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Zero-field splitting and line shape of the ODMR of self-trapped excitons in NaBr

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Abstract. The optically detected electron paramagnetic resonance (ODMR) spectrum of self-trapped excitons (STEs) in NaBr was measured using a microwave frequency of 25.9 GHz and compared with that measured previously at 24.0 GHz. In lock-in detected ODMR only one structureless non-Gaussian line was observed for each frequency. From the field positions of the lines obtained in the previous and new measurements a zero-field splitting of $D = 1.7$ T was derived. On the basis of transient ODMR measurements in KBr it is shown that the shape of the ODMR line does not follow the V_K-centre nuclear spin statistics of the STE because of the dependence of the lifetimes on the nuclear spin states. Similar effects seem to occur in all alkali bromides.

1. Introduction

Recent work has considerably clarified the structure of the self-trapped exciton (STE) in a number of alkali halides. There are now good reasons to classify the STEs into the so-called type II (weakly off centre) and type III (strongly off centre) STEs, that is to be primitive and possibly nearest-neighbour Frenkel defect pairs, respectively. Concerning the so-called type I STEs, which include those in NaBr and NaI, both calculations and optical transition studies are not clearly conclusive as to the symmetry of the system (strictly on centre versus marginally off centre without a centre of inversion) (Song and Williams 1996).

In order to clarify this situation concerning the type I STEs, the first electron paramagnetic resonance (EPR) study of the triplet state of the STE (Song and Williams 1996) using optical detection via luminescence had been made in NaBr (Rogulis *et al* 1995). The microwave frequency used was 24 GHz (K band), the detection mode was the standard lock-in technique, and the spectrum consisted of a structureless non-Gaussian line centred at $g = 2$ with a halfwidth of about 135 mT. The spectrum showed a different structure compared to those in KCl or KBr, and that seemed not surprising. In the latter cases clearly resolved hyperfine (hf) structures, typical for V_K centres, were obtained. In NaBr, the observed ODMR line shape, which was 'flat' at the centre, was interpreted as being the result of a closely separated pair of Gaussian lines, and the small separation was attributed to the zero-field splitting. The D parameter was estimated to be about 23 mT (Rogulis *et al* 1995).

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In a more recent work, Kan'no *et al* (1996) have studied the EPR of the STE in NaBr using a pulse technique and microwaves of 9 GHz (X band). They obtained a single line with somewhat less flattened top, which was centred at 1.45 T. Kan'no *et al* failed to observe the second line expected for a fine-structure split triplet spectrum within their available magnetic field range. This seemed to indicate a possibly very large D value. In an attempt to estimate the D value, Kan'no *et al* (1996) combined their line with the one obtained by Rogulis *et al* (1995) and thus estimated the D parameter to be about 1.7 T, much larger than in other bromides (265 mT in KBr and 185 mT in RbBr). However, Kan'no *et al* (1996) had to assume a g value, which was taken to be $g = 2$.

In this report, we present new results obtained with two different microwave frequencies in the K-band (24 GHz and 25.9 GHz). Based on our new studies, we also obtained a large D value of 1.68 T, which is close to that proposed by Kan'no *et al* (1996) as described above.

In view of the proposal of Kan'no *et al*, we undertook to investigate the reason for having observed an apparent 'double' line with the standard ODMR technique, which has previously lead to the determination of a small D value. Previous experiments on KBr (Marrone *et al* 1973, Wasiela *et al* 1973) indicated that also there the line shape does not follow the expectation from the hf structure. We, therefore, undertook transient ODMR experiments in order to find the reason for the non-Gaussian line shapes. They were performed on KBr because of the better signal-to-noise ratio compared to NaBr. It turned out that the lifetimes of the different nuclear spin states of the V_K centre are different. In ODMR experiments with lock-in detection at audio-frequency between a few hertz and 100 kHz, these lifetime differences influence the ODMR line intensities.

In summary, we have found that in our previous work (Rogulis *et al* 1995) and in the work of Kan'no *et al* (1996) only one fine-structure component of the STE ODMR spectrum was observed due to the unusually large D value.

2. Experimental details

The pure NaBr crystals were grown with the Czochralski method. The NaBr powder was treated before crystal growth with Br_2 to avoid oxygen contamination. The extremely pure KBr crystal was provided by G McDugle (Eastman Kodak). The optically detected electron paramagnetic resonance was measured as a microwave induced change of the luminescence intensity in a computer controlled custom built K-band spectrometer (24–25.9 GHz). The details of the stationary lock-in detected ODMR for the x-ray induced luminescence have been described previously (Rogulis *et al* 1995).

The time resolved ODMR measurements were performed with a PC controlled transient recording board triggered by the microwave switch controller. As a microwave switch a p–i–n diode was used with a response time of 50 ns. The ODMR effect was monitored with a time resolution switching the microwave power on and off. 65 000 scans for each cycle (switching on and off the microwave power) were measured.

