

Optical Detection of NQR: Crystal Field and Matrix Effects on Halogenated Organic Molecules*

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Electron spin polarization or alignment achieved in the excited triplet state of organic molecules can be transferred into nuclear spin polarization (alignment) during an optical pumping cycle. Due to this effect, quadrupole resonance (NQR) investigations of nuclei with concentrations of 10^{-5} molar are possible in the electronic singlet ground and excited triplet state in one and the same experiment by the applied optical pumping cycle. By this conventional NMR sensitivity is enhanced by several orders of magnitude, enabling investigations of defect site structures in molecular crystals.

1. Introduction

One of the topics in the investigation of the physics of molecular crystals is the change of the crystal field and symmetry due to lattice defects [1, 2]. These defects arise either due to the presence of different molecules at various concentration ratios in mixed molecular crystals or due to lattice strain or dislocations during the crystal growing process. Nuclei with a quadrupolar moment are sensitive to changes in the electric field gradient tensor at the locus of the nuclei. When the crystal field changes all over the crystal or at well defined regions within the crystal lattice this shows up as an intermolecular contribution to the quadrupole resonance frequency.

Usually the intermolecular contributions to the electric field gradient tensor are small as compared to the intramolecular parts, but as has been shown, can nevertheless be investigated especially by chlorine and bromine nuclear quadrupole resonance (NQR) [3].

Of special interest is the situation where crystal field changes are limited to a restricted region of the crystal, so-called defect sites. Usually, conventional NQR fails in the low concentration limit due to sensitivity reasons to investigate these defect sites. On the other hand, the individual quadrupole

nuclei are ideal probes to investigate the defect site structure and its symmetry in quite a detail because each nucleus might feel a different electric field. If it is feasible to gather information from quite a lot of different electric field gradient tensors, it is in principle possible to obtain a crystal field contour plot of the lattice defect in question.

Two conditions have to be met to achieve this goal. The first one is that the NQR sensitivity is high enough to detect small concentrations of quadrupole nuclei. The second one is, that the applied technique is sensitive to only those nuclei which belong to well defined defect sites. Both conditions are ideally met by the method of optically detected NQR (ODNQR) for a variety of halogenated organic molecular crystals. This technique evaluated recently [4, 5] improves the sensitivity by about 5 orders of magnitude as compared to conventional NQR [6]. Moreover, because it is related with well defined optical active defect centers it is exactly sensitive to those nuclei which are closely connected to this defect center. Examples of such investigations of the influence of the crystal field of low concentrated defect sites on the quadrupole transition frequencies will be reported in this contribution.

2. Pumping Scheme of the Optical Detection of NQR

In zero magnetic field experiments the nuclear quadrupole interaction is a first order effect whereas the isotropic and anisotropic hyperfine interaction mix electronic and nuclear spin functions

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only in second order. By this mixing simultaneous electron-nuclear spin transitions become partly allowed. This – as is well known – results in additional lines in the optically detected magnetic resonance (ODMR) spectra which can be observed separately from the pure electronic spin transitions in the optically excited electronic triplet state in the case of the $I = 3/2$ nuclear spins of Cl and Br [5].

When pumping these transitions by saturating microwave fields, the initial selective population of the electronic sublevels – which is due to the symmetry dominated intersystem crossing selection rules – is transferred to the nuclear sublevels. Speaking in terms of spin temperature concepts this means that the nuclear and electronic spin subsystems equalize their temperatures when linked by the “forbidden” transitions. Since electron and nuclear spin lattice relaxation are strongly suppressed at low temperatures (1.5 K) the achieved nuclear spin alignment is conserved after the decay of the triplet state and is stored in the singlet ground state until re-excitation. The re-excitation of molecules which are now in a preferred nuclear spin configuration results in a change of the phosphorescence intensity and a decrease of the “forbidden” ODMR-transition. By subsequent pumping cycles the nuclear spin alignment is further increased, finally reaching an equilibrium value. In our experiments the mean pumping cycle time is in the order of 10 ... 100 s. A more detailed description of this kind of optical pumping cycle, the nuclear alignment and the experimental set-up is given elsewhere [4, 7].

