

## Nuclear Quadrupole Resonance\*

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A resonance phenomenon which is closely related to NMR is nuclear quadrupole resonance (NQR), which was discovered in 1950 by Dehmelt and Krüger. All nuclei with a spin  $\geq 1$  possess in addition to the magnetic moment, an electric quadrupole moment  $eQ$ , which measures the deviation of the distribution of the positive charge in the nucleus from spherical symmetry. While  $e$  is the elementary charge,  $Q = r \int (3\cos\theta - 1)\rho d\tau$  has the dimension  $\text{cm}^2$  and is defined to be positive for a cigar-shaped nucleus and negative for a disc-shaped nucleus ( $\rho$  is the charge density per volume,  $r$  is the distance of the volume element  $d\tau$  from the origin, and  $\theta$  is the angle between the radius vector and the axis of quantization of the spins).

In non-cubic crystals and in almost all molecules the nuclei are situated in an inhomogeneous electric field  $q$  which is given by the second derivative of the electric potential in a given direction, for instance, the direction  $z$  of a chemical bond,  $q_{ZZ} = \delta^2 V/z^2 = V_{ZZ}$ . A nucleus with a quadrupole moment can orient itself only in certain discrete angles with respect to the field gradient, each of which corresponds to a discrete energy value. The quadrupole coupling constant  $e^2 qQ$  is the quantity which is measured directly in an NQR experiment. If the electric field gradient is not axially symmetric with respect to the  $z$ -axis, the deviation is given by the asymmetry parameter  $\eta = (V_{YY} - V_{XX})/V_{ZZ}$ .

In NQR magnetic dipole transitions are induced, in analogy to NMR, by a magnetic radiofrequency field which fulfills the resonance condition  $h\nu = \Delta E_Q$  between energy levels  $E$ , the

energy of which is determined by electric interactions. If the nuclear quadrupole moment  $eQ$  is known, a measurement of NQR renders the value of the field gradient  $q$ , and hence information on quantities like ionic character and hybridization of a bond, which are correlated to  $q$ . The measurement of NQR is facilitated by the fact that it can be performed in a polycrystalline solid; on the other hand, it can be tedious to search for the absorption lines in a large frequency region since the frequency to be expected can be predicted only very approximately in many cases. When investigating nuclei with a small quadrupole moment such as deuterons where the quadrupole interaction is typically in the range between 100 and 200 kHz, the sensitivity becomes very low. In this case it is much more recommendable to measure the quadrupole splitting in an NMR experiment. If this measurement is performed with single crystals, it becomes possible to determine the complete quadrupole tensor and its orientation with respect to the molecular frame. Since the orientation of the quadrupole tensor is closely related to the bond direction in molecular crystals, measurements of the quadrupole interaction renders information on structural parameters which is frequently considerably more precise than X-ray data particularly for deuterons.

After this general introduction I would like to discuss two experiments which were recently performed in our Institute. The first one concerns the investigation of sodium nitroprusside SNP,  $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}\cdot 2\text{H}_2\text{O}$ . I shall restrict myself to the quadrupole interaction of the  $^{14}\text{N}$  nucleus.

Why did we select SNP for our studies? The recent discovery by Mössbauer spectroscopy of a new state in this crystal has attracted a considerable amount of interest in this compound (1-5). The Mössbauer spectrum of Fe normal SNP consists of one pair of quadrupolar split lines. If

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a crystal of SNP is irradiated with intense laser light at a temperature,  $T \leq 150$  K under appropriate polarization conditions (1), a new state develops which differs in two properties from the normal state. First, one observes a change of the optical absorption spectrum of SNP which can be seen with the bare eye as a bleaching of the crystal. Simultaneously with this bleaching two extra Mössbauer lines appear which correspond to a quadrupole interaction of the  $^{57}\text{Fe}$  nucleus which is about 40% larger than in the normal state (Figure 1). This new state seems to persist indefinitely even after switching off the laser as

