

**Calculations of the EFG tensor in DTN using the GIPAW
method with CASTEP and Quantum Espresso software**
and applications of DFT to NQR spectroscopy

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JAN 2015 Department of Physics - UF

Calculations of the EFG tensor in DTN using the GIPAW method with CASTEP and Quantum Espresso software

One important difference between NQR and NMR is that for NQR, the transition frequency is site specific and cannot be chosen by the experimenter. In NMR studies, the excitation frequency of the nucleus is just the gyromagnetic ratio times the applied field. Thus, the difficulty in NMR is controlling the uniformity of the applied static \mathbf{B} . However, the experimenter is free to choose an operating frequency by adjusting \mathbf{B} . For NQR, the transition frequency is proportional to the electric field gradient (EFG) at the nuclear site, which is entirely a property of the substance and a function of temperature. While it is theoretically possible to apply a prescribed EFG in the lab, it is unfeasible as the EFG's in crystal structures are often on the order of many kV/m^2 . Thus the particular difficulty in NQR spectroscopy is *locating the resonance in the first place*, which is difficult if not hopeless if the apparatus runs at a fixed frequency and the search space is several orders of magnitude in frequency.

The home made pulsed superheterodyne spectrometer used in the trial experiments has proven to have excellent resolution. However, it has essentially no ability to perform frequency sweeps as is done in continuous wave methods. The operator must choose a relatively narrow band (< 1 MHz) to target, and design a custom bridge, tank, and receiver configuration just for small band. Band switching is non-trivial with high resolution pulsed techniques.

At one time, it was not possible to calculate the EFG for all but the simplest of structures. However, DFT calculations have become very potent and accessible in the last decade. Beginning in June of 2013, Calculations of the EFG tensor in *dichloro-tetrakis-thiourea-nickel* $\text{NiCl}_2[\text{SC}(\text{NH}_2)_2]_4$ were made using the GIPAW method with closed source *CASTEP* software (by then graduate student Dr. Tim Green at Oxford University, with advisor Dr. Jonathan = Yates). Then in October of 2013, Dr. Ari Seitsonen and I repeated the calculation at ETH in Zurich using the open source DFT-GIPAW package *Quantum Espresso* (QE).

The two calculations show good agreement in many respects and indicate that the ^{35}Cl resonance frequencies in DTN are likely about an order of magnitude lower than initially believed. Because chlorine NQR transitions occurred around 30 MHz in both para-dichlorobenze and NaClO_3 , DTN was initially thought to be likely to show ^{35}Cl NQR in the 29-31 MHz band. This was tested first by Robert Baker (REU Student, 2010) and then in 2012-2013 by myself to no avail.

There is no particular reason ^{35}Cl should have to have a resonance in this 30 MHz band. ^{35}Cl NQR measurements have been made in many materials below 18 MHz and above 60 MHz. A high degree of symmetry in a given structure can result in very low NQR frequencies, with correspondingly very poor S/N. Though all nuclei with spin $S \geq 1$ are guaranteed to have at least one non-zero NQR transition frequency, NQR is not always found. This is likely due to poor S/N when the EFG is small and the transition frequency is very low.

Evidence for the validity of the DFT calculations is that the prediction for NaClO_3 ^{35}Cl NQR matches observation remarkably well.

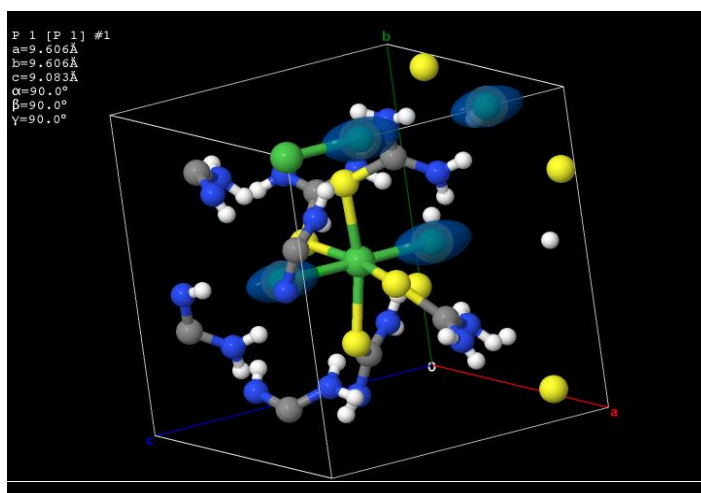


Figure 1 – unit cell of DTN with EFG level curves surrounding ^{35}Cl .