The observed final decrease of the forbidden ODMR transition amounts up to 80% of the initial intensity. By resonant irradiation of NQR frequencies in the ground or excited state this decrease is completely reversed with rf powers of about 0.5 Watt. When sweeping the rf, optically detected NQR (ODNQR) spectra are obtained.

Figure 1 shows such an ODNQR transition of ^{35}Cl for p-dichlorobenzene doped 10^{-4} molar in p-dibromobenzene at 1.5 K. The center frequency is 34.878 MHz. In this special experiment the resonance transition has been measured in two different ways. Open circles represent the intensity change of the ODMR transition as a function of the NQR-frequency. Filled circles at a given rf-power correspond to the rate at which the nuclear spin alignment is destroyed. By this latter method always the true NQR lineshape is observed, whereas the line-

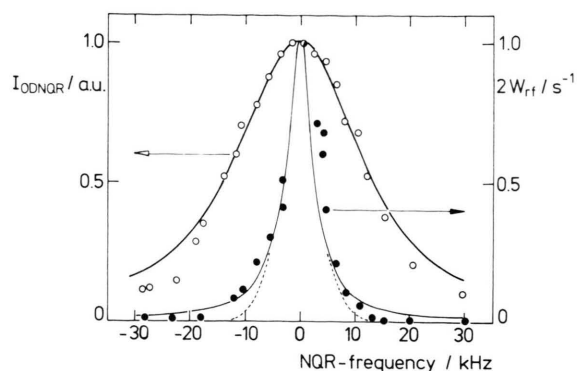


Fig. 1. ODNQR transition in S_0 at 1.5 K for DCB in DBB. Spectra have been obtained as a function of frequency measuring the intensity of the lines (open circles) or the rate of dealignment (closed circles). Full lines correspond to a Lorentz line-shape, dashed lines to a Gauss line-shape. Center frequency is 34.878 MHz.

width connected with the ODNQR intensity is broadened due to the principles of the applied pumping cycle, as will be discussed elsewhere [6].

3. Matrix Effects on the ODNQR of Chlorinated Benzene

The improvement of sensitivity described above makes it possible to investigate the influence of the matrix on NQR resonance frequencies also at very low concentrations. As has been reviewed recently [3], the influence of the crystal field when going from the gas phase to the solid state is two-fold. Firstly, chemically equivalent positions in a molecule become non-equivalent if the molecule enters a crystallographic site which has a lower symmetry than the molecule itself. This is true as well for pure molecular crystals as for molecules diluted in molecular crystals. Secondly, the resonance transitions exhibit a frequency shift. As has been demonstrated this gas-to-crystal shift is in the order of 5% mostly to lower frequencies, whereas the induced differences of resonance frequencies for chemically equivalent positions are about 1% for halogenated benzenes [3].

Additionally to already reported NQR investigations ODNQR offers the possibility to extend the concentration range far below 1% as has not yet been reported for conventional NQR. These very low concentrations are necessary to exclude aggregate formation which cannot be neglected at con-

Table 1. NQR transition frequencies $\nu = 1/2 e^2 q Q (1 + 1/3 \eta^2)^{1/2}$ in MHz for ^{35}Cl .

Guest/Host	$\nu (S_0)$	$\bar{\nu}$	$\Delta\nu_{\text{max}}$
TCB/TCB ^a	36.702, 36.738, 36.843, 36.898	36.795	0.196
TCB/TMB	37.329, 37.348	37.339	0.019
TCP/TCB	36.837, 36.928, 36.969, 37.049	36.946	0.212
TCP/TMB	36.850, 36.941, 36.973, 37.047	36.953	0.197
	37.337, 37.374	37.356	0.037

^a Ref. [8].

centrations of 1% and above. Additionally, also those matrices with a limited solubility can be used. It is obvious that with such low concentrations the amount of material needed is considerably reduced.