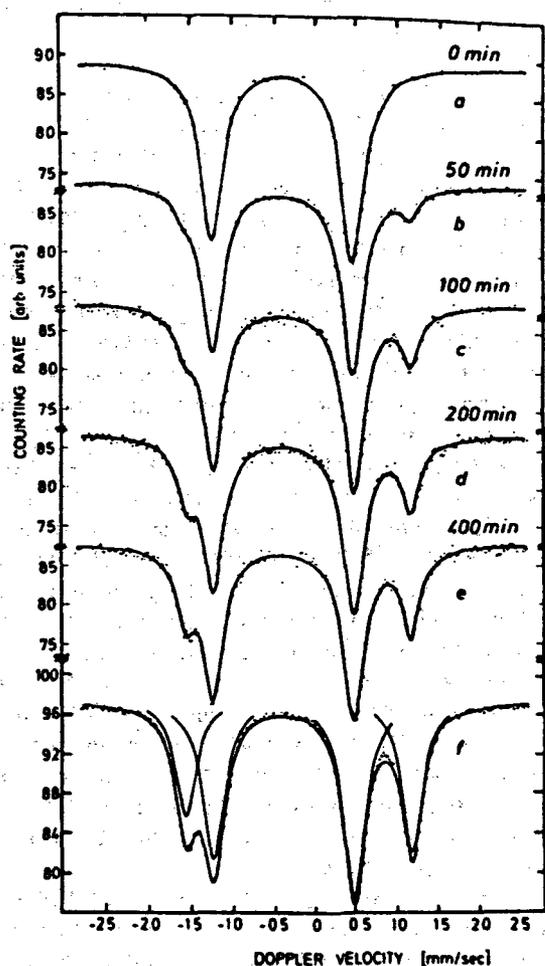


Figure 1. Mössbauer spectrum of sodium nitroprusside at 100 K with increasing irradiation time (U. Hauser et al.).

long as the temperature is kept below 150 K.

The nature of this new state in SNP in terms of its electronic and nuclear configuration is still unknown. However, it may safely be expected that one of the principal axes of the electric field gradient (EFG) is parallel to a good approximation to the CN or NO bond direction. Any rearrangement of the subgroups (CN, NO) of SNP are expected to affect the orientation of these subgroups and hence to manifest itself in the quadrupole interaction of the NMR spectrum. In addition, any change in the electronic configuration of these groups is expected to influence the quadrupole coupling constants QCC of the respective N nucleus.

In a first step we have measured the full quadrupole coupling tensors at all the nitrogen sites in the normal state of SNP (6). This is, of course, a necessary basis of the study of the new state by NMR, but it turned out that it is interesting by itself because it demonstrates a remarkable sensitivity of nitrogen NMR to orientations of molecular subgroups in crystals.

For a better understanding of the NMR results, let us first have a look at the structure of SNP as determined by Manoharan and Hamilton in 1963 (7) and refined by Bottemley and White in 1979 (8) (Figure 2). Crystals of SNP are orthorhombic, space group  $P_{21}nm$ ,  $a = 6.198$ ,  $b = 11.897$ ,  $c = 15.557$ , with two pairs of SNP complexes  $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO} \cdot 2\text{H}_2\text{O}$  per unit cell (Figure 2). The total number of  $^{14}\text{N}$  nuclei per unit cell is 24, but since the two complexes in each cell are related by inversion symmetry there are only 12 magnetically nonequivalent sites in an SNP crystal; hence the  $^{14}\text{N}$  spectra of a single crystal of SNP consists in general of 12 pairs of resonance lines.

Furthermore, all of the complexes in SNP are related by twofold screw axes which leads to a further reduction of the resonance lines in certain planes. Hence it suffices when discussing the results to consider one single complex. Moreover, nitrogens  $\text{N}_2$  and  $\text{N}_{2m}$  and  $\text{N}_3$  and  $\text{N}_{3m}$  in each NP complex are related by a mirror plane which reduces the number of independent  $^{14}\text{N}$  quadrupole coupling tensors  $e^2qQ/h$  to four. We designate them  $q_{\text{N}_0}$ ,  $q_{\text{N}_1}$ ,  $q_{\text{N}_2}$ , and  $q_{\text{N}_3}$ . Note that the NO-bond direction is not perpendicular to the plane spanned by the  $\text{N}_2$  and  $\text{N}_3$  nitrogens.

