Optically detected magnetic resonance of the self-trapped exciton in NaBr

U Rogulis†§, J-M Spaeth† and K S Song‡

† Fachbereich Physik, Universität-GH Paderborn, Warburger Strasse 100, D-33098 Paderborn, Germany
‡ Department of Physics, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

Abstract. The optically detected electron paramagnetic resonance spectrum of the self-trapped exciton in NaBr is measured using x-ray excitation of the triplet luminescence. The zero-field splitting parameter was found to be $D = (23 \pm 2.5)$ mT, an order of magnitude smaller than that of KBr and RbBr. The self-trapped exciton in NaBr is believed to be of type I, i.e. the electron and hole occupying an on-centre geometry in contrast to the off-centre configuration of type III, found in most alkali halides. For an explanation of the small D value measured one has to assume, however, that also in NaBr the electron and hole are split as in a primitive F–H pair, with the distance between them of about 1.5–3 Å.

1. Introduction

Self-trapped excitons (STEs) in alkali halides are of fundamental importance for atomic processes induced by electronic excitations, including the photochemical formation of F centres (an electron trapped at an anion vacancy) and H centres (a halogen$_2^-$ molecular ion on an anion site, oriented along a $\langle 110 \rangle$ direction). STEs were studied extensively with a variety of spectroscopic techniques (for a recent review see e.g. Song and Williams 1993). It is now generally agreed that in alkali halides the STEs can be visualized as a primitive F–H centre pair which undergoes a radiative transition emitting π polarized light from a spin triplet state and a σ-polarized light from a singlet state. According to a series of calculations, the STEs are off centre along the $\langle 110 \rangle$ directions, i.e. the centres of the F and H centres are displaced from each other along a $\langle 110 \rangle$ direction (Song et al 1989, Song and Baetzold 1992, Shluger et al 1991). The stable F–H centre pairs are created dynamically at low temperature in those crystals in which the off-centre motion is accompanied by large relaxation energy. These crystals also have a large Stokes shift of the π band, which can be as much as 70% of the free exciton absorption energy. STEs of this kind have been classified as of type III (Kan'no et al 1990). They occur in the fluorides, KCl, RbCl, KBr, RbBr and RbI. In contrast, the STEs in NaBr and NaI are characterized by a small Stokes shift ($\sim$20%) and a very small F centre formation yield at low temperature. They are classified as of type I. The STEs in NaCl and KI are in between (type II).

Recent experiments have greatly contributed in confirming this general picture of the STE and its relation to the primary lattice defects created under radiation. They include the

§ Permanent address: Institute of Solid State Physics, University of Latvia, 8 Kengaraga Street, LV-1063 Riga, Latvia.

resonant Raman scattering (RRS) of the STE in a number of crystals (Suzuki *et al* 1994), transient absorption of the STE in the group I crystals (Hirota *et al* 1991), femtosecond pulse work on the F centre creation (Tokizaki *et al* 1991) and observation of correlated F–H pairs in KBr at low temperature (Meise *et al* 1994). In particular, the RRS has shown that in type II and III crystals the hole of the STE is practically an H centre with its stretching mode frequency identical with that of the isolated H centre. On the other hand, in type I material, the frequency is the same as in a V_k centre (a hole shared between adjacent halogen ions along a $\langle 110 \rangle$ direction). This seems to indicate that whether or not the molecule-ion occupies a one-anion site or two-anion sites determines whether or not the frequency of the stretching mode is that of an H or V_k centre.