Table 1 clearly shows for sym-tetrachlorobenzene (TCB) and sym-tetrachloropyrazine (TCP) that the differences of resonance frequencies of chemically equivalent chlorine positions are dependent on the symmetry of the host matrix. For TCB the appearance of 4 different transition frequencies has already been reported [8] and explained as being due to the triclinic crystal symmetry at temperatures below 77 K. When changing the matrix to sym-tetramethylbenzene (TMB) which is monoclinic also at low temperatures, only two different resonance frequencies are observed, reflecting the fact that a TMB vacancy has inversion symmetry. The same arguments hold for TCP, for which no NQR data have been published yet. For this guest molecule, two distinguishable subsets of resonance frequencies are observed in TCB. These subsets can clearly be assigned because due to the principles of ODNQR, the NQR transitions are preselected by choosing a discrete microwave and/or optical transition, as has been described in the foregoing section. From these additional informations, the subset with the lower $\bar{\nu}$ is assigned to a molecule which is somewhat more influenced by the matrix (e.g. a stronger temperature dependence of optical transitions is observed), but the detailed nature of this “distortion” is not known.

The presented data also show that $\bar{\nu}$ is shifted considerably more to lower frequencies in the halogenated host matrix as compared to the methylated benzene host TMB. At the same time $\Delta\nu_{\text{max}}$ becomes less in TMB by a factor > 5 , again reflecting that the loss in molecular symmetry is induced by the crystal field. From investigations in an external magnetic field it is known [7] that TCP is not enter-

ing the TMB lattice substitutionally but exhibits a rotation in the molecular plane by 4° which is reflected by the two times larger $\Delta\nu_{\text{max}}$ as compared to TCB in TMB.

Contrary to the situation of the tetrahalogenated benzenes, para-dichlorobenzene (DCB) shows up only one resonance transition either at very low or very high concentrations. This is in agreement with the fact that the host matrices p-dibromobenzene (DBB), p-dimethylbenzene (DMB) and DCB itself have inversion symmetry of the lattice vacancy. Matrix effects on DCB have been investigated quite intensively. NQR results are reported for 3.5 mol% DCB in various host matrices [10] with a variation of resonance frequencies not more than ± 25 kHz at 195 K. Our result at 1.5 K with 0.1 mol% DCB in DBB is +47 kHz and is in agreement with +14 kHz reported in [10]. An intensive concentration dependent investigation of chlorobenzenes in bromobenzenes [11, 12] shows only small but very distinct frequency variations and the appearance of a multi-line spectrum at concentrations above 5 and below 95 mol%. From preliminary results [13, 14] on DCB in DBB we believe that such distinct resonance frequencies can be explained by aggregate formation as a function of concentration.

Contrary to the situation of DCB in various hosts where – as already mentioned – only minor frequency shifts relative to pure DCB crystals are reported as a function of the host matrix, the situation is quite contrary for DCB in DMB. This can be recognized from Table 2 where the frequency shifts relative to pure DCB NQR data have been plotted for various concentrations of DCB. The outstanding result is that the frequency shift is more than 1 MHz for a low concentrated DMB crystal, which is for organic molecules by far the largest shift due to crystal field effects reported so far [3]. But also for very high concentrations a shift, which is similar in

Table 2. Difference of ^{35}Cl NQR transition frequencies $\Delta\nu$ in MHz as a function of DCB concentration.

[c]/mol%	$\Delta\nu$	T /[K]
0.1 ^a	1.079	1.5 K
13.4 ^b	–0.095/0.200	195 K
37.5 ^b	–0.055	195 K
98.7 ^b	0.440	

^a DMB [5]. ^b DMB [10].