3. Experimental results

3.1. Lock-in detected ODMR

The ODMR spectra of the STEs in NaBr are shown in figure 1, for two different microwave frequencies—at 24 GHz (figure 1(a), reported earlier by Rogulis *et al* (1995)) and 25.9 GHz (figure 1(b)). We observe a shift of the broad resonance line to lower magnetic fields by

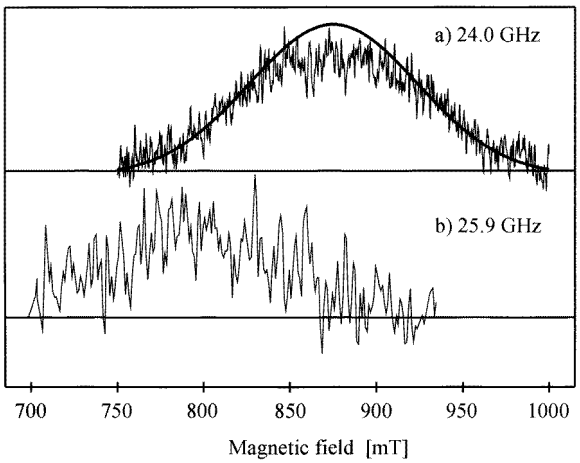

Figure 1. Optically detected EPR spectra of the triplet STE in NaBr for $B \parallel [110]$, $T = 1.6$ K. (a) $\nu_{EPR} = 24.0$ GHz. The solid line is a calculated Gaussian single line. The experimental line shape appears as a Gaussian line with a 'flattened' top. (b) $\nu_{EPR} = 25.9$ GHz.

76 mT when the microwave frequency increases. If this shift was determined by the Zeeman splitting, then the line shift would be expected to higher magnetic fields upon increase of the microwave frequency.

The obtained shift to lower field could be explained by a very large value of the zero-field splitting D. From the determination of the resonance fields from figure 1(a) and (b), we obtained the following spin Hamiltonian parameters:

$$g = 1.80 \pm 0.2 \qquad D = 1.66 \pm 0.2 \text{ T}.$$

We obtained a higher precision in the determination of the parameters when taking into account our resonance fields together with the resonance field obtained by Kan'no *et al* (1996):

$$g = 1.87 \pm 0.05 \qquad D = 1.68 \pm 0.05 \text{ T}.$$

Further, in figure 1(a), we evaluated the halfwidth of our ODMR spectrum, under the assumption that there is one Gaussian-like spectrum with a 'flattened' (depressed) central part. In such a way we obtained a halfwidth of 122 mT. This value is close to that found by Kan'no *et al* (1996). We tried to find the reason for the flattened lineshape measured with our conventional lock-in technique.

Because of the low signal to noise of the ODMR spectrum no full angular dependence could be measured; from this in principle, the zero field splitting could also have been determined.

3.2. Transient ODMR experiments in KBr

We used transient ODMR experiments to follow the dynamical relations between the relaxation times in different hf transitions of the ODMR spectra. We had to use the ODMR of the STE of a KBr crystal for the transient ODMR experiments instead of our NaBr crystal, since the signal-to-noise ratio in NaBr was too bad.

In figure 2, the spectrum of the lock-in detected ODMR is shown for the KBr crystal for $B_0 \parallel [110]$, the axis of the STE. Similar to earlier observations by Marrone *et al* (1973)

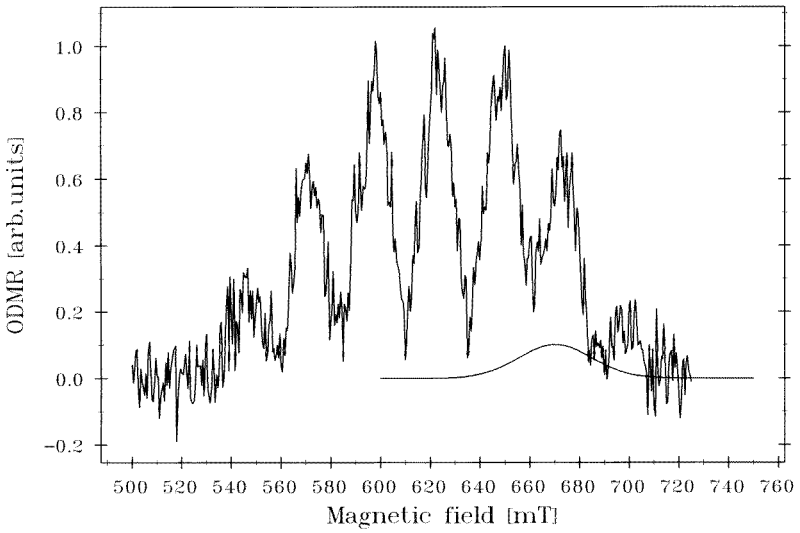

Figure 2. The optically detected EPR spectrum of the triplet STE in KBr for $B \parallel [110]$, $T = 1.6$ K, ($\nu_{EPR} = 25.5$ GHz). The solid line centred at 670 mT is the calculated EPR spectrum of STEs in perpendicular orientation.

and Wasiela *et al* (1973) we observe in figure 2 that all three 'middle' components have about the same relative intensities (middle line depression) rather than the statistical relation 3:4:3, as could be expected. At the higher-magnetic-field side of the spectrum in figure 2 also the resonances from the other perpendicular STE orientations appear (simulated with parameters taken from Wasiela *et al* (1973). In KBr the 'flattened' central part is seen more clearly than in NaBr where the signal-to-noise ratio is much worse. However, the line shape in NaBr is clearly non-Gaussian (see figure 1(a)).