The single crystals of SNP were provided by Professor Haussuhl of Köln University, which we gratefully acknowledge. The NMR spectra were recorded by FT techniques using a superconducting magnet with a field  $B = 8.4$  Tesla, corresponding to a Larmor frequency  $\nu_L(^{14}\text{N}) = 25.7$  MHz. The full  $^{14}\text{N}$  spectrum spans a range

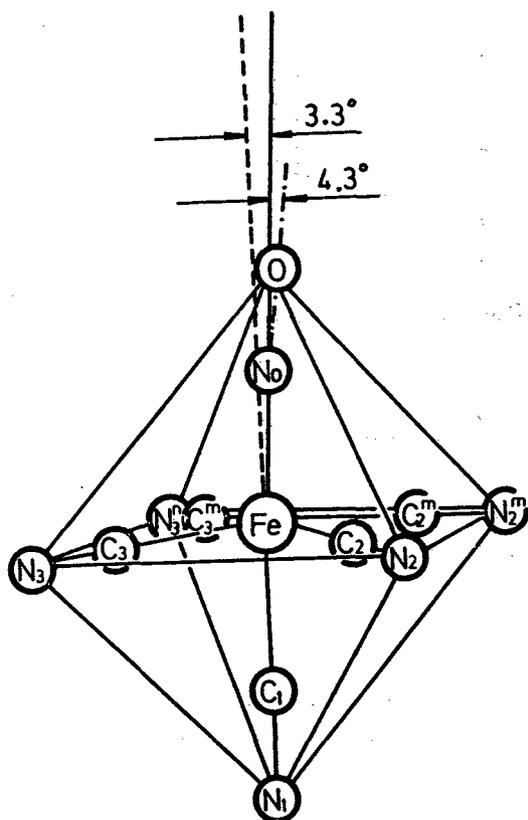


Figure 2. Structure of the nitroprusside ion  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$ .

of up to 5 MHz. Since the spectral range of our  $3 \mu\text{s}$  pulse as well as the bandwidths of the probe and receiver are far less than 5 MHz, the full  $^{14}\text{N}$  spectrum had to be recorded in spectral slices. (Figure 3 shows how different slice spectra with ample overlap were combined to a full spectrum.)

The very marked sensitivity of the nitrogen NMR to orientations of molecular subgroups is illustrated in Figure 4. It shows a part of the  $^{14}\text{N}$  spectra when  $B_0$  is almost (a and b) and exactly (c) parallel to the c-axis of the crystal. We estimate on the basis of the width of the  $^{14}\text{N}$  lines which is about 3 KHz, and on the slope of the quadrupole splittings versus rotation angle that  $B_0$  must be parallel to c to better than 0.03 for the quadruples of lines to fully coalesce.

The rotation patterns of the line splittings of the  $^{14}\text{N}$  NMR spectra are shown in Figure 5. We are now faced with the task of determining which of the traces in the "a", "b", and "c"

rotation patterns shown in the figure belongs to a certain  $^{14}\text{N}$  site. This task is easy for  $\text{N}_0$  and  $\text{N}_1$ . Since their bond directions are perpendicular to the c-axis, the traces belonging to  $\text{N}_0$  and  $\text{N}_1$  should pass through an extremum at  $B_0 \parallel c$ . The "a"- and "b"-rotation patterns contain indeed two traces which possess these properties. Knowing their values for  $B_0 \parallel a$  and  $B_0 \parallel b$  enables us to identify the traces belonging to  $\text{N}_0$  and  $\text{N}_1$  in the "c"-rotation pattern as well. However, at this stage we do not know which belongs to  $\text{N}_0$  and which to  $\text{N}_1$ . By an analogous procedure we could attribute the rotation patterns which belong to the  $\text{N}_2$  and  $\text{N}_3$  sites and to work out the quadrupole coupling components and the asymmetry parameters; they are compiled in Table 1. A comparison of the components in the second row of Table 1 with the sets of principal components of  $\text{N}_2$  and  $\text{N}_3$  indicates that this set must belong to the quadrupole coupling tensor at the  $\text{N}_1$  site.

The next step would be to record the  $^{14}\text{N}$  NMR spectra of the new state and to evaluate the  $^{14}\text{N}$  electric field gradients in this state. For doing this we are faced with the problem that we have to work with thin discs of single crystals, while the work in the normal state discussed so far was performed using rods of a diameter of  $d = 10 \text{ mm}$  and a length  $l$  of about 15-20 mm. In the beginning we used discs of a thickness below 1 mm because with the light intensity which we considered tolerable for the crystal ( $200 \text{ mW/cm}^2$ ), it takes already at least a day to populate 90% of the maximum population of the new state (50% of the NP complexes). Such thin slices require, because of the low sensitivity of  $^{14}\text{N}$  NMR, more than 1000 FIDs in order to achieve the same signal-to-noise ratio as obtained with the large sample with a single shot. After an irradiation time  $\sim 3 \text{ h}$  at 120 K the  $^{14}\text{N}$  NMR absorption spectrum vanished. After reheating the sample to rt the original spectrum of the normal state reappeared showing that the change of the  $^{14}\text{N}$  NMR spectrum is a reversible process analogous to the changes in the optical transmission and in the  $^{57}\text{Fe}$  Mössbauer spectrum. Although it is possible with relaxation times of the order of seconds to make measurements with more than a thousand FIDs, it is rather tedious. Hence we have tried to use thicker discs of about 5 mm length and increased the light intensity to about 700 mW. The result of this experiment was similar; after an irradiation time of about 24 h the intensity of the  $^{14}\text{N}$  NMR spectrum was strongly reduced although it did not vanish completely with thicker samples.