Additionally, since both DFT packages output the full EFG tensor, the NQR transitions for ^{14}N were also predicted by the same calculations. There are sixteen nitrogen nuclei in each unit cell of DTN (right). DTN contains 4 independent thiourea molecules in each unit cell, each having 4 nitrogen centers. The NQR frequencies calculated by CASTEP and QE for ^{14}N in DTN match very well with those observed in pure thiourea from literature (David H. Smith and R. M. Cotts). The paper by Smith and Cotts quotes NQR in ^{14}N in pure thiourea NQR at 2.6 MHz and 2.0 MHz for inequivalent sites at room temperature. In the absence of any DFT calculation, the ^{14}N resonance in pure thiourea would be a best first guess as to the NQR transition for ^{14}N in DTN.

As the NQR frequency at a given nuclear site is directly proportional to V_{zz} (the electric field gradient, or stretching), crystals with a high degree of symmetry will have low NQR frequencies. Inspection of the crystal structure superficially indicates a widely symmetric nuclear distribution about the chlorine sites, as the thiourea groups are distributed symmetrically and the structure parameters show each Cl is roughly equidistant to both adjacent Ni nuclei.

The quadrupole coupling constant and NQR transitions

The quadrupole coupling constant C_q is defined as

$$C_q = e \cdot V_{zz} \cdot Q / h \quad [1]$$

where V_{zz} is the largest absolute eigenvalue, e is the electron charge, Q is the quadrupole moment and h is Planck's constant.

We consider a nucleus of spin S and define

$$A = e V_{zz} Q / (4S(2S-1)) \quad [2]$$

where S is spin and Q is the quadrupole moment. Then the NQR frequency or (frequencies) are given by

$$f_{\text{nqr}} = 3 |A| / h (2 |m| + 1) \quad [3]$$

where m is the lowest of the two levels m and $m+1$ over which a transition has occurred. For integral spins there are S unique transitions. For half integral spins there are $I - 1/2$ unique transitions.

NQR is observed in nuclei with $I=3/2$, $I=5/2$ and $I=7/2$. For $I=1/2$, there are no transitions. The $I=5/2$ and $I=7/2$ are perhaps more complicated, but for $I=3/2$ there is a degeneracy that causes there to be one frequency of half the quadrupole coupling constant, which makes the single transition frequency in the case of $I=3/2$ equal to one half the quadrupole coupling constant $C_q = e V_{zz} Q / h = e^2 Q q / h$.

NQR Frequencies for half-integral spins

Chlorine has $I=3/2$ so there is only 1 transition. Using $I=3/2$ in the formula above, we obtain

$$f_{\text{nqr}} = (1/2) e V_{zz} Q / h = (1/2) C_q \quad [4]$$

for axially symmetric field gradients. For non-axially symmetric gradients, we define the asymmetry parameter $\eta = (V_{xx} - V_{yy}) / V_{zz}$. $\eta=0$ in the axially symmetric case, where V_{zz} is the only nonzero component. When η is non-zero, the transitions for $I=3/2$ are

$$f_{\text{nqr}} = (1/2) eV_{\text{zz}}Q/h * (1 + 1/3 \eta^2)^{1/2} \quad [5]$$

For $l=5/2$ and $\eta=0$ there are of course 2 lines

$$f_{\text{nqr}[5/2 \rightarrow 3/2]} = (3/10) eV_{\text{zz}}Q/h \quad [6]$$

$$f_{\text{nqr}[3/2 \rightarrow 1/2]} = (3/20) eV_{\text{zz}}Q/h \quad [7]$$

since in the axially symmetric case, there are just $S - 1/2$ transitions.