There remain, however, a few intriguing questions. One of them is whether or not the type I STE is truly on-centre with the symmetry of the D_{2h} point group. In this symmetry, the hole and the electron would share the same centre of symmetry along $\langle 110 \rangle$. None of the above experiments shed light directly on this point, except possibly the transient absorption in NaBr and NaI (Hirota *et al* 1991). In sharp contrast to other materials, the lowest absorption was found to be in the infrared region, at less than 0.2 eV. Earlier calculations assuming the D_{2h} symmetry have all shown that the lowest absorption band, corresponding to a_g–b_{3u} electron states, is in the range of 0.5 eV in sharp disagreement with the then available data in type II and III crystals which were around 2.0 eV. This was considered as a sign showing that in type I the STE is occupying a truly on-centre geometry. A recent all-electron *ab initio* Hartree–Fock calculation of the STE triplet states in NaBr for both on-centre and off-centre geometries (Baetzold and Song 1993) shows that indeed the absorption energy is better accounted for with the on-centre geometry, but the recombination luminescence is in better agreement if the off-centre geometry is assumed. Also, the adiabatic potential energy calculation indicates that the on-centre geometry is unstable in NaBr also. This problem is difficult to decide on the grounds of calculations alone due to the possibility of configuration interaction in the on-centre geometry and the limited size of the quantum cluster used in all such calculations.

A quantity which is sensitive to the relative displacement between the F centre and the H centre forming the triplet state from which the π emission occurs is the zero-field splitting parameter D. This was shown previously for the alkali fluorides (Song *et al* 1990). It was the purpose of this paper to measure the zero-field splitting for the STEs in NaBr as well as the Br hyperfine (HF) interactions of the halogen molecular ions and to investigate whether or not they can be explained with the on-centre model for the type I STEs.

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 optically detected electron paramagnetic resonance (ODEPR) was measured as a microwave-induced change of the luminescence intensity in a computer-controlled custom-built K band spectrometer (24 GHz). The NaBr crystal could be x-irradiated at 1.5 K *in situ* in the cavity of the ODEPR spectrometer. The x-ray-induced fluorescence was measured with a photomultiplier. For spectral resolution several interference filters were used. The x-ray tube (60 kV, 15 mA) was placed at a distance of about 15 cm from the sample; the x-rays were passed through a Be window. It was necessary to carefully shield the static magnetic field generated by two superconducting solenoids within the tail of the helium cryostat of the ODEPR spectrometer during the spectrometer operation, since otherwise the x-ray tube did not function properly. Because of the shielding the absolute value of the magnetic field was less well known than

usual resulting in a larger error of the absolute g value ($\pm 10^{-2}$). However, field differences could be measured with the usual accuracy.