Our working hypothesis for this behaviour is

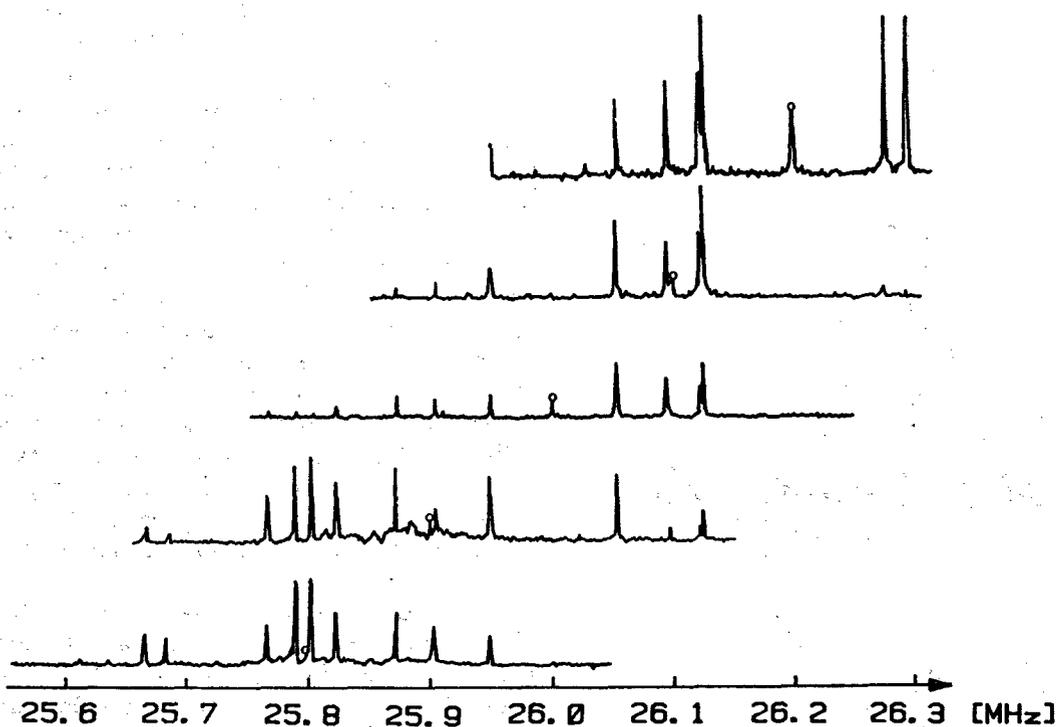


Figure 3.  $^{14}\text{N}$  slices spectra of sodium nitroprusside (SNP) at 25.7 MHz ( $B_0 = 8.4$  Tesla)..

Table 1.

$^{14}\text{N}$  Quadrupole Coupling Tensor Components  
of Sodium Nitroprusside (SNP).

Site	$e^2q_{11}Q/h$ (MHz)	$e^2q_{22}Q/h$ (MHz)	$e^2q_{33}Q/h$ (MHz)	$\eta = \frac{q_{22} - q_{11}}{q_{33}}$
$\text{N}_0$	1.155	1.084	2.239	0.032
$\text{N}_1$	1.791	1.773	3.560	0.005
$\text{N}_2$	1.867	1.651	3.489	0.062
$\text{N}_3$	1.897	1.756	3.635	0.038

at present that the "new state" is paramagnetic and that the  $^{14}\text{N}$  NMR lines are broadened beyond detectability by their interaction with the

unpaired electrons. This hypothesis is, however, not in agreement with preliminary results obtained by ESR in Professor Elschner's

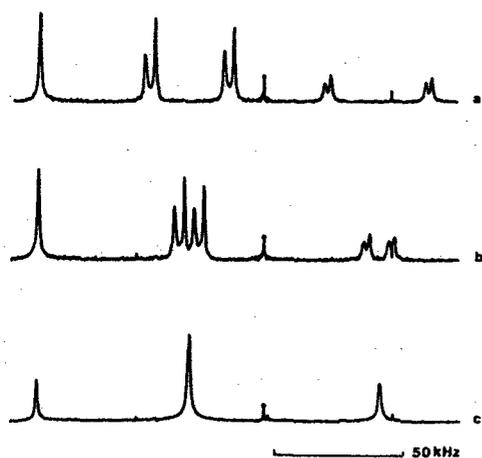


Figure 4.  $^{14}\text{N}$  spectra of SNP when  $B_0$  is near (a and b) and exactly (c) parallel to the  $c$ -axis of the crystal.