NQR frequencies for integral spins

For integral spins, we use the formula [2] again. For $l=1$ and an axially symmetric field gradient ($\eta=0$), the NQR transition frequency is

$$f_{\text{nqr}} = (3/4) eV_{\text{zz}}Q/h = (3/4) C_q \quad [8]$$

For non-axial field gradients, there are two transitions for $l=1$ given by

$$f_{+} = (3/4) eV_{\text{zz}}Q/h (1 + \eta/3) \quad [9]$$

$$f_{-} = (3/4) eV_{\text{zz}}Q/h (1 - \eta/3) \quad [10]$$

RESULTS

Castep was used to calculate the EFG tensor for each atom in sodium chlorate. Like any DFT calculation, the computed coupling constant corresponds to the value of C_q at absolute zero. The results for the relaxed case are given below.

NaClO₃ - CASTEP

CASTEP C_q DATA (sodium chlorate – 35Cl)

Cl 1 C_q :	57.6881 (MHz)	f_{nqr} :	28.8441 (MHz)
Cl 2 C_q :	58.1146 (MHz)	f_{nqr}:	29.0573 (MHz)
Cl 3 C_q :	57.6881 (MHz)	f_{nqr} :	28.8441 (MHz)
Cl 4 C_q :	57.6882 (MHz)	f_{nqr} :	28.8440 (MHz)

EXPERIMENTAL C_q DATA (sodium chlorate – room temperature NQR)

35Cl f_{nqr} :	29.9366 MHz;	C_q :	59.8732 MHz
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DTN – CASTEP AND QE

CASTEP EFG DATA (DTN – 35Cl) – relaxed

Cl 1	Cq: 8.4298 (MHz)	Eta: 0.1272
Cl 2	Cq: 0.1705 (MHz)	Eta: 0.5898
Cl 3	Cq: 0.1866 (MHz)	Eta: 0.5340
Cl 4	Cq: 8.4513 (MHz)	Eta: 0.1264

QE EFG DATA (DTN – 35Cl) - relaxed

Cl 1	Cq= 9.4969 MHz	Eta=-0.00000
Cl 2	Cq= -0.9388 MHz	Eta= 0.00000
Cl 3	Cq= 9.4869 MHz	Eta= 0.00000
Cl 4	Cq= -0.9298 MHz	Eta= 0.00000

CASTEP EFG DATA (DTN – 35Cl) – unrelaxed

Cl 1	Cq: -15.7965 (MHz)	Eta: 0.0089
Cl 2	Cq: -16.9778 (MHz)	Eta: 0.0048
Cl 3	Cq: -16.9515 (MHz)	Eta: 0.0048
Cl 4	Cq: -15.8271 (MHz)	Eta: 0.0089

CASTEP EFG DATA (DTN – 14N) – relaxed

N 1	Cq: -3.7067 (MHz)	Eta: 0.3400
N 2	Cq: -3.3560 (MHz)	Eta: 0.4226
N 3	Cq: -3.6918 (MHz)	Eta: 0.3463
N 4	Cq: -3.3621 (MHz)	Eta: 0.4256
N 5	Cq: -3.6917 (MHz)	Eta: 0.3468
N 6	Cq: -3.3533 (MHz)	Eta: 0.4231
N 7	Cq: -3.7068 (MHz)	Eta: 0.3410
N 8	Cq: -3.3535 (MHz)	Eta: 0.4228
N 9	Cq: -3.6920 (MHz)	Eta: 0.3466
N 10	Cq: -3.3611 (MHz)	Eta: 0.4251
N 11	Cq: -3.7067 (MHz)	Eta: 0.3409
N 12	Cq: -3.3524 (MHz)	Eta: 0.4230
N 13	Cq: -3.7073 (MHz)	Eta: 0.3399
N 14	Cq: -3.3563 (MHz)	Eta: 0.4225
N 15	Cq: -3.6927 (MHz)	Eta: 0.3469
N 16	Cq: -3.3523 (MHz)	Eta: 0.4227