magnitude compared to the differences of $\alpha(\beta)$ -phase DCB as compared to γ -phase DCB [15] is observed. Additional information is obtained from Ref. [16] which reports the influence of various parasubstituted benzenes doped into DCB, demonstrating that DMB plays a special role concerning the NQR matrix effects on DCB. It should be mentioned that assuming a gas-to-solid shift of $\sim (-5\%)$ for DCB [17], the NQR data of DCB in DMB are very close to the gas phase data. This is supported by a calculation according to a model by Bersohn [18] of the electric field at the position of the DCB chlorine atoms due to C-CH₃, C-Br or C-Cl dipole moments from which it is concluded that the NQR frequencies – opposite to Bersohn's result for trichlorobenzene – should be lowered for halogene containing matrices but should become slightly higher for DMB [19] as compared to gas phase data. However, calculations of this kind suffer from the simplicity of this model. Additionally it has been shown that in some systems frequency shifts are more correlated with volume effects than with electric dipole moments [16]. To get a better insight into a systematic behavior of DCB in DMB careful concentration dependence experiments have to be performed. ODNQR is of special interest in these systems because different molecular aggregates can be preselected via optical transitions [14].

4. Defect Structures in Molecular Crystals

As has already been pointed out in the preceding section for DCB doped with small amounts of guest molecules [16], such doped systems exhibit a broadening or even frequency shift of the NQR resonance transitions. This can be interpreted as an overall crystal strain [16]. This strain is felt by those abundant nuclei being more distant from the doped molecule which is responsible for the creation of the defect center within the molecular crystal. The concentration of those host nuclei which feel the strongest NQR frequency shift because they are next-neighbouring to the guest molecule, is mostly much too low to be detected by conventional NQR. However, those nuclei are most suitable to be detected by ODNQR. If the corresponding difference of resonance frequencies of local and distant nuclei is larger than the linewidth, nuclear spin alignment obtained during an optical pumping cycle

is limited to the next-neighbouring molecules because their resonance frequency is detuned from that of the bulk (undistorted) nuclei. This corresponds to a spin diffusion bottle neck. An additional necessary condition aside from the bottle neck is that a non-vanishing hyperfine interaction exists between the nuclei in question and the electron spin of the excited triplet state in order to transfer the electron spin alignment to the nuclei as described in Section 2. It should be pointed out, however, that although excited triplet states are involved in the pumping cycle, the information obtained by ODNQR concerns singlet ground and excited triplet states as well.

One example of a lattice distortion has already been reported for a single crystal of DBB doped with quinoxaline (*Q*) [4]. *Q* fits the crystal structure of DBB so badly that it gives rise to a strong distortion of the next-neighbouring DBB host molecules. This distortion is felt by the bromine nuclei resulting in frequency shifts of up to 1.5 MHz relative to the bulk nuclei because of the altered crystal field. Thus 6 “distorted” bromine nuclei have been observed for each molecule in the DBB unit cell which has been substituted by *Q* [4, 20]. A closer inspection of the crystal structure reveals that 4 of them belong to 4 translationally equivalent next-neighbouring host molecules [20] whereas the other two belong to probably two translationally inequivalent molecules [21].

From the above reported bromine ODNQR data it is evident that in the *Q*/DBB mixed crystal the detailed nature of a crystal lattice distortion can be investigated.

The situation is somewhat different for a DBB crystal doped with DCB. It is well known from crystallographic data that the crystal structure of DCB is not too much different from that of DBB. This is reflected by the fact that we could not achieve a measurable nuclear spin alignment of host bromine nuclei via an optical pumping cycle. This is valid despite the fact that we did observe hyperfine interaction of host bromine nuclei with the excited triplet state of DCB. From this we have to conclude that DCB induces shifts of the bromine NQR frequencies of neighbouring molecules which are less than the NQR linewidth of about 100 kHz. This implies that changes in the crystal field felt by bromine nuclei are negligible, which is not surprising because of the similarity of the crystal structures.

So far we have discussed the situation where a lattice distortion has been induced by doped guest molecules. The situation is somewhat different for pure molecular crystals which exhibit structural defects. These defects may be due to lattice strain, dislocations or unknown impurities. If these defects are small in concentration, they may not show up in X-ray or NQR spectroscopy. However, very often optical spectroscopy shows up emission from such defect centers – often referred to as X-traps. The emission wavelength is in these situations shifted to the red as compared to the emission of the band states of the pure crystal. The corresponding energy shifts are in the order of $10 \dots 100 \text{ cm}^{-1}$.