Institute in Darmstadt, which seem to indicate that the new state is not paramagnetic. Hence it is fair to say that the disappearance of the  $^{14}\text{N}$  NMR spectrum, when generating the new state, is not understood.

The second example which I would like to discuss is the quadrupole coupling tensor of the  $^{17}\text{O}$  nucleus in benzophenone (BPh), both in the ground state and in the excited state. In order to increase the sensitivity of our measurements we used BPh molecules in which the rare  $^{17}\text{O}$  isotope was enriched from 0.037 to 50%.

In order to interpret our results we require two different coordinate systems as shown in Figure 6. The first ( $xyz$ ) is a coordinate system defined by the planar  $-\text{C}_1-\text{C}(\text{O})-\text{C}_1'$  fragment of BPh with  $z$  parallel to the  $\text{C}=\text{O}$  bond, in agreement with the  $\text{C}_2$  symmetry of the molecule,  $y$  in the plane of this fragment perpendicular to the  $\text{C}=\text{O}$  bond, and  $x$  normal to this plane. The second ( $q_{11}, q_{22}, q_{33}$ ) is the principal axes system of the  $^{17}\text{O}$  quadrupole coupling tensor. Further coordinate systems, such as the symmetry axes of the crystal and the principal axes of the fine structure tensor of BPh are not relevant for the discussions within the scope of this article.

The ground state of BPh was studied in our Institute by U. Haerberlen and W. Scheubel with a single crystal of BPh using NMR at high field (84.5 kG  $\sim$  48 MHz). The experimental procedure and the evaluation of the data have been separately presented as a poster at this

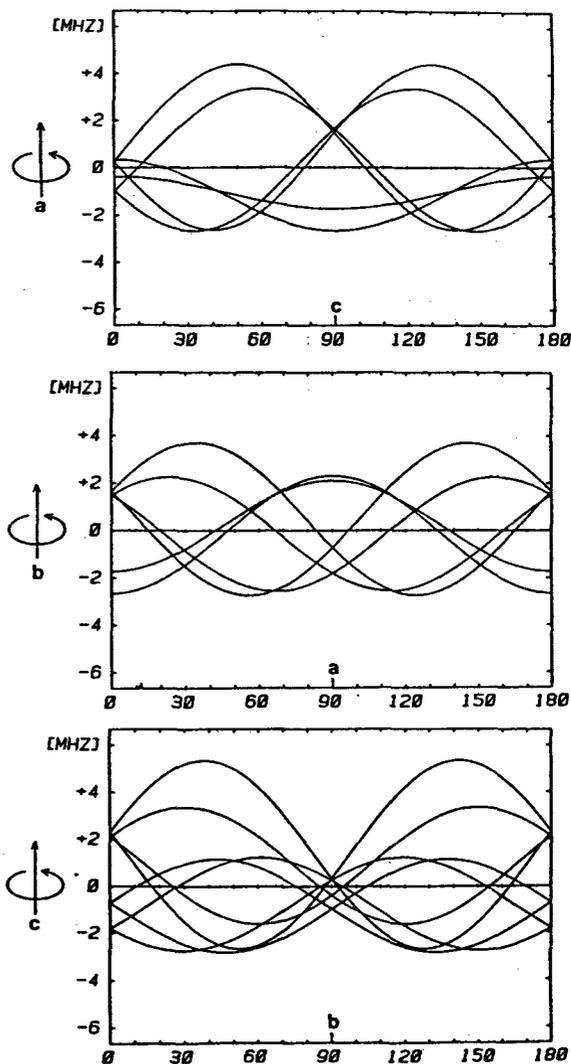


Figure 5. Orientational dependence of the quadrupole splittings  $e^2qQ$  of the  $^{14}\text{N}$  resonances in SNP.

conference. The results are summarized in Figure 7. The value of  $e^2qQ/h = 10.808$  MHz,  $\eta = 0.369$ . The deviation of the main axis of the quadrupole coupling tensor from the molecular symmetry axes are not more than one degree, in particular the  $q_{22}$ -axis is parallel to the  $\text{C}=\text{O}$  bond direction within the experimental error of 0.4. Note that the tensor component  $e^2q_{22}Q/h$  parallel to the  $\text{C}-\text{O}$  bond direction is not the largest one as one might expect, but the smallest.