CASTEP EFG DATA (DTN – 14N) – unrelaxed

N1	Cq: 3.0165 (MHz)	Eta: 0.8408
N2	Cq: -2.6850 (MHz)	Eta: 0.9198
N3	Cq: 3.0154 (MHz)	Eta: 0.8423
N4	Cq: -2.6885 (MHz)	Eta: 0.9216
N5	Cq: 3.0164 (MHz)	Eta: 0.8419
N6	Cq: -2.6841 (MHz)	Eta: 0.9213
N7	Cq: 3.0179 (MHz)	Eta: 0.8414
N8	Cq: -2.6854 (MHz)	Eta: 0.9186
N9	Cq: 3.0188 (MHz)	Eta: 0.8421
N10	Cq: -2.6833 (MHz)	Eta: 0.9207
N11	Cq: 3.0214 (MHz)	Eta: 0.8411
N12	Cq: -2.6802 (MHz)	Eta: 0.9177
N13	Cq: 3.0199 (MHz)	Eta: 0.8406
N14	Cq: -2.6798 (MHz)	Eta: 0.9189
N15	Cq: 3.0198 (MHz)	Eta: 0.8417
N16	Cq: -2.6788 (MHz)	Eta: 0.9203

QE EFG DATA (DTN – 14N) - relaxed

N 45	Cq= -3.5069 MHz	eta= 0.36826
N 46	Cq= -3.5084 MHz	eta= 0.36870
N 47	Cq= -3.5084 MHz	eta= 0.36870
N 48	Cq= -3.1864 MHz	eta= 0.38355
N 49	Cq= -3.1864 MHz	eta= 0.38355
N 50	Cq= -3.1880 MHz	eta= 0.38408
N 51	Cq= -3.1864 MHz	eta= 0.38355
N 52	Cq= -3.1864 MHz	eta= 0.38355
N 53	Cq= -3.1880 MHz	eta= 0.38408
N 54	Cq= -3.5069 MHz	eta= 0.36826
N 55	Cq= -3.5084 MHz	eta= 0.36870
N 56	Cq= -3.5084 MHz	eta= 0.36870
N 57	Cq= -3.5069 MHz	eta= 0.36826
N 58	Cq= -3.1880 MHz	eta= 0.38408
N 59	Cq= -3.1880 MHz	eta= 0.38408
N 60	Cq= -3.5069 MHz	eta= 0.36826
Q= 2.04 1e-30 m^2		

Calculating NQR frequencies from simulation data

We can calculate the expected NQR transition frequencies for ^{14}N in thiourea using equations [9] and [10] for this non-axial spin 1 case.

We begin by using the data from D. H. Smith, R. M. Cotts (October 1964, J. Chem. Phys, vol 41, Num. 8). There C_q is provided, as well as the asymmetry parameter, from which we can obtain 4 NQR transition frequencies at 0K (2 transitions for each of 2 inequivalent sites):

KNOWN ^{14}N NQR TRANSITIONS FROM Smith, Cotts, known C_q (THIOUREA, 0 K)

N 1	C_q : 3099.6 (KHz)	Eta: .3903	f_{+} : 2.627 MHz
N 2	C_q : 3099.6 (KHz)	Eta: .3903	f_{-} : 2.022 MHz
N 3	C_q : 3121.6 (KHz)	Eta: .3954	f_{+} : 2.649 MHz
N 4	C_q : 3121.6 (KHz)	Eta: .3954	f_{-} : 2.032 MHz

```
In[1] :=
{
  {
    3099.6*3/4*(1 + .3903/3),
    3099.6*3/4*(1 - .3903/3)
  }, {
    3121.6*3/4*(1 + .3954/3),
    3121.6*3/4*(1 - .3954/3)
  }
}

Out[1] :=
{{2627.14, 2022.26}, {2649.77, 2032.63}}
```

We should want to apply the same method to the values obtained through GIPAW for the 16 nitrogen sites in DTN. CASTEP and QE both predicted two inequivalent ^{14}N sites in DTN (instead of 16) which is in line with Cotts' findings in pure thiourea. This suggests that the EFG at the ^{14}N sites in DTN should be roughly similar to that found in pure thiourea.

