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Structure of LiNO$_3$: Point Charge Model and Sign of the ^{7}Li Quadrupole Coupling Constant

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The crystal structure of LiNO$_3$ is determined by single-crystal X-ray diffraction. The structure is isomorphous with that of calcite; lithium is coordinated by oxygen in a trigonally-elongated octahedron. A positive sign of the ^{7}Li quadrupole coupling constant is deduced from a simple point charge model with the following assumptions: (1) only contributions from the six oxygen atoms of the inner coordination sphere are included, and (2) the charge assigned to each oxygen atom is negative. This result is compared to the low-temperature ^{7}Li NMR work of Kuhns and Waugh (*J. Chem. Phys.* **1992**, *97*, 2166–2167), in which the sign of the ^{7}Li quadrupole coupling constant was found to be positive.

Introduction

Recently, Kuhns and Waugh[1-3] measured the sign of the ^{7}Li quadrupole coupling constant in LiNO$_3$ by a technique which is generally applicable to most quadrupolar nuclei, very low temperature and very high field NMR.[4-6] Heretofore, NQR and NMR results, with only a few exceptions,[7-11] are confirmed to the reporting of the absolute value of the quadrupole coupling constant; in gas-phase microwave spectroscopy, the sign of the quadrupole coupling constant is readily obtained.[12] However, the value of the NQR and NMR data is greatly increased with the knowledge of the sign of the quadrupole coupling constant. We discuss the Kuhns and Waugh results for LiNO$_3$ with the use of a point charge model based upon the X-ray crystal structure of LiNO$_3$, which is reported herein. Also, a point charge model for LiNO$_3$ is compared to that for NaNO$_3$; the isomorphous crystal structure and sign of the ^{23}Na quadrupole coupling constant have been determined previously.[8,13] LiNO$_3$ was correctly reported in 1928 to have the G1 (calcite) structure;[14] however, no high-resolution single-crystal structure determination has subsequently appeared. Briefly, the objective of this line of research is to use the *sign* of a quadrupole coupling constant to deduce the *direction* of a site distortion away from, for example, ideal tetrahedral or octahedral symmetry. The recent ^{7}Li NMR result for a simple material, LiNO$_3$, provides a useful introduction. On the basis of recent calculations by Huggins and Ellis[15] and Tossell,[16] potential applications are likely in the ^{27}Al NMR spectroscopy of zeolites.

Theory

The quadrupolar coupling constant, $e^2q_{zz}Q/h$, is a product of the nuclear electric quadrupole moment, Q, and the largest element of the electric field gradient tensor at the nuclear site, q_{zz}. In contrast to other NMR parameters, such as chemical shifts and *J*-coupling constants which are difficult to model from first principles, the value of the quadrupole coupling constant can be estimated by simple electrostatic modeling of the ligands about a quadrupolar nucleus. Each ligand is assigned a point charge, and using the geometry of the first coordination sphere, the electric field gradient is calculated. Point charge models were used early in the history of NQR for modeling the magnitude of the ^{23}Na quadrupole coupling constant in sodium salts[2] and were recently used in the analysis of ^{2}H quadrupole coupling constants in bridging metal hydrides.[17]

There are two special cases, ideal tetrahedral and ideal octahedral, for which the electric field gradient at the metal site is exactly zero; hence, the quadrupole coupling constant is zero.[18-20] Deviations from tetrahedral or octahedral symmetry will yield electric field gradients that can be either positive or negative. In principle, an NMR experiment that yields the sign of the quadrupole coupling constant can be used to determine the direction of distortion away from ideal tetrahedral or octahedral symmetry. Additional details of electric field gradients, with an emphasis on deuterium, have been published in a tutorial.[21]

Consider a six-coordinate quadrupolar nucleus, ML$_6$, in a nominally octahedral environment that can undergo compression or expansion along a 3-fold axis, i.e., trigonal distortion. We use one of the angles, $\angle$L–M–L, to describe the distortion of the octahedral environment such that compression leads to an acute

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(1) Kuhns, P. L.; Waugh, J. S. *J. Chem. Phys.* **1992,** *97,* 2166–2167. Note: There is a typographical error in the reported magnitude of the ^{7}Li quadrupole coupling constant; the formulas are correct. Bersohn[2] reports a value of 39.2 kHz, which is consistent with the ^{7}Li NMR spectrum shown in the work of Kuhns and Waugh.