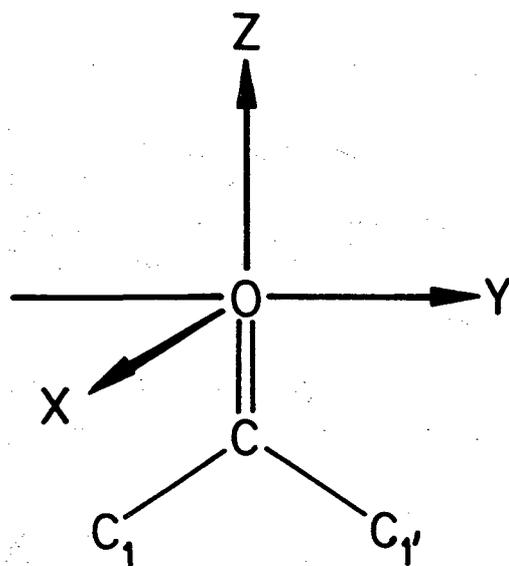


Figure 6. Fragment of benzophenone defining a local  $C_{2v}$  symmetry.

We shall later compare the  $^{17}\text{O}$  quadrupole couple tensor and its orientation with respect to the molecular framework in the ground state and in the excited state of BPh.

These investigations were performed with a single crystal of BPh at rt. In distinction to these experimental conditions K. P. Dinse and G. Wackerle of our Institute have investigated a mixed crystal of BPh in dibromodiphenyl ether at 1.2 K using Optical Nuclear Double Resonance (ONDOR) (9). They used a stabilized single mode laser with a short-term stability of a few hundred KHz and a power incident on the sample of 30 mW in combination with a radiofrequency power of 1 W. This stability of the laser is sufficient since recently the same authors have succeeded in obtaining the first photon echo of a very similar mixed crystal, i.e. dibromo-BPh in DDE; with this method it was possible to determine  $T_2$  to be  $1\mu\text{s}$ , corresponding to a linewidth of the order of 1 MHz in an inhomogeneous line of about 50 GHz. In other words the homogeneous linewidth is three or four times larger than the jitter of the laser. The  $^{17}\text{O}$  enriched synthesis and the growing of the mixed crystals was done in our Institute by H. Zimmermann starting

Table 2.

Benzophenone- $^{17}\text{O}$  Quadrupole Coupling Tensor Components.

Molecular State	Experimental Method	$e^2q_{11}Q/h$ (MHz)	$e^2q_{22}Q/h$ (MHz)	$e^2q_{33}Q/h$ (MHz)	Asymmetry Parameter $\eta = \frac{q_{22} - q_{11}}{q_{33}}$
Ground State	NMR <sup>a</sup>	(-) 7.396	(-) 3.412	(+) 10.808	0.369
	Laser-RF Double Res. <sup>b</sup>	(-) 7.596	(-) 3.437	(+) 11.033	0.377
Excited State	ODENDOR <sup>c,d</sup>	+ 8.70	- 0.86	- 7.80	0.80

a) Scheubel et al., 6th Spec. Coll. Ampère. b) Reference (9). c) Wackerle et al., *J. Chem. Phys.* **76** 2275 (1982). d) Principal tensor axes rotated by  $20^\circ$  about the C=O bond direction.

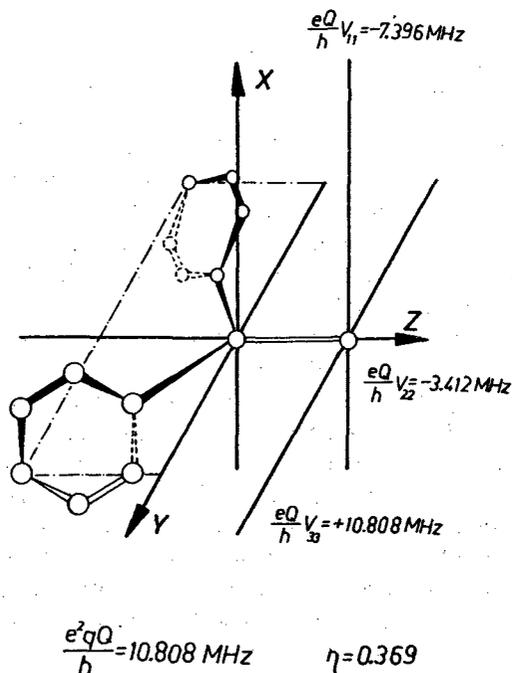


Figure 7. EFG tensor at the  $^{17}\text{O}$  site of benzophenone.