CASTEP EFG DATA (DTN – ^{14}N , 0 K) – relaxed

N 1	$ C_q $: 3.70 MHz	Eta: .3450	$f_{+}=3.094$ MHz; $f_{-}=2.456$ MHz
N 2	$ C_q $: 3.35 MHz	Eta: .4235	$f_{+}=2.867$ MHz; $f_{-}=2.157$ MHz

```
In[2] :=
{
  {
    3700*3/4*(1 + .3450/3),
    3700*3/4*(1 - .3450/3)
  }, {
    3350*3/4*(1 + .4235/3),
    3350*3/4*(1 - .4235/3)
  }
}

Out[2] :=
{{3094.13, 2455.88}, {2867.18, 2157.82}}
```

QE EFG DATA (DTN – 14N, 0 K)

N 1	Cq = 3.5084 MHz;	Eta= 0.36870;	f_+=2.954 MHz;	f_-=-2.308 MHz
N 2	Cq = 3.1864 MHz;	Eta= 0.38355;	f_+=2.695 MHz;	f_-=-2.083 MHz

```
In[3] :=
{
  {
    3508*3/4*(1 + .3687/3),
    3508*3/4*(1 - .3687/3)
  }, {
    3186*3/4*(1 + .3836/3),
    3186*3/4*(1 - .3846/3)
  }
}
Out[3]:=
{{2954.35, 2307.65}, {2695.04, 2083.17}}
```

Chlorine NQR in DTN from GIPAW

Recall that for chlorine, $I=3/2$ and we calculate the transition frequencies with equation [5]

$$f_{\text{nqr}} = (1/2) eV_{zz}Q/h * (1 + 1/3 \eta^2)^{(1/2)} \quad [5]$$

CASTEP EFG DATA (DTN – 35Cl, 0 K) – relaxed

Cl 1	Cq: 8.4298 (MHz)	Eta: 0.1272	f_nqr = 4.226 MHz;
Cl 2	Cq: 0.1705 (MHz)	Eta: 0.5898	f_nqr = 94.85 KHz;
Cl 3	Cq: 0.1866 (MHz)	Eta: 0.5340	f_nqr = 101.84 KHz;
Cl 4	Cq: 8.4513 (MHz)	Eta: 0.1264	f_nqr = 4.236 MHz;

```
In[4] :=
{
  {
    8430/2*(1 + .1272^2/3)^(1/2),
    8451/2*(1 + .1264^2/3)^(1/2)
  }, {
    170/2*(1 + .5898^2/3),
    186/2*(1 + .5340^2/3)
  }
}
Out[4]:=
{{4226.35, 4236.74}, {94.8561, 101.840}}
```

The calculation of the EFG at the 35Cl sites in DTN showed the largest disparity between the results of CASTEP and QE. The obtained values of Cq are similar, but QE returned $\eta=0$ for 35Cl in DTN, where as CASTEP returned significant non-axial components and η as high as .5898 for one of the chlorine sites.

QE EFG DATA (DTN – 35Cl) - relaxed

Cl 1	Cq= 9.4969 MHz	Eta=0.00000	f_nqr = 4.750 MHz
Cl 2	Cq= -0.9388 MHz	Eta=0.00000	f_nqr = 469 KHz
Cl 3	Cq= 9.4869 MHz	Eta=0.00000	f_nqr = 4.650 MHz
Cl 4	Cq= -0.9298 MHz	Eta=0.00000	f_nqr = 465 KHz

```
In[5] :=
{
  {
    9500/2*(1 + 0^2/3)^(1/2),
    9300/2*(1 + 0^2/3)^(1/2)
  }, {
    939/2*(1 + 0^2/3),
    930/2*(1 + 0^2/3)
  }
}
Out[5] :=
{{4750, 4650}, {469, 465}}
```

For NaClO₃, CASTEP arrived at an average NQR frequency (over 4 sites) of 28.9 MHz, in direct support of experimental results well known for over 40 years.

For chlorine in DTN, CASTEP found a non-axial EFG at the 35Cl sites and calculated NQR at 8.5 MHz (unrelaxed) and 4.2 MHz (relaxed), along with a very low resonance on the order of 100 KHz. In contrast, QE found no asymmetry parameter for 35Cl in DTN. QE does however still roughly agree with CASTEP as QE predicts 35Cl NQR in DTN at 4.7 MHz and around 500 KHz.

For 14N in DTN, the CASTEP relaxed calculation yields $f_{+} = 2.456$ MHz and $f_{-} = 2.157$ MHz for inequivalent sites in the relaxed EFG calculation for 14N. QE agrees well with $f_{+} = 2.308$ MHz $f_{-} = 2.083$ MHz. In pure thiourea, the corresponding known transitions for 14N NQR are $f_{+} = 2.627$ MHz and $f_{-} = 2.022$ MHz.