In figure 3, the transient ODMR spectra are shown for the middle line and two adjacent ones. We have analysed the decay relations of these three spectra. We obtained these by switching microwaves 'on'; the amplitude of the middle line is somewhat higher than that for the adjacent ones, but the subsequent decay of the middle line is faster than for the other lines. The ratios of the initial amplitudes of the middle line to the two other lines in figure 3 are 1.33:1 (which is close to the expected 4:3 for the statistical distribution of the hf lines) and 1.15:1 (not exactly 4:3, but higher than 1:1).

We therefore observed experimentally that the lifetimes of the different ODMR components are different and depend on the nuclear spin states. In the conventional lock-in technique the averaged values of the ODMR line intensities are measured. Numerical integration of our time resolved patterns in figure 3 leads to the same final intensity of all the three middle lines: this is what is observed in lock-in technique experiments. Thus, the lock-in technique gives 'wrong' intensities of the ODMR lines and the total lineshape of the ODMR is determined by lifetime effects of transitions in different nuclear spin states.

3.3. Simulation of the transient ODMR experiments

In order to understand the common feature observed for most of the STEs in alkali halides that the hf split ODMR transitions do not have the intensity ratio expected from the statistical distribution of the occupation of the m_I states, we have to analyse the ODMR effect

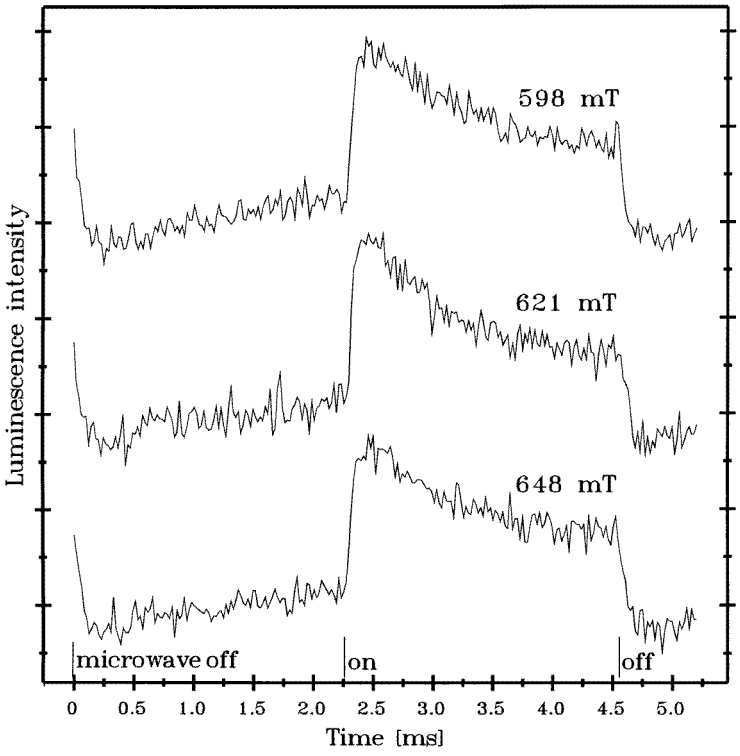

Figure 3. Time resolved ODMR spectra of KBr for $B \parallel [110]$ for the middle line (621 mT) and two adjacent ones (598 mT and 648 mT).

quantitatively. The intensity of the $m_I = 0$ transition is usually depressed and does not have the predicted ratio of 4:3 in comparison with the neighbouring $m_I = \pm 1$ transitions. The only exception is the STE in KCl, having much smaller hf interactions with the two central nuclei of the molecule. In order to calculate the ODMR effect and to analyse its transients we solved a rate equation system. Since we ignored coherence effects, we do not need to use the density matrix formalism.