3. Experimental results

In the x-ray fluorescence band of the STEs, the ODEPR spectrum was measured for $B_0 \| [110]$ as a microwave-induced increase of the luminescence intensity. The ODEPR spectrum is shown in figure 1. It consists of a rather broad line around $g \sim 2$. The signal-to-noise ratio is rather poor. This is not altogether surprising. Apart from a rather high noise of the x-ray intensity (5–10%), the rather short radiation lifetime of 0.48 μs for the triplet STEs in NaBr prevents good EPR signals. Because of the microwave power available of only 50–100 mW in the cavity, the time for a spin-flip is only of the order of magnitude of the radiative life time of the STEs. Therefore, no efficient spin flip-induced fluorescence intensity changes can be obtained. The ODEPR line shows indications of a structure. Its line shape is 'flat' around $g \sim 2$ (at $B \approx 850$ mT), showing that this is not a single line of Gaussian shape as expected for a single inhomogeneously broadened EPR line (see below). In order to be sure to have measured the spectrum of the STE, we measured the optical excitation spectrum of the EPR spectrum by setting the magnetic field to the centre of the EPR line (850 mT). We used several interference filters with half width of about 22 nm and 25% transmission to spectrally resolve the luminescence. Figure 2 shows the optical excitation spectrum of the ODEPR line. The peak at ~270 nm agrees with the published peak of the π luminescence of the STE in NaBr at 266 nm (Song and Williams 1993, table 5.8). Also the band width is in fair agreement with that of the STE (0.46 eV) within experimental accuracy, which is not very high due to the filter width. The x-ray fluorescence intensity was not intense enough to measure the excitation spectrum through a monochromator.
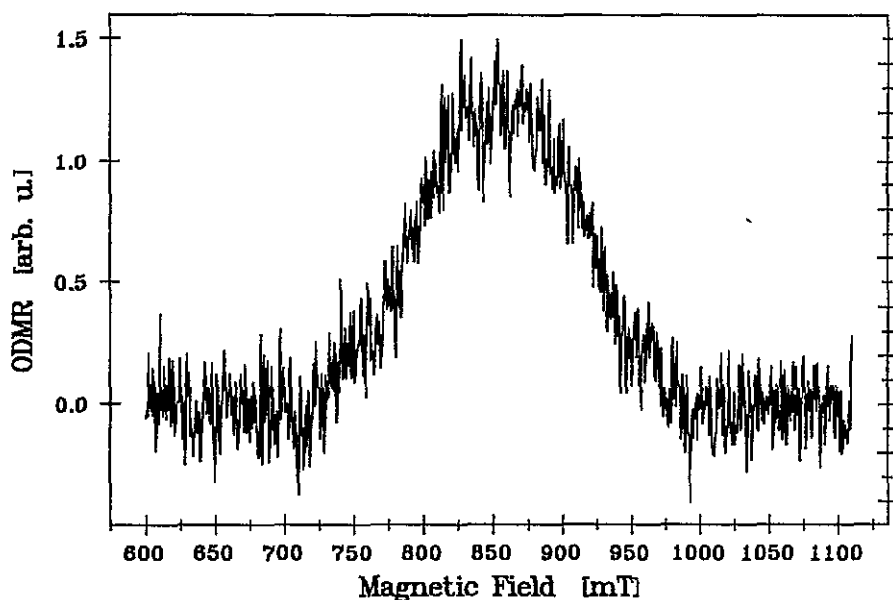

Figure 1. Optically detected EPR spectrum of the triplet STE in NaBr for $B\|[110]$, $T = 1.6$ K, ($\nu_{ESR} = 24$ GHz).
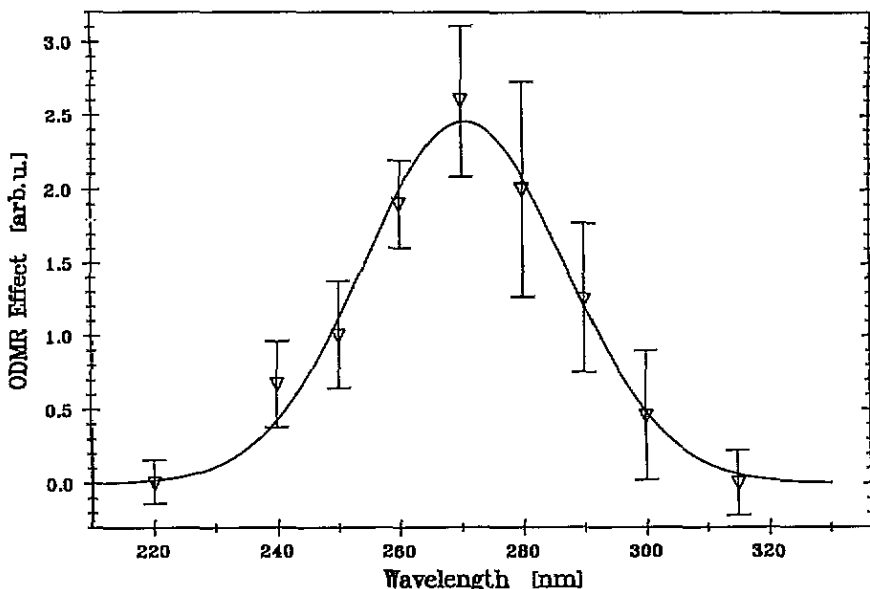
Figure 2. Excitation spectrum of the ODEPR line measured at $B = 850$ mT using a set of interference filters of 25% transmission and a half width of about 22 nm. $T = 1.5$ K, $\nu_{ESR} = 24$ GHz.