DATA SUMMARY

14N

CALCULATED 14N NQR TRANSITIONS IN DTN
FROM CASTEP RELAXED EFG DATA
DTN – 14N NQR – CASTEP – 0K

N1	Cq : 3.70 MHz; Eta: .3450; f ₊ : 3.094 MHz
N1	Cq : 3.70 MHz; Eta: .3450; f ₋ : 2.456 MHz
N2	Cq : 3.35 MHz; Eta: .4235; f ₊ : 2.867 MHz
N2	Cq : 3.35 MHz; Eta: .4235; f ₋ : 2.157 MHz

CALCULATED 14N NQR TRANSITIONS IN DTN FROM
QE RELAXED EFG DATA
DTN – 14N NQR – QE – 0 K

N1	Cq : 3.5084 MHz; Eta: 0.36870; f ₊ : 2.954 MHz
N1	Cq : 3.5084 MHz; Eta: 0.36870; f ₋ : 2.308 MHz
N2	Cq : 3.1864 MHz; Eta: 0.38355; f ₊ : 2.695 MHz
N2	Cq : 3.1864 MHz; Eta: 0.38355; f ₋ : 2.083 MHz

CALCULATED 14N NQR TRANSITIONS IN PURE THIOUREA
FROM KNOWN COUPLING CONSTANT
Smith, Cotts – THIOUREA - 0 K

N1	Cq: 3.0996 MHz; Eta: .3903; f ₊ : 2.627 MHz
N2	Cq: 3.0996 MHz; Eta: .3903; f ₋ : 2.022 MHz
N3	Cq: 3.1216 MHz; Eta: .3954; f ₊ : 2.649 MHz
N4	Cq: 3.1216 MHz; Eta: .3954; f ₋ : 2.032 MHz

35Cl

CALCULATED 35Cl NQR TRANSITIONS IN DTN
FROM CASTEP RELAXED EFG DATA
DTN – 35Cl NQR – CASTEP – 0 K

Cl 1	Cq: 8.4298 MHz; Eta: 0.1272; f _{nqr} : 4.226 MHz;
Cl 2	Cq: 0.1705 MHz; Eta: 0.5898; f _{nqr} : 94.85 KHz;
Cl 3	Cq: 0.1866 MHz; Eta: 0.5340; f _{nqr} : 101.84 KHz;
Cl 4	Cq: 8.4513 MHz; Eta: 0.1264; f _{nqr} : 4.236 MHz;

CALCULATED 35Cl NQR TRANSITIONS IN DTN
FROM QE RELAXED EFG DATA
DTN – 35Cl NQR – QE – 0 K

Cl 1	Cq : 9.4969 MHz; Eta: 0.00000; f _{nqr} : 4.750 MHz
Cl 2	Cq : 0.9388 MHz; Eta: 0.00000; f _{nqr} : 469 KHz
Cl 3	Cq : 9.4869 MHz; Eta: 0.00000; f _{nqr} : 4.650 MHz
Cl 4	Cq : 0.9298 MHz; Eta: 0.00000; f _{nqr} : 465 KHz

CALCULATED 35Cl NQR TRANSITIONS IN NaClO₃
FROM CASTEP RELAXED EFG DATA
SODIUM CHLORATE – 35Cl NQR – CASTEP – 0 K

Cl 1	Cq: 57.6881 MHz f _{nqr} : 28.8441 (MHz)
Cl 2	Cq: 58.1146 MHz f _{nqr} : 29.0573 (MHz)
Cl 3	Cq: 57.6881 MHz f _{nqr} : 28.8441 (MHz)
Cl 4	Cq: 57.6882 MHz f _{nqr} : 28.8440 (MHz)

EXPERIMENTAL 35Cl NQR TRANSITIONS in NaClO₃
SODIUM CHLORATE
35Cl NQR – EXPERIMENT – ROOM TEMPERATURE

35Cl	f _{nqr} : 29.9366 MHz; Cq: 59.8732 MHz (? Temperature)
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14N