We made four simplifications. (i) We neglect the influence of the spin–lattice relaxation. This is justified because the lifetimes of the excited triplet states are much smaller than the spin–lattice relaxation time at the measurement temperature of 1.5 K. This can also be seen directly from the decay of the ODMR, which can be described by the difference of two exponentials, each reflecting the lifetime of the excited state involved in the ODMR transition (Chan 1982) (see figure 4; see below for an explanation). (ii) We only take into account the two triplet levels which are connected by the microwave transition. The third level does not influence the ODMR effect as it is decoupled from the two other states because of the neglect of the spin–lattice relaxation. (iii) We consider the hf levels separately. In other words, we solve the rate equations, consisting of only two states for the different m_I sublevels with different lifetimes, each of which are estimated by a fit to the measured transients. (iv) We assume that all triplet levels are optically pumped at the same rate. This means that we introduce only one parameter P for the pumping probability. With these simplifications, one hf subsystem of the triplet can be described with the following rate

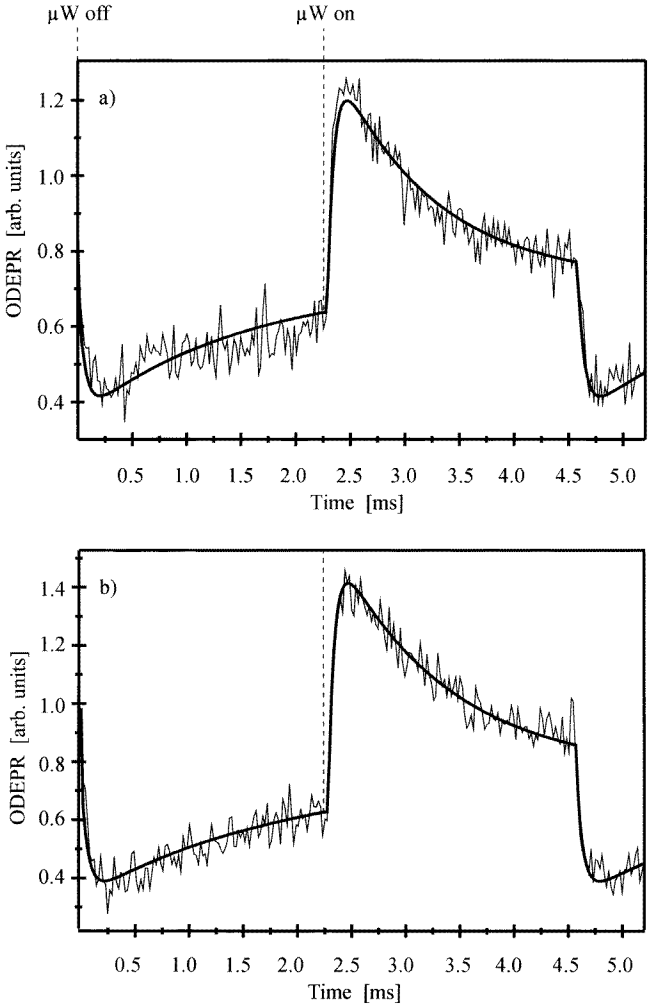

Figure 4. Simulation of the transient ODMR experiments of the STE in KBr (a) for the middle hf line at 621 mT ($m_I = 0$) and (b) for the side line at 598 mT ($m_I = 1$).

equations:

$$\frac{\mathrm{d}N_{f,s}}{\mathrm{d}t} = P(N - N_f - N_s) \pm \mu(N_s - N_f) - \frac{1}{\tau_{f,s}} N_{f,s} \tag{1}$$

with N_f the population of the fast excited state, N_s the population of the slow excited state (bottleneck), N the population of the ground state, P the optical pumping probability, μ the transition probability induced by the microwaves, τ_f the lifetime of the fast excited state, and τ_s the lifetime of the slow excited state (see figure 5 for a schematic illustration of the parameters).

After Barry (1992) the solution of the rate equations (1) is

$$N_{f,s}(t) = A_{f,s} + B_{f,s} \exp(\lambda_1 t) + C_{f,s} \exp(\lambda_2 t) \tag{2}$$

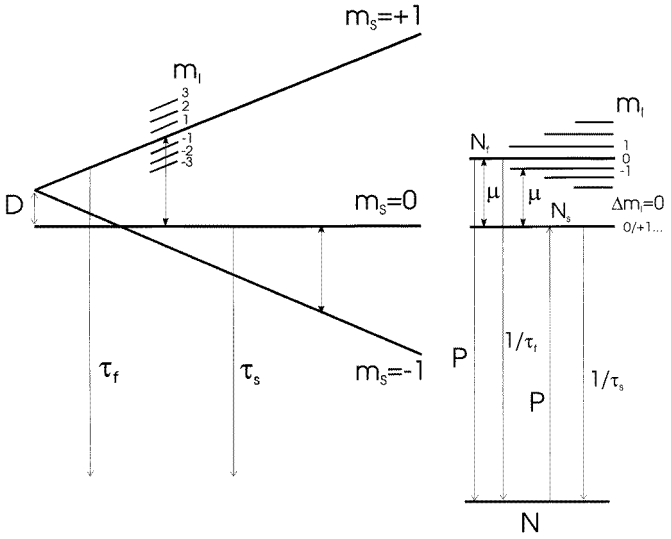

Figure 5. A schematic illustration of the parameters for the simulation of the transient ODMR experiments.