One of these examples is 1,4-dibromonaphthalene (DBN) which shows several of these X-trap phosphorescence emissions. The intensities and emission wave-lengths depend strongly on the method of crystal preparation [22], suggesting that the corresponding defect centers are due to structural defects of the crystal lattice. The ODMR of the excited triplet state is well known and has been studied in quite detail [23]. When pumping microwave transitions which involve nuclear as well as electronic spin transitions the bromine nuclei can be spin aligned at sufficient microwave power within a time of about 3 s.

Although the phosphorescence emission of distinct defect centers can be clearly resolved, this is difficult for the ODMR transitions of DBN. The only way to obtain the magnetic resonance spectra definitely belonging to a specific defect center, ODMR has to be performed on spectroscopically well resolved lines which, however, reduces the signal to noise ratio with respect to ODNQR experiments considerably. Thus we have performed ODNQR experiments by observing changes of the total phosphorescence when sweeping the frequency in the region of ^{81}Br NQR transitions. The result is shown in Figure 2. Because the same symmetry approximations as for DCB are valid with respect to fine structure and hyperfine structure, the interpretation is easily performed [5]. Two completely different kinds of ODNQR transitions are observed, namely those occurring in the excited triplet state T_1 and those in the singlet ground state S_0 . Starting with the transitions in S_0 , three lines are observed which we attribute to three different defect centers. This is supported by the fact that in this crystal exactly three predominant

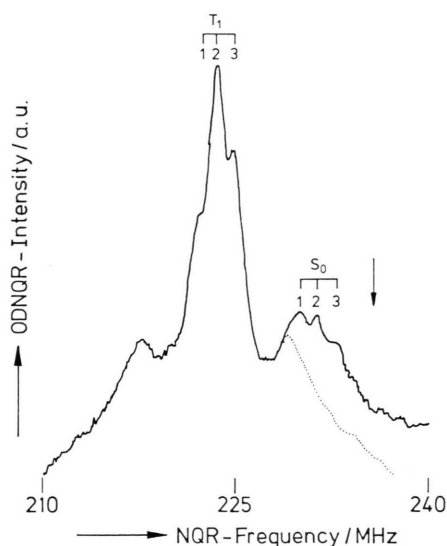


Fig. 2. ^{81}Br ODNQR transitions in T_1 and S_0 . The dotted line represents the mirror symmetry which is expected from the analysis [5]. The arrow indicates the expected NQR transition for an undistorted molecule.

Center No.	$\nu(S_0)$	$\nu(T_1)$
1	230.1	222.5
2	231.3	223.5
3	232.9	225.8
DBN ^a	≥ 235.0	

Table 3. NQR transition frequencies in MHz for ^{81}Br of Dibromonaphthalene.

^a Ref. [24].

phosphorescence centers are observed. These three ^{81}Br transition frequencies are shifted to lower frequencies as compared to the corresponding NQR transition reported for the bulk nuclei of DBN [24] which is indicated by an arrow in Figure 2.

Besides an overall frequency shift, ODNQR transitions in T_1 show up additional lines due to in zero external magnetic field second order hyperfine interaction. This can be analyzed according to [5] and will not be discussed here. From this analysis it is clear that the center line is almost free of contributions due to hyperfine interaction which is reflected in a rather narrow line-width. The splitting of this line we observe in Fig. 2 is thus also due to three different defect centers as already observed in the phosphorescence emission and the ODNQR in S_0 . The ^{81}Br ODNQR transition frequencies are collected in Table 3. The shift of the NQR transitions in S_0 of the defect centers as compared to the

one of the undistorted DBN molecules is up to 5 MHz. This means that lattice defects result in changes of the crystal field at the ^{81}Br positions. The shifts are quite considerable and even stronger than those reported for doped DBB.