with a guest concentration of BPh of 2000 ppm, although one should keep in mind that the final guest concentration is typically one order of magnitude lower as was verified by the GLC analysis.

The results obtained with the ONDOR method, i.e. by monitoring the phosphorescence when changing the population of the nuclear sublevels by irradiating the appropriate radiofrequency, are shown in Table 2, together with those obtained by NMR in a neat single crystal at rt. Since this is a zero-field experiment without an axis of preference, it is not possible to determine the orientation of the quadrupole tensor components with respect to the molecular framework. The difference of about 2% is mainly due to the temperature difference since the measurements by NMR of neat single crystals were performed at rt while the ONDOR measurements were performed at 1.2 K with mixed crystals, the latter difference probably being less important than the temperature. The ONDOR results are more suitable for comparison with the results in the photoexcited triplet state since they are obtained as well with mixed crystals at 1.2

K. Considering the small difference it can be safely assumed that the orientation of the quadrupole coupling tensor with respect to the molecular framework does not change with temperature.

The measurements of the quadrupole interaction in the excited triplet state were performed in our Institute by K. P. Dinse and G. Wackerle in collaboration with D. Pratt using Optical Detection of Magnetic Resonance (ODMR) and Optical Detection of Electron Nuclear Double Resonance (ODENDOR) both in zero field and in high magnetic field (10). The samples used were perdeuterated  $^{17}\text{O}$ -enriched BPh in DDE in order to reduce the linewidth. Figure 8 shows the phosphorescence spectrum of this mixed crystal

### BENZOPHENONE PHOSPHORESCENCE

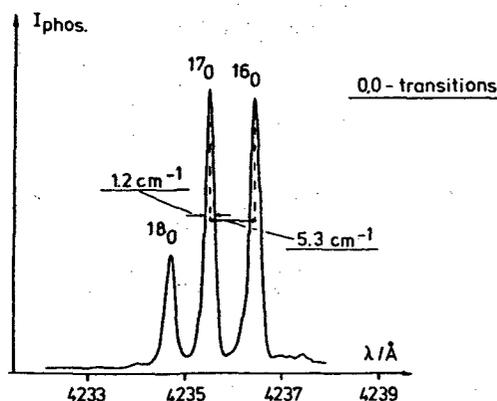


Figure 8. 500 ppm  $^{17}\text{O}$ -benzophenone- $\text{d}_{10}$  in a DDE single crystal.  $[^{17}\text{O}] = 50\%$ . Monochromator resolution  $\Delta = 0.9 \text{ cm}^{-1}$ ,  $T = 1.2 \text{ K}$ .

in the vicinity of the (0,0) band at 1.2 K. The relative intensities of the three bands correspond to the isotopic enrichment factors.

Since the most important results, i.e. the quadrupole coupling tensor and its orientation with respect to the molecular framework including the signs, were obtained with the ODENDOR experiment, I shall restrict myself here to the discussion of this experiment. Dinse and Wackerle observed in zero field the change in the ODMR intensity when sweeping the radiofrequency in the range from 0-30 MHz. For the

high-field experiments they used a spectrometer which was developed in our Institute for measuring microwave induced optical nuclear polarization. The crystal was mounted on a cone wheel which could be turned by a full  $2\pi$  angle around a vertical axis which could be oriented arbitrarily with respect to  $B_0$ . It was placed into a cylindrical  $TE_{1,1,2}$  X-band cavity into which an rf coil with 5 turns and a diameter of 13 mm was inserted.