with

$$\lambda_{1,2} = -P - \mu - \frac{1}{2}\left(\frac{1}{\tau_f} + \frac{1}{\tau_s}\right) \pm \sqrt{(P-\mu)^2 + \left(\frac{1}{\tau_f} - \frac{1}{\tau_s}\right)^2}. \tag{3}$$

$A_{f,s}$, $B_{f,s}$, and $C_{f,s}$ are functions of the pumping probability, the microwave transition probability, the lifetimes, and the initial conditions N_f^0 and N_s^0:

$$\begin{aligned} A_{f,s} &= \frac{PN(2\mu + 1/\tau_{s,f})}{\lambda_1\lambda_2} \\ B_{f,s} &= \frac{PN(2\mu + 1/\tau_{s,f})}{\lambda_1(\lambda_1 - \lambda_2)} + \frac{PN + (\mu - P)N_{f,s}^0 + (\lambda_1 + P + \mu + 1/\tau_{s,f})N_{f,s}^0}{\lambda_1 - \lambda_2} \\ C_{f,s} &= -\frac{PN(2\mu + 1/\tau_{s,f})}{\lambda_2(\lambda_1 - \lambda_2)} - \frac{PN + (\mu - P)N_{f,s}^0 + (\lambda_2 + P + \mu + 1/\tau_{s,f})N_{f,s}^0}{\lambda_1 - \lambda_2}. \end{aligned} \tag{4}$$

The transient ODMR signal can be calculated as

$$\mathrm{ODMR}(t) = \frac{1}{\tau_f}N_f(t) + \frac{1}{\tau_s}N_s(t). \tag{5}$$

In the following, using KBr as an example, we analyse the ODMR effect of the STE using the solution of the rate equations as derived above.

Figure 4 illustrates a fit of equation (5) to the measured transients for the $m_I = 0$ and $+1$ transitions. To improve the accuracy of the fitting procedure, solutions were calculated for both cases, microwaves on and off ($\mu > 0$ and $\mu = 0$, respectively). The initial conditions, in other words the actual populations N_s^0 and N_f^0 at the beginning of each period (microwaves on and off, respectively), depend on what happened in the previous period and what happened in all periods prior thereto. These populations were calculated iteratively. After optimization of the parameters for the pumping probability P and the microwave transition probability μ, they were kept constant for all three transitions ($m_I = 0, \pm 1$).

Table 1. Parameters of the fit of the transient ODMR measurements.

m_I	P (s^{-1})	μ (s^{-1})	τ_f (ms)	τ_s (ms)
+1	1.5	450	0.06 ± 0.01	1.9 ± 0.06
−1	1.5	450	0.06 ± 0.01	1.9 ± 0.1
0	1.5	450	0.06 ± 0.015	1.5 ± 0.1

Calculations showed that variations in μ are negligible for the different hf sublevels. For the transition $m_I = 0$ the measured transient used for the fit was scaled down by a factor of $\frac{3}{4}$ to compensate for the statistics of coupling of the two nuclear spins which do not enter the rate equations. The parameters obtained by the fit are listed in table 1. The agreement between this fit and the measured transients of the ODMR is excellent. The fit could reproduce the fact that the ODMR effect of the $m_I = 0$ transition is smaller if the gain due to the statistics of nuclear spin coupling (factor $\frac{4}{3}$ with respect to the $m_I = \pm 1$ transitions) is taken into account. One important result is that the lifetimes of the bottlenecks (slow component, τ_s) of the hf subsystems are different while the fast component (τ_f) does not change within experimental error. The lifetimes of the bottlenecks of the $m_I = \pm 1$ subsystems are both equal to 1.9 ms within experimental error, whereas the lifetime of the $m_I = 0$ transition is 1.5 ms. Because of the 'faster' bottleneck of the $m_I = 0$ hf subsystem with respect to the other hf subsystems, the ODMR effect is smaller. This results in a depression of the stationary ODMR spectrum for the $m_I = 0$ line. To demonstrate this we calculated the total area of the ODMR transients, being a measure of the signal obtained with lock-in detection. The ratio of the areas of the transients follows exactly the ratio of the ODMR lines measured with lock-in detection in ordinary stationary ODMR experiment.

Below, we discuss the reason for the faster decay of the bottleneck for the $m_I = 0$ situation. It is shown that the mixing of the spin wavefunctions of the triplet levels is the maximum for this hf subsystem and that this mixing reduces the lifetime of the bottleneck.