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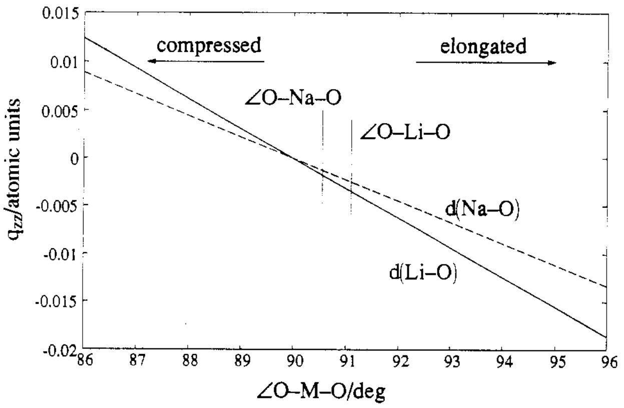

Figure 1. Electric field gradient in an ML_6 unit as a function of trigonal distortion calculated from eq 1. K_i is set to −1 for each of the six oxygen sites. The results for two different M–O distances are shown: (—) *d*(Li–O); (- - -) *d*(Na–O). The two vertical markers denote experimental ∠O–M–O values for $LiNO_3$ and $NaNO_3$.

∠L–M–L angle and an ideal octahedral environment has a value of ∠L–M–L = 90°. It is convenient to assign the *z* axis of a Cartesian coordinate system to be collinear with the 3-fold axis. The electric field gradient along the *z* axis is given by

$$q_{zz} = \sum_i K_i \frac{3z_i^2 - r_i^2}{r_i^5} \qquad (1)$$

where K_i is the assigned charge at each *i*th ligand and r_i is the metal–ligand distance; it is convenient to use atomic units. Atomic units are common in the output of properties packages such as GAUSSIAN 90,[22] and calculated values have been tabulated for many molecular species.[23] The traces shown in Figure 1 are values of q_{zz} calculated as a function of ∠L–M–L for two different metal–ligand distances corresponding to the $LiNO_3$ and $NaNO_3$ structures. As required by ideal octahedral symmetry, the value of q_{zz} is zero at an angle of 90° for both traces.[18–20] We note that an elongated ML_6 unit has a negative value for q_{zz} when each ligand site is modeled with a negative charge. Because of the 3-fold symmetry in this example, another NMR parameter called the asymmetry parameter, η,[17] will always be zero and will not be discussed further.

There are some problems with the point charge model. First, there is an ambiguity in the charge to be used to model a ligand. While there is a tendency to use a negative charge to represent a ligating oxygen atom, based perhaps upon the concept of a formal oxidation state, averaging of the $1/r^3$ electric field gradient operator may actually emphasize the oxygen nuclear charge more than the oxygen core and valence electrons; hence, the oxygen may best be represented by a partial positive charge. Second, there is the issue of polarization of the core and valence electrons on the quadrupolar nucleus by the surrounding point charges. In molecular orbital calculations that use an extended basis set (double ζ plus one higher angular momentum orbital), most polarization effects are automatically included.[24,25] However, the simple point charge model does not allow for polarization. In the early history of NQR, polarization was estimated using Sternheimer antishielding factors which were obtained from atomic Hartree–Fock wave functions.[26] On the basis of tabulated values for the Sternheimer antishielding factors, polarization affects the magnitude but, for most ions, does not change the sign of the quadrupolar coupling constant.[2] Because the values of the Sternheimer antishielding factors are approximate, we do not include this effect in the point charge model. In summary, we intend to use the point charge model only for a qualitative analysis to assess the sign of the effective charge on the ligating oxygens. A third problem is the issue of termination of the sum at the first coordination sphere.[2,25] Here, the sum is terminated early for convenience and in recognition of the problems mentioned above.

