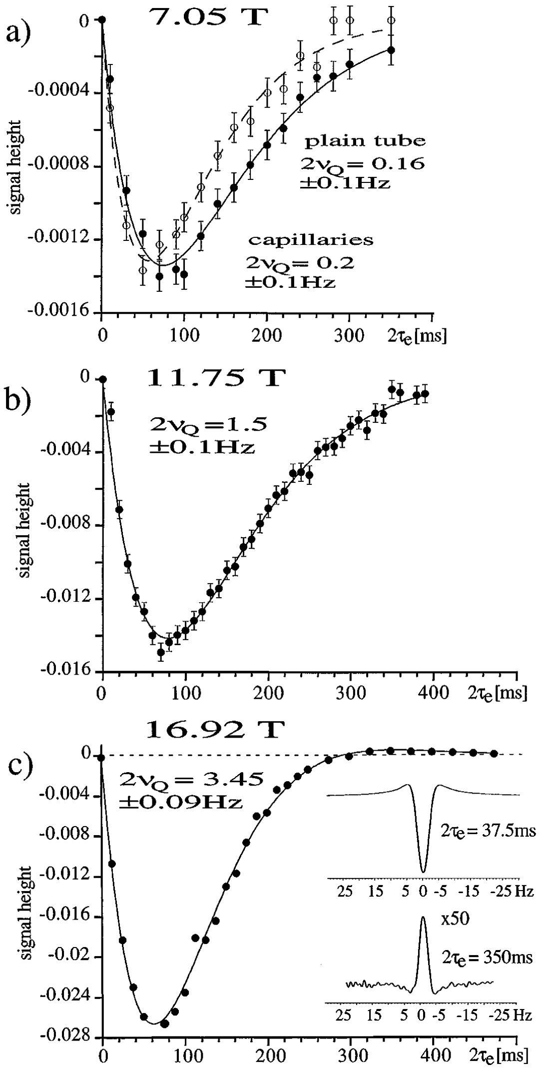
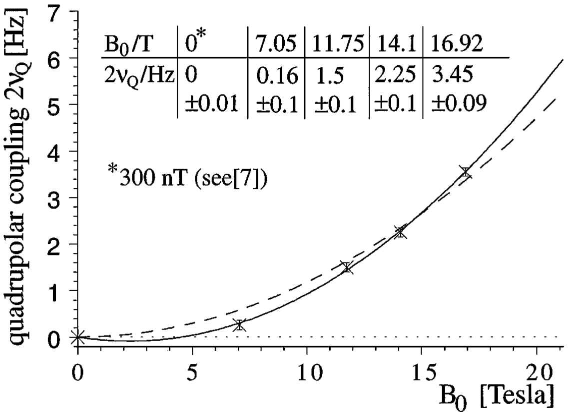


FIG. 3. DQF measurements [using pulse sequence Eq. (3)] at three different field strengths on liquid xenon contained in a 9 mm i.d. single crystal sapphire tube at 285 K. Comparison of measurements at 7.05 T in a plain tube (open circles) to a capillary filled tube (closed circles) did not indicate a dramatic alteration in quadrupolar splitting as in Figs. 1(a) and 1(d). Only the 16.92 T data exhibits an inversion of the signal which leads to a reliable determination of the coupling constant.



B_0/T	0*	7.05	11.75	14.1	16.92
$2\nu_Q$/Hz	0 ±0.01	0.16 ±0.1	1.5 ±0.1	2.25 ±0.1	3.45 ±0.09

*300 nT (see[7])

FIG. 4. Field dependence of the Xe-131 quadrupolar splitting from liquid experiments as described in Fig. 3. The data indicate a dependence of the splitting in the vicinity of B_0^2 (best fit: dashed line). The best fit using a linear and quadratic term (solid line) suggests a linear term 5 times larger than the quadratic term with opposite sign.

measurements at higher field strengths with magnets currently under construction.

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