For the triplet state (electron spin $S = 1$) of an STE for the magnetic field parallel to the $\langle 110 \rangle$ orientation one expects to observe an EPR spectrum consisting of two line groups separated by the zero-field splitting, each group having a resolved structure because of the HF interaction with two equivalent halogen nuclei or being inhomogeneously broadened by this interaction. For example, such a spectrum was observed in KBr (Wasiela *et al* 1973a, Marrone *et al* 1973). Thus, the ODEPR spectrum should be described by a spin Hamiltonian of the form

$$\mathcal{H} = \mu_B B_0 gS + SFS + \sum_{i=1,2} I_i A_i S \tag{1}$$

where the terms represent the electronic Zeeman energy, the fine-structure interaction and the hyperfine (HF) interaction with the two central halogen nuclei of the molecular ion (V_k or H centre). In NaBr, one would expect a seven-line HF structure due to the interaction with the two equivalent Br nuclei of the V_k centre (both isotopes ^{79,81}Br have $I = \frac{3}{2}$ and about equal abundances, with only a small ($<10\%$) nuclear g factor difference). For $B \| [110]$ these two groups should be separated by the fine structure interaction. Assuming an axial fine-structure tensor F, the splitting is expected to be given by $2D = F_{zz}$, where D represents the zero-field splitting parameter (see e.g. Song and Williams 1993, ch 5.4). The measured spectrum can be explained with a g factor of $g = (2.01 \pm 1 \times 10^{-2})$, the zero-field splitting constant of $D = (23 \pm 2.5)$ mT and a Br HF interaction $A_{zz} = (28 \pm 2)$ mT (the isotope difference was neglected).

Figure 3 compares the calculated spectrum with the experimental one. In figure 3(b) and 3(c) the two Br HF structures are shown (with an unrealistic small line width for the sake of clarity and neglecting the small isotope differences), which are displaced from each other by $2D$. Assuming an individual line width of 25 mT for the Br HF lines, one obtains the calculated spectrum in figure 3(a) (continuous line), which shows very good agreement with the experimental one. The experimental line shape would be Gaussian for $D = 0$,
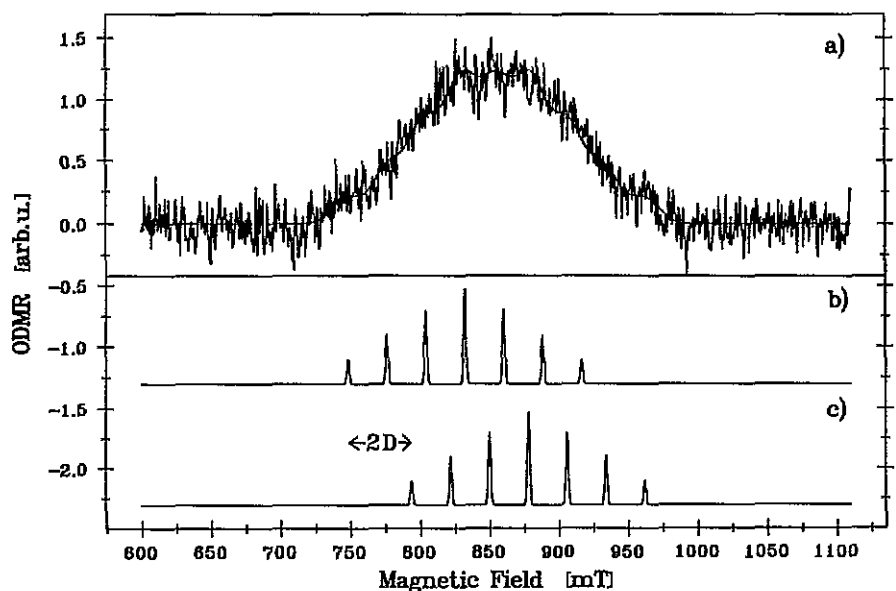
Figure 3. Comparison of the calculated and experimental ODEPR spectrum of the STE in NaBr for $B_0 \| [110]$. (b) and (c) stick spectra of the two Br hyperfine septets for two equivalent Br nuclei, split by the zero-field splitting of $2D$; (a) experimental and calculated spectrum (solid line) with $g = 2.01$, $D = 23$ mT, $A_{zz} = 28$ mT, the single Br HF lines had a width of 25 mT.