The results of the ODENDOR experiments are given in Figure 9. The ODMR spectrum

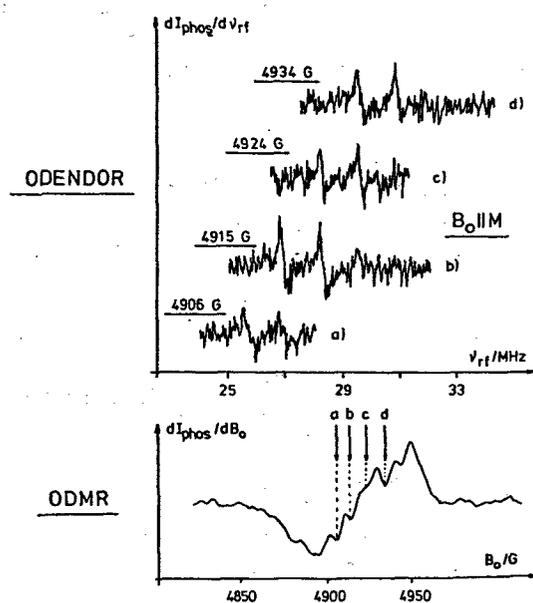


Figure 9. Magnetic resonance of  $^{17}\text{O}$ -benzophenone- $d_{10}$ .

consists of six hyperfine components with a separation of about 26 MHz which are not well resolved at high power. The field was then positioned at one of the resonance fields and the change in the ODMR intensity was monitored when the rf field was swept from 25 to 35 MHz. Five  $\Delta m = \pm 1$  ENDOR transitions within the  $m_S = +1$  sublevel were obtained in agreement with expectations for a  $S = 1$ ,  $I = 5/2$  system with differences between the first-order hyperfine coupling of  $1.36 \pm 0.01$  MHz, which were found to be equal within experimental error.

The evaluation of these experimental data leads to the quadrupole coupling tensor components shown in Table 2, together with the

quadrupole coupling tensor components in the ground state of BPh discussed above. As mentioned before, the results for the quadrupole coupling tensor in the ground state obtained with NMR and with ONDOR differ by only 2%. This difference is due to the different temperatures—remember that the NMR measurements were performed at rt and the ONDOR measurements at 1.2 K. The signs of the quadrupole coupling tensor components are set in parenthesis since they are not determined experimentally but are the result of INDO calculations.

The most interesting result given in Table 2 is the striking difference of the quadrupole coupling tensor in the excited triplet state as compared to the ground state. The smallest component is still along the molecular z-axis, parallel to the C=O bond direction, but it is close to zero, leading, of course, to a very large asymmetry parameter  $\eta = 0.80$ . Note that the signs are not set in parenthesis because they could be determined experimentally. The largest component is in the excited triplet state along the  $q_{1,1}$  axis of the quadrupole coupling tensor. However, it is not anymore in the plane of the fragment of the three carbon atoms and the oxygen atom, Figure 6, but the  $q_{1,1}$  and  $q_{3,3}$  axes are rotated around the C=O bond direction by  $20^\circ$ .

The quadrupole data show that the first excited triplet state is an  $\pi^*$  state in which one electron is transferred from the oxygen 2p-type lone pair orbital to a  $\pi^*$  orbital. The change in the direction of the largest component of the field gradient tensor is consistent with this description. However, a quantitative analysis shows that considerably less than one electron (about 2/3) is transferred out of the n orbital on excitation.

BPh is not a planar molecule. Due to steric hindrance the benzene rings are twisted in the ground state by  $28^\circ$  out of the plane of the fragment  $-\text{C}_1-\text{C}(\text{O})-\text{C}_1'$ . The orientation of the quadrupole tensor shows that this out-of-plane twisting of the benzene rings in a conrotatory fashion causes a rotation of the n- and  $\pi$ -type orbitals of the oxygen atom as well leading to a more favorable interaction of the n orbital with the  $\pi$  orbitals of the rings. This result was neither experimentally nor theoretically anticipated; it proves that triplet benzophenone is not a pure  $\pi^*$  state: since both the n and  $\pi$  orbitals of the carbonyl group are mixed with the aromatic  $\pi$  system, it has both  $\pi^*$  and  $\pi\pi^*$  character in agreement with the so far unexplained fact that the transition to the excited state is much less forbidden than one would expect for a transition to a pure  $\pi^*$  state. However, this is more

theoretical chemistry than magnetic resonance and I shall not discuss it any further.

Let me finish by summarizing the main conclusion of this paper: quadrupole interactions in the ground state and in the excited state of molecules can be investigated in addition to pure NQR by NMR, ODMR, ONDOR, and ODENDOR. The results, either by themselves or in combination with other data, in particular the hyperfine interaction between the quadrupole nuclei and the unpaired electrons of the excited states, provide interesting information on the electronic structure of these molecules both in the ground state and in the excited state.

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