Now, we discuss some limiting cases. In our experiments, we excited optically the STE with an x-ray tube. The intensity and thus the pumping rate of the x-rays is very low. Therefore, the following conditions are certainly valid for our experiments:

$$P \ll \frac{1}{\tau_f}, \frac{1}{\tau_s}$$

and therefore

$$N \gg N_f, N_s. \tag{6}$$

Then, if the microwave power is switched off ($\mu = 0$), the time behaviour of the ODMR transients simply reflects the lifetimes τ_f and τ_s of the involved excited states, if the spin–lattice relaxation is negligible. Under this condition the difference between the exponentials of the fast decay (with τ_f) and the slow recovery (with τ_s) of the photoluminescence is measured. The fast decay results in a lowering of the photoluminescence intensity to a level lower than the stationary value without microwave transitions. The slow recovery to this stationary state without microwave excitation occurs with τ_s, the lifetime of the bottleneck. For this simple case the rate equations (1) can be simplified:

$$\frac{\mathrm{d}N_{f,s}}{\mathrm{d}t} = PN - \frac{1}{\tau_{f,s}} N_{f,s}. \tag{7}$$

The solutions are

$$N_{f,s} = PN\tau_{f,s} + (N^0_{f,s} - PN\tau_{f,s}) \exp\left(-\frac{t}{\tau_{f,s}}\right) \tag{8}$$

and the transient ODMR signal is

$$\mathrm{ODMR}(t) = 2PN + \frac{1}{\tau_s}(N^0_s - PN\tau_s)\ \exp\left(-\frac{t}{\tau_s}\right) + \frac{1}{\tau_f}(N^0_f - PN\tau_f) \exp\left(-\frac{t}{\tau_f}\right). \tag{9}$$

At $t = 0$ the microwaves induce transitions between both levels. Therefore, the population of the slow level is smaller than the stationary value for $\mu = 0$ ($N^0_s < PN\tau_s$) and that of the fast level is larger ($N^0_f > PN\tau_f$). Thus, the prefactor of the exponential with the fast lifetime is positive, while for the slow lifetime it is negative, resulting in a difference of exponentials as mentioned above. If spin–lattice relaxation were important, the ODMR transients would be more complicated than the simple difference of exponentials with the fast and the slow lifetime.

The lifetimes we estimated from such decay experiments are consistent with the values we obtained from the fit of (2) to the whole ODMR transient, consisting of periods where the microwaves are switched on and off. Moreover, we found that the rise time of the photoluminescence after switching on the microwaves is equal to the lifetime of the fast excited states. From equation (3) it can be easily seen that this can only happen if the microwave transition probability μ is small in comparison to the lifetime τ_f of the fast levels. This is not the case for the slow levels. Here μ is of the order of $1/\tau_s$ (from the fit, $\mu = 450\ \mathrm{s}^{-1}$ and $1/\tau_s \approx 670\ \mathrm{s}^{-1}$ and $530\ \mathrm{s}^{-1}$, for the $m_I = 0$ and ± 1 transition, respectively). This can be seen in the different recovery times after switching off the microwaves in comparison to the decay of the ODMR transient to the stationary value after switching on (recovery time $= \tau_s = 1.5$ ms for $m_I = 0$ and 2 ms for $m_I = \pm 1$ in comparison to the decay times of the ODMR transients of 0.9 and 1.0 ms, respectively). For the conditions in our experiments ($P \ll 1/\tau_{f,s}$, $\mu \ll 1/\tau_f$, $\mu \sim 1/\tau_s$) the time behaviour of the ODMR effect after switching on the microwaves is

$$\lambda_1 = -\mu - \frac{1}{\tau_s} \qquad \lambda_1 = -\frac{1}{\tau_f}. \tag{10}$$

Under saturating microwave transitions the decay time of the ODMR transient to a stationary value after switching on would be $\frac{1}{2}(1/\tau_f + 1/\tau_s)$ (Barry 1992) which can be easily seen from (3). With our estimated lifetimes this decay would be of the order of 0.1 ms, which was not measured.

4. Discussion

4.1. Line shape of the ODMR of the STEs

Our observations and their analysis in KBr are thought to have the same reason as the observations made with stationary ODMR in NaBr. We propose the same reason for the 'flattened' lineshape of the STEs in NaBr and KBr seen with the lock-in technique. We found that the lifetimes of the STE hf lines are different for the different nuclear spin states. We note that at the first moment of the switching 'on' of the microwaves the ratio of the amplitudes of the ODMR effect for different hf lines is close to the ratios, which are expected from the V_K-centre nuclear spin statistics. In the ODMR experiments with a pulse technique (Kan'no *et al* 1996) less depression of the ODMR lineshape has been observed.

We note that the same 'flattened' lineshape has been found in all of the other conventional lock-in measurements on STEs in alkali bromides with NaCl-type structure—KBr (Wasiela *et al* 1973, Marrone *et al* 1973) as well as RbBr (Mori *et al* 1978) (in hf line groups for the 0° oriented STEs, where the overlaps with the 90° oriented STEs have not significantly influenced the middle lines of the hf spectrum). Such 'flattened' lineshapes of the ODMR spectra of the STE seem to occur in bromides, but not in the chlorides (e.g. KCl (Block *et al* 1978)). The hf interaction parameters for V_K centres are much larger in bromides than in chlorides, which may lead to a larger influence of the nuclear spin states on the lifetimes of the STE hf components. We have performed some experiments with probably not so pure KBr crystals where the amplitude of the middle hf line became even lower than that of the two adjacent ones. The ODMR measurements presented in figures 2–4 were performed on extremely pure KBr crystals.