Table 1. Crystal, Experimental, and Refinement Data for Lithium Nitrate

mol formula	$LiNO_3$
fw	68.95
a, Å	4.6920(3)
c, Å	15.2149(13)
V, Å^3	290.08(4)
Z	6
D_{calcd}, g cm^{-3}	2.368
radiation	Mo Kα
λ, Å	0.710 73
cryst syst	trigonal, hexagonal axes
space group	$R\bar{3}c$
μ, cm^{-1}	2.3
cryst dimens, mm	0.18 × 0.52 × 0.83
color	colorless
min rel transm, %	93.51
temp, °C	24
scan type	ω–2θ
θ limits, deg	1–60
no. of reflcns	488
no. of obsd reflcns	305
observn criterion	$I > 3\sigma(I)$
no. of parameters refined	11
R $(=\sum\lvert\Delta F\rvert/\sum F_o)$	0.030
R_w $(=(\sum w(\Delta F)^2/\sum wF^2)^{1/2})$	0.046
max resid density, e Å^{-3}	0.31
min resid density, e Å^{-3}	−0.18

The conversion factor between the quadrupole coupling constant in SI units and the electric field gradient is given by

$$e^2 q_{zz} Q/h = q'_{zz} \frac{e^2 Q}{4\pi\epsilon_0 a_0^3\, h} \qquad (2)$$

where the field gradient, q'_{zz}, is in atomic units, *e* is the electric charge in coulombs, ϵ_0 is the vacuum permittivity, a_0 is the Bohr radius in meters, and *h* is Planck's constant. *Q* is obtained from experimental measurements of quadrupole coupling constants in atoms or small molecules and combined with high-quality atomic or molecular orbital calculations;[27] the literature was recently reviewed.[28]

Experimental Section

A crystal of $LiNO_3$ (Aldrich) was grown from a melt and mounted in a capillary in a nitrogen-filled glovebag. While the crystal was not entirely single, the diffraction pattern from the predominant individual was well resolved from other scattering. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer equipped with Mo Kα radiation and a graphite monochromator. Data reduction included corrections for Lorentz, polarization, background, and absorption effects. Absorption corrections were based on ψ scans. The structure was refined by full-matrix least squares procedures based on *F*. Calculations were carried out using the Enraf-Nonius MolEN programs.[29] Crystal, experimental, and refinement data are given in Table 1. Atomic coordinates are listed in Table 2, and selected distances and angles are shown in Figure 2.

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Table 2. Coordinates and Equivalent Isotropic Thermal Parameters for Lithium Nitrate

atom	x	y	z	B_{eq},[a] Å^2
Li	0	0	0	1.62(4)
N	0	0	$^1/_4$	0.807(9)
O	0.2667(1)	0	$^1/_4$	1.12(1)

[a] The equivalent isotropic thermal parameter is defined by the equation $B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$.

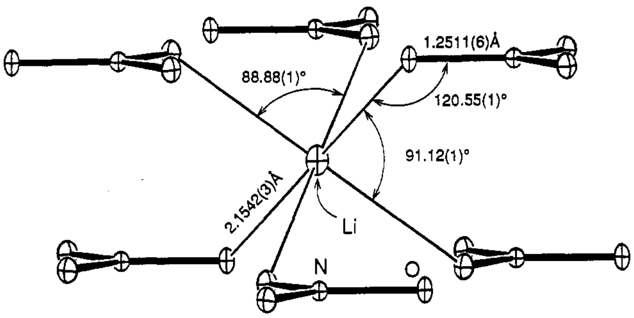

Figure 2. Crystal structure of lithium nitrate and selected distances and angles.

Table 3. Electric Field Gradients at Selected Sites

site	$e^2q_{zz}Q/h$, MHz	Conversion factor, MHz au^{-1}	q_{zz}, atomic units	Q, 10^{-31} m^2 [a]
$^7LiNO_3$	+0.0392[b]	−9.422	−0.0042	−40.1
$^{23}NaNO_3$	−0.334[c]	23.64	−0.0141	100.6(20)
$[O_3{}^{27}AlOH]^{4-}$	+11.17[d]	32.97	0.3388	140.3(10)
$[O_5{}^{27}AlOH]^{8-}$	+6.716[d]	32.97	0.2037	140.3(10)
$[Ph_4P][^2HW_2(CO)_{10}]$	0.0541[e]	0.672	0.0805	2.860(15)

[a] We take our Q's from ref 28. [b] References 1 and 2. [c] Reference 8. [d] Reference 15 (corrected for sign error). [e] Reference 17 (sign is believed to be positive).