5. Conclusion

Besides the fact that ODNQR enhances the sensitivity for NQR of Cl and Br in the situation of low concentrated molecules, it has shown to be a valuable tool to investigated crystal field effects on quadrupole nuclei of molecules diluted in molecular crystals even at very low concentrations. Additionally, with this method it is possible to investigate in quite detail defect structures in molecular crystals either induced by dopants or by lattice strain,

especially if additional external magnetic fields are applied. In this situation quadrupole nuclei serve as a probe to investigate crystal fields. A condition sine qua non is that electronic triplet states are necessary to transfer electron spin alignment into nuclear spin alignment. However, not necessarily optical detection of NQR has to be applied, but also conventional NQR can be considerably improved making use of the experimentally observed nuclear spin alignment of up to 80%. By this also low concentrated nuclei should be observable. However, two conditions have to be obeyed: Firstly, temperatures have to be low enough in order to suppress nuclear spin-lattice relaxation as compared to the optical pumping cycle in the order of a few seconds. Secondly, a spin diffusion bottle neck is demanded if one is interested in locally limited nuclear reservoirs.

- [1] A. I. Kitaigorodsky, *Mixed Crystals*, Springer-Verlag, Berlin 1984.
- [2] E. A. Silinsh, *Organic Molecular Crystals*, Springer-Verlag, Berlin 1980.
- [3] A. Weiss, *Crystal Field Effects*, in: *Topics in Current Chemistry* **30**, Berlin 1972.
- [4] C. v. Borczyskowski and E. Boroske, *Chem. Phys.* **35**, 367 (1978).
- [5] K. P. Dinse and C. v. Borczyskowski, *Chem Phys.* **44**, 93 (1979).
- [6] C. v. Borczyskowski, submitted to *Chem. Phys.*
- [7] C. v. Borczyskowski and E. Fallmer, *Chem. Phys. Lett.* **102**, 433 (1983).
- [8] L. Guibé and E. A. C. Lucken, *Mol. Phys.* **14**, 79 (1968).
- [9] C. v. Borczyskowski, *J. Lumin.* **31/32**, 570 (1984).
- [10] R. Baer and C. Dean, *J. Chem. Phys.* **31**, 1690 (1959).
- [11] G. K. Semin and I. M. Alymov, *Phys. Stat. Solid A* **1976**, K111.
- [12] G. K. Semin, I. M. Alymov, and T. L. Khotsyanova, in: *Magn. Res. and Rel. Phenomena*, Springer-Verlag, Berlin 1979.
- [13] J. Grimm, T. Kirski, C. v. Borczyskowski, and D. Stehlik, in: *Proceed. of XIII. Coll. Amp. Zürich 1984*.
- [14] C. v. Borczyskowski, J. Grimm, and T. Kirski, *J. Physique* (in press).
- [15] I. P. Biryukov, M. G. Voronkov, and I. A. Safin, *Tables of NQR Frequencies*, Jerusalem 1969.
- [16] S. Kojma, S. Ogawa, M. Minematsu, and M. Tanaka, *J. Phys. Soc. Japan* **13**, 446 (1955).
- [17] D. R. Lide and D. E. Mann, *J. Chem. Phys.* **28**, 572 (1958).
- [18] R. Bersohn, *J. Appl. Phys.* **33**, Suppl. **1**, 286 (1962).
- [19] C. v. Borczyskowski, *Proceed. of XIII Coll. Amp. Zürich 1984*.
- [20] C. v. Borczyskowski and E. Boroske, *J. Lumin.* **18/19**, 477 (1979).
- [21] C. v. Borczyskowski, *Chem. Phys. Lett.* **68**, 146 (1979).
- [22] J. M. J. Vankan and W. S. Veeman, *Chem. Phys. Lett.* **89**, 258 (1982).
- [23] R. M. Hochstrasser and A. H. Zewail, *Chem. Phys.* **4**, 142 (1972).
- [24] E. A. C. Lucken, *Nuclear Quadrupole Coupling Constants*, Academic Press, New York 1969.