4.2. Lifetimes of different nuclear spin states

We found that the lifetimes for the fast and slow components in KBr are very close to those published by Mukai *et al* (1989). Let us discuss the reason for the observed lifetime shortening of the middle hf line of the ODMR of the STE in the slow decay component (bottleneck). Our explanation is based on the idea that the radiative lifetimes of the hf sublevels are changed when mixing with other hf sublevels belonging to the nearby triplet sublevels.

The hf Hamiltonian term considered here is

$$H_{hf} = a(I_Z S_Z + (S_+ I_- + S_- I_+)/2). \tag{11}$$

The second term of the hf interaction is the term mixing the various m_I levels between the three sublevels of m_s. Thus it raises or lowers m_I by unity as follows:

$$I_+|I, m_I\rangle = \sqrt{I(I+1) - m_I(m_I+1)}|I, m_I + 1\rangle \tag{12}$$

$$I_-|I, m_I\rangle = \sqrt{I(I+1) - m_I(m_I-1)}|I, m_I - 1\rangle. \tag{13}$$

The $m_s = 0$ state is purely a triplet in the absence of a magnetic field. The long-lifetime component of the triplet originates from this state. We estimated the lifetimes of the sublevels through perturbation theory. We found that in our present model the lifetimes of the long-lifetime component have a trend to increase from the central to the side lines, which is in agreement with the experimental fit shown in table 1. We analysed in the present model also the lifetimes of the short-lifetime components arising in our experiment from the $m_s = +1$ state. In this case the perturbation contributes only a small change in the wavefunction. The mixing term of the hf interaction Hamiltonian does not modify the lifetimes within experimental precision. This is what we observed by the experimental fit shown in table 1.

4.3. Analysis of the D value of the STE in NaBr

The main point which sets NaBr apart from the other two bromides is the magnitude of the D parameter. It is 1.7 T in NaBr compared with 0.265 and 0.185 T, respectively, in KBr and RbBr. There is therefore almost an order of magnitude difference. The case of KBr and RbBr has been satisfactorily understood in terms of the large off-centre geometry of the STE which makes the STE more like a second-nearest-neighbour F–H pair. One of the principal points of interest is whether an STE in NaBr is in the strictly on-centre geometry, with the point group D_{2h} symmetry, or slightly off centre with C_{2v} symmetry.

Several aspects are well established regarding these geometries. First, in the on-centre case the hole distribution is equal on the two bromide ions while it is strongly polarized when it is weakly off centre (Song and Williams 1996). The bromide ion, which is closer to the localized electron, carries more hole. The other point is that the electron wavefunction is quite different in the two geometries. In the on-centre case the wavefunction is very extended (Song and Williams 1996), while in the off-centre case the wavefunction is much more compact, similar to that of the ground state of an F centre.

The zero-field splitting parameter D is made up of two contributions, D_{ss} and D_{so}, representing the dipole–dipole and spin–orbit interactions, respectively. The first term can be estimated from an approximate knowledge of the wavefunctions of the electron and hole as well as their separation in the lattice. In the NaCl lattice along the $\langle 110 \rangle$ axis, D_{ss} is negative (Song *et al* 1990). For large separation it varies as d^{-3} where d is the separation of the two dipoles. D_{so} has been derived by Fowler *et al* (1973) for the on-centre case:

$$D_{so} = \xi^2 \Delta / 4E_{\perp}^2 \tag{14}$$

where ξ is the spin–orbit splitting, Δ the exchange energy and $E_{\perp}$ the energy difference between σ_u and π_u states. This formula has been derived for the on-centre geometry, the only model of the STE at the time. On the other hand, it is reasonable to apply it to the strongly off-centre STE such as in KBr and RbBr. Indeed, in those STEs the hole centre of the STE is a more or less well formed H centre occupying a single cation site. In such cases, the hole population is found equally distributed on the two halide ions (Song and Williams, 1996).

The problem is that this formula has not been tested for a weakly off-centre geometry STE such as might be the case in NaBr. Based on this information we attempt to estimate the two contributions to D and determine the nature of the STE in NaBr as indicated by the ODMR.

(i) *The on-centre STE.* Using the 14 above and values of the parameters ($\xi = 0.306$ eV, $\Delta = 0.04$ eV, $E_{\perp} = 1.95$ eV for the V_K centre), D_{so} is found to be $\cong$2000 mT. From a theoretical estimation of $D_{ss} = -20$ to -160 mT, we obtain $D \cong 1980$ to 1840 mT. These values are close to the new value obtained here, 1.7 T, if we assume that $D > 0$. As we argued already in our previous paper (Rogulis *et al* 1995) the wavefunction of the electron which was used ($\alpha = 0.002$ to 0.01 in units of Bohr radius squared) in obtaining D_{ss} seems incompatible with the short triplet lifetime in NaBr.