which is not observed, and would show a splitting into two separate broad lines for a larger D. Whether or not there is also a (small) deviation from axial symmetry for the zero-field splitting as found, e.g. in KBr, we cannot say. The ODEPR lines of other STE orientations are usually much weaker; they could not be detected here (see e.g. Song and Williams 1993, ch 5.4).

In figure 4 an attempt is shown to explain the spectrum assuming that the two Br nuclei of the V_k centre are not equivalent, a situation which may occur for a small displacement between the F centre and the V_k centre. A reasonable explanation of the measured spectrum could be obtained for the following set of data: $A_{zz1} = (24 \pm 2)$ mT, $A_{zz2} = (31 \pm 2)$ mT and $D = (24 \pm 2.5)$ mT. (The individual line width was again 25 mT.) With this set of data, the mathematical overall difference between the measured and calculated spectrum was the same as for the assumption of two equivalent Br nuclei as made above but the weak structure of the measured spectra may seem a little better represented by the simulation assuming equivalent nuclei. However, this is hard to decide.

The sign of the fine structure splitting D could not be measured, since attempts to measure the magnetic circular polarization of the emission were not successful.

4. Discussion

4.1. Zero-field splitting parameter

We have two parameters which could give us in principle indications as to the precise nature of the symmetry of the STE in NaBr: the zero-field parameter D and the hyperfine interaction parameter A_{zz}. In this section we first discuss the zero-field parameter D, which
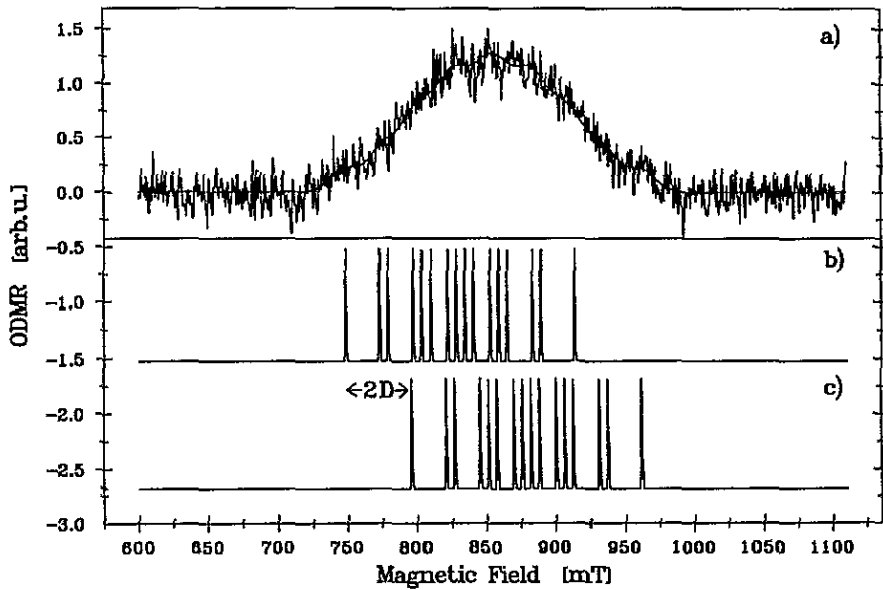
Figure 4. Comparison of the calculated and experimental ODEPR spectrum of the STE in NaBr for $B_0 \| [110]$. (b) and (c) stick spectra of two inequivalent Br nuclei split by the zero-field splitting of $2D$; (a) experimental and calculated spectrum (solid line) with $g = 2.01$, $D = 24$ mT, $A_{zz1} = 24$ mT, $A_{zz2} = 31$ mT; the single Br HF lines had a width of 25 mT.