Results and Discussion

$LiNO_3$ is isomorphous with calcite and $NaNO_3$, consisting of alternate layers of lithium ions and planar nitrates. The coordination of Li by six nitrate ions is shown in Figure 2. The nitrate groups are arranged in such a way that all those in a given layer differ in orientation by 60° from the nitrates in adjacent nitrate layers. Lithium is coordinated by six oxygen atoms in a trigonally-elongated octahedron. The octahedron is created by three oxygen atoms in nitrates in one layer and three nitrates in an adjacent layer. The lithium sites have $\bar{3}$ (S_6) symmetry and, for the six oxygens coordinated to lithium, differ slightly from ideal octahedral geometry. The LiO_6 unit is elongated such that the layer-to-layer ∠O–Li–O = 91.12(1)°. The Li–O distance is 2.1542(3) Å. Other atoms are more distant from lithium; the closest nitrogen approach is 2.9910(3) Å, and the next closest oxygen approach is 3.2421(3) Å. The structure of $NaNO_3$ at room temperature is isomorphous with that of $LiNO_3$. The NaO_6 unit is slightly elongated such that ∠O–Na–O = 90.56(3)°. The Na–O distance is 2.4049(8) Å.[13]

By converting from the quadrupole coupling constant to the electric field gradient, one can compare the data for $LiNO_3$ with that of other sites. The objective here is to assess the range and sign of electric field gradients. Some representative values for several quadrupolar nuclei are listed in Table 3. The electric field gradient at Li in $LiNO_3$ is near zero, as expected for the nearly perfect local octahedral symmetry about Li. The small remaining electric field gradient is negative, in agreement with the point charge analysis for the LiO_6 unit, provided the effective charges on the oxygens are negative (see Figure 1). Interestingly, the magnitude of the electric field gradient at the Na nucleus in $NaNO_3$ is larger than that for the Li nucleus even though the Na site in $NaNO_3$ is closer to octahedral symmetry relative to Li in $LiNO_3$; the magnification of the electric field gradient created by the ligating oxygen atoms is attributed to polarization of the Na core and valence electrons, i.e, the Sternheimer antishielding effect.[2,26] The experimental value of q_{zz} for Na is 11-fold larger than is predicted by the point charge model. Because it is difficult to reliably integrate the polarization effects into a point charge model, application of point charge moodels is generally limited to qualitative analyses or to sites for which polarization is minimal, for example, deuterium.[17]

Upon distortion of the local symmetry from perfect octahedral or tetrahedral, the magnitude of the field gradient increases. Recently, Huggins and Ellis[15] calculated electric field gradients at Al sites in a number of aluminum oxide model clusters using the GAUSSIAN 90 program and a D95 basis set.[22,24] For Al, the D95 basis set is a double-ζ basis set which obviates the need for a Sternheimer correction factor; thus, some polarization effects are included in this calculation, a significant advantage over the point charge model. However, even with a double-ζ basis set, there are substantial differences between calculated and experimental electric field gradients such that the calculations are best used to search for trends connecting spectroscopy with structure rather than exact matches. Listed in Table 3 are results for tetrahedral and octahedral hydroxyoxyaluminas from the Huggins and Ellis work. For both Al sites, the asymmetric environment caused by the hydroxy ligand yields a nonzero value for the electric field gradient. The magnitude is larger for the tetrahedral species, and this much can be understood from the perspective of the point charge model. For the tetrahedral species, the hydroxy ligand is one of four ligands about the Al site whereas, for the octahedral species, it is one of six ligands and, in the simple summation of point charges, will have a diluted effect. In more complex aluminum oxide species, i.e. dimers, the sign of the calculated electric field gradient is sometimes found to be negative. The point is that the sign of the ^{27}Al quadrupole coupling constant is related to local structure.

Conclusions

The very low temperature work of Kuhns and Waugh that yielded directly the sign of the ^7Li quadrupole coupling constant is likely just the first of many such works. Very high magnetic field, very low temperature NMR spectrometers are being planned (National High Magnetic Field Laboratory) or are under construction (LSU).[30] Given a wealth of data, especially ^{27}Al results, the task then becomes establishing the connection between spectroscopy and structure either with a simple point charge model as used herein or with extensive lattice sums, as used for bifluoride salts by Bacskay and Gready.[25]

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Supplementary Material Available: A table of anisotropic thermal parameters (1 page). Ordering information is given on any current masthead page.

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