(ii) *The off-centre STE.* Instead of estimating D_{so} directly from the above equation, we attempt to find 'reasonable' values of D_{so}, which can give acceptable values of D_{ss} and d_{H-F}. We have examined a range of D_{so} between 1000 and 3000 mT. We assumed that D is positive, following Kawata *et al* (1992). When we accept that the off-centre shift can only be very moderate in NaBr, we found that the set $D_{ss} \cong -1300$ mT and $D_{so} \cong +3000$ mT is most reasonable. Corresponding to this D_{ss} value the separation between the electron and hole centres is estimated to be small, about 1 Å. These data are shown in table 2.

As we can see the most uncertain element is D_{so} for NaBr in the weakly off-centre geometry. Equation (14) is valid for both the on-centre and the strongly off-centre case. The main difference between an H centre and a V_K centre (of an on-centre STE) is in the hf interacting level difference $E_{\perp}$ between the σ_u and π_u states. $E_{\perp}$ is considerably larger in an H centre (see figure 6) (Stoneham 1975). In the absence of a suitable theory to treat a polarized H centre, we will rely on the general relationship between D_{so} and other parameters contained in (14) to understand the reason for the much larger D_{so} value in NaBr compared to those in KBr and RbBr. As we stated above, the hole centre of a weakly

Table 2. A comparison of experimental zero-field splitting parameters with theoretical estimates for three alkali bromides.

	d_{H-F} (Å)	D (mT)	D_{so} (mT)	D_{ss} (mT)
NaBr	~ 1	1700	3000	−1300
Kbr	5	+ 265	665	−400
RbBr	6	+ 185	405	−220

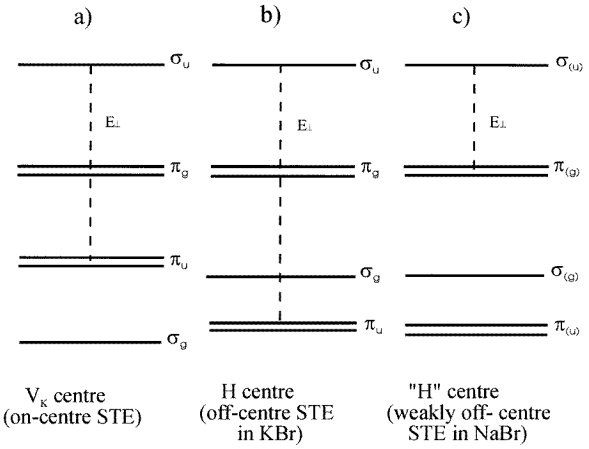

Figure 6. X_2^- energy levels. Broken lines indicate the spin–orbit coupling of the levels. (a) V_K centres (on-centre STE). (b) H centre (after Stoneham (1975)) (off-centre STE). (c) 'H' centre (weakly off-centre STE) in NaBr.

off-centred STE is strongly polarized and it should not be considered to be a regular H centre. The centre of inversion is lost in such a case and as a result σ_u and σ_g as well as π_u and π_g are substantially mixed. This situation is schematically shown in figure 6(c). The mixing pairs of levels repel in energy to some extent. One principal effect of this mixing is in the contribution to D_{so}. Not only the original pair, $\sigma_{(u)}$–$\pi_{(u)}$, contribute, but also the pair $\sigma_{(u)}$–$\pi_{(g)}$ could contribute to D_{so}. Indeed, the latter could be dominant, because of the smaller energy difference. This could explain the much larger value of D_{so} for NaBr which we chose above.

5. Conclusion

Our new measurements with the frequency of 25.9 GHz together with the previous measurement using 24.0 GHz have shown that the zero-field splitting of the STE in NaBr is indeed very large in agreement with the recent results of Kan'no *et al* and not small as we had concluded from our previous measurement at 24 GHz. The non-Gaussian line shape with a depression in the middle has been reinterpreted. The line originates in one fine-structure transition only, but its shape deviates from the Gaussian line form expected from unresolved hf interactions with the two Br nuclei of the V_K centre. The depression in the middle is a consequence of the different radiative lifetimes of the nuclear spin sublevels together with the lock-in technique used to observe the ODMR spectrum. The $m_I = 0$

sublevel of the bottleneck state ($m_s = 0$) experiences a relative shortening in the radiative lifetime compared to the other m_I sublevels. This shortening occurs because of larger admixtures of nuclear sublevels in the $m_s = \pm 1$ manifold into the $m_s = 0$, $m_I = 0$ state compared to the other m_I, $m_s = 0$ levels because of the large Br hf interactions. This effect was demonstrated by transient measurements of the ODMR of the STE in KBr. The shortened lifetime of the m_I sublevels leads to a 'weakening' of the bottleneck condition and therefore to a reduced signal measured in the lock-in technique. This effect occurs in all bromides, with a large hf interaction as seen from the ODMR line shapes and not in the chlorides, with a smaller hf interaction. The large D value is interpreted to be due to a STE in an off-centre configuration, where the separation between the electron and the hole centre is small, estimated to be approximately 1 Å.

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