contains two parts:

$$D = D_{so} + D_{ss}$$

where D_{so} is the spin–orbit contribution and D_{ss} the dipole–dipole term (Song and Williams 1993). The zero-field splitting parameter D is very useful in determining the geometry of the F centre relative to the H centre, and also the distance separating the two centres when the spin–orbit coupling is weak or negligible (Song *et al* 1990). In the alkali halides D_{so} is positive and D_{ss} is negative (Song and Williams 1993). Unfortunately, in the bromides the spin–orbit contribution D_{so} dominates over the dipole–dipole term D_{ss} and the analysis used in Song *et al* (1990) is not applicable until we have estimated the contribution of the spin–orbit term D_{so}. This is attempted in the following separately for the on-centre (D_{2h} point group) and off-centre (point group C_{2v}) geometries. The knowledge that the wavefunctions of the excited electron are very different in the two geometries (Song and Leung 1989, Song and Baetzold 1992, Shluger *et al* 1991) is important for the present analysis. The wavefunction is very diffuse in the on-centre case and we have used a Gaussian with $\alpha \cong 0.002$ (au) in $\exp(-\alpha r^2)$, while for the off-centre case $\alpha \cong 0.05$ (au) typically, as for an F centre. D_{so} was derived by Fowler *et al* (1973) earlier for the on-centre case:

$$D_{so} = \zeta^2 \Delta / 4E_\perp^2. \tag{2}$$

Here, Δ is the exchange energy and ζ is the spin–orbit coupling parameter. $E_\perp$ is the energy splitting between the Σ_u^+ ground state and the Π_u excited state and is taken from that of the V_k centre ($= 1.95$ eV) (Wasiela *et al* 1973b) and Δ is known for the free exciton (0.370 eV). Δ of the STE (off centre) is systematically smaller than in the free exciton by a factor of between $\frac{1}{3}$ and $\frac{1}{30}$ (Song and Williams 1993). For those where data are available, Δ is of the order of 10 meV. However, in the on-centre STE it is expected to be smaller than in free excitons because of the diffuse nature of the electron wavefunction. As Δ in this

case is impossible to estimate in an independent way, we simply scaled Δ from a maximum of 0.04 to a minimum of 0.004 eV to get a range of D_{so}: 2030 mT to 203 mT. Taking $D_{ss} = |D| - D_{so}$, and acknowledging that we do not have the sign of D, D_{ss} is found to be in the range of $-(2000\pm23)$ mT to $-(200\pm23)$ mT. On the other hand, we have evaluated D_{ss} using a simplified basis of Gaussians. The hole is represented by p-like Gaussians centred on the two sites of Br_2^-, with $\alpha_h = 0.3$ (au) and the excited electron centred at the mid-point of Br_2^- with $\alpha_e = 0.002$–0.01. We obtained $D_{ss} = -22$ mT to -160 mT. This shows that the value of D_{ss}, including its sign (negative), could be explained only with a diffuse excited electron and for a very small value of Δ. We will come back to this result below.

For the off-centre geometry, the electron is strongly localized on one anion site and it polarizes the H centre (Br_2^-) strongly if close (<1 Å) (Song and Baetzold 1992). As the formula above for D_{so} was derived for the on-centre symmetry, we are not using it. Instead, we try to estimate it from those of KBr and RbBr assuming that we have reasonable values for the D_{ss} for these bromides. Indeed, earlier calculations as well as a semiempirical fit of the triplet π band lifetimes as a function of the distance between the F and H centres give a good correlation (Song and Chen 1989). We use those values of d_{H-F} for KBr and RbBr (5 and 6 Å respectively) to arrive at D_{ss} of -400 and -220 mT respectively (d_{H-F} is the distance between the centre of the F centre and the midpoint of the Br_2^- molecule). From the experimental values of D, $+265$ and $+185$ mT for KBr and RbBr respectively, one obtains D_{so}: 665 and 405 mT. By extrapolating these data, we assume that D_{so} of NaBr, in the off-centre geometry is in the range of 800 to 1000 mT. From the measured $|D|$ value of 23 mT, we can deduce the range of d_{H-F}: 1.5–3.0 Å with which we can fit D_{ss}. These data are assembled in table 1.