CALCULATED 14N NQR TRANSITIONS IN DTN

FROM CASTEP RELAXED EFG DATA

DTN – 14N NQR – CASTEP – 0K

N 1	Cq :	3.70 MHz;	Eta: .3450;	f ₊ : 3.094 MHz
N 1	Cq :	3.70 MHz;	Eta: .3450;	f ₋ : 2.456 MHz
N 2	Cq :	3.35 MHz;	Eta: .4235;	f ₊ : 2.867 MHz
N 2	Cq :	3.35 MHz;	Eta: .4235 ;	f ₋ : 2.157 MHz

CALCULATED 14N NQR TRANSITIONS IN DTN FROM

QE RELAXED EFG DATA

DTN – 14N NQR – QE – 0K

N 1	Cq :	3.5084 MHz;	Eta: 0.36870;	f ₊ : 2.954 MHz
N 1	Cq :	3.5084 MHz;	Eta: 0.36870;	f ₋ : 2.308 MHz
N 2	Cq :	3.1864 MHz;	Eta: 0.38355;	f ₊ : 2.695 MHz
N 2	Cq :	3.1864 MHz;	Eta: 0.38355;	f ₋ : 2.083 MHz

CALCULATED 14N NQR TRANSITIONS IN PURE THIOUREA

FROM KNOWN COUPLING CONSTANT

Smith, Cotts – THUOUREA - 0 K

N 1	Cq:	3.0996 (MHz);	Eta: .3903;	f ₊ : 2.627 MHz
N 2	Cq:	3.0996 (MHz);	Eta: .3903;	f ₋ : 2.022 MHz
N 3	Cq:	3.1216 (MHz);	Eta: .3954;	f ₊ : 2.649 MHz
N 4	Cq:	3.1216 (MHz);	Eta: .3954;	f ₋ : 2.032 MHz

35Cl

CALCULATED 35Cl NQR TRANSITIONS IN DTN FROM CASTEP RELAXED EFG DATA

DTN – 35Cl NQR – CASTEP – 0 K

Cl 1	Cq: 8.4298 (MHz);	Eta: 0.1272;	f_nqr: 4.226 MHz;
Cl 2	Cq: 0.1705 (MHz);	Eta: 0.5898;	f_nqr: 94.85 KHz;
Cl 3	Cq: 0.1866 (MHz);	Eta: 0.5340;	f_nqr: 101.84 KHz;
Cl 4	Cq: 8.4513 (MHz);	Eta: 0.1264;	f_nqr: 4.236 MHz;

CALCULATED 35Cl NQR TRANSITIONS IN DTN FROM QE RELAXED EFG DATA

DTN – 35Cl NQR – QE – 0 K

Cl 1	Cq : 9.4969 MHz;	Eta: 0.00000;	f_nqr: 4.750 MHz
Cl 2	Cq : 0.9388 MHz;	Eta: 0.00000;	f_nqr: 469 KHz
Cl 3	Cq : 9.4869 MHz;	Eta: 0.00000;	f_nqr: 4.650 MHz
Cl 4	Cq : 0.9298 MHz;	Eta: 0.00000;	f_nqr: 465 KHz

CALCULATED 35Cl NQR TRANSITIONS IN NaClO₃ FROM CASTEP RELAXED EFG DATA

SODIUM CHLORATE – 35Cl NQR – CASTEP – 0 K

Cl 1	Cq: 57.6881 (MHz)	f_nqr: 28.8441 (MHz)
Cl 2	Cq: 58.1146 (MHz)	f_nqr: 29.0573 (MHz)
Cl 3	Cq: 57.6881 (MHz)	f_nqr: 28.8441 (MHz)
Cl 4	Cq: 57.6882 (MHz)	f_nqr: 28.8440 (MHz)

EXPERIMENTAL 35Cl NQR TRANSITIONS in NaClO₃

SODIUM CHLORATE

35Cl NQR – EXPERIMENT – ROOM TEMPERATURE

35Cl	f_nqr: 29.9366 MHz;	Cq: 59.8732 MHz
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(not T-corrected)

The difference between the relaxed and unrelaxed calculation lies in the structural data preparation. In the unrelaxed case, structure data from direct measurements in literature is fed directly into CASTEP and used. In the relaxed case, the structure parameters itself are adjusted using GIPAW, and then the EFG is calculated.