Table 1. Comparison of experimental zero-field splitting parameters with theoretical estimates for three alkali bromides.

	d_{H-F} (Å)	D (mT)	D_{so}	D_{ss}
NaBr	1.5–3.1	[23]	1000–800	-1020 to -780
KBr	5	$+265$	665	-400
RbBr	6	$+185$	405	-220

From the above discussion, it appears that both models are capable of accounting for the observed $|D|$ value of 23 mT, much smaller than in KBr and RbBr. However, when the lifetime of the π band in NaBr of 4.8×10^{-7} s is compared to those in the other two of 1.3×10^{-4} s and 1.8×10^{-4} s, respectively, it becomes clear that the very diffuse on-centre electron wavefunction is incompatible with such a short lifetime. An estimate of the lifetime of the π band as a function of α_e of the excited electron yields that for a value of $\alpha_e = 0.002$ a value of $\tau = 10^{-3}$ s is expected, while for $\alpha_e = 0.01$ τ becomes 10^{-5} s. We, therefore, conclude here on the basis of the D value analysis, although it was semiquantitative, that the triplet STE in NaBr is probably of C_{2v} symmetry with a relatively small shift of $Q_2 \approx 1$ Å from the on-centre position, where $Q_2 = d_{H-F} - a/\sqrt{2}$, a being the nearest-neighbour distance (Song and Williams 1993, ch 5).

4.2. Hyperfine structure

A dominant contribution to the HF interaction parameter A_{zz} will be due to the V_k centre part of the STE. For the V_k centre in NaBr itself $A_{zz} = 44$ mT (Shoemaker 1973). Since the spin

Hamiltonian of equation (1) refers here to an $S = 1$ system, the HF parameters of electron and hole are scaled by one half, i.e. the V_k contribution alone would be 22 mT, assuming *that the two Br nuclei are equivalent. If we assume that the two Br nuclei are inequivalent,* the situation is similar to that in the fluorides, such as in CaF$_2$. Indeed, according to theoretical calculations on NaBr (Song and Williams 1993, ch 5), at the off-centre shift of about 1.5 Å *($d_{H-F} \cong 3.6$ Å), the hole charge is distributed as 60 against 40%. If we scale* the HF parameters of the V_k centre according to this weight and scale again by $\frac{1}{2}$, then one obtains 26 and 18 mT, which can be compared to 31 and 24 mT obtained above as a possible fit. The discrepancy can be attributed in part to the contribution of the F centre which is very close to one Br atom. If, on the other hand, we assume a hole distribution of 55 against 45%, then the A_{zz} are 24 mT and 20 mT. One should note that the wavefunction *of the excited electron localized on the anion site is strongly distorted according to ab initio* calculations and the contribution of the F centre to the HF point contact term may not follow from that of a simple exponential decay.

The HF interaction parameter estimate requires careful consideration of the details of the electron wavefunction at an ionic site, e.g. the amplification factor (Seidel and Wolf 1968). Beside, the electron wavefunction is quite distorted compared to that of a regular F centre.

On the other hand, if we assume that the STE in NaBr is on-centre with the symmetry of D$_{2h}$ point group, then A_{zz} is fitted to be 28 mT which is larger than half the V_k value by about 6 mT. This discrepancy cannot be explained by a diffuse excited electron. The HF contribution of a diffuse electron with $\alpha_e = 0.002$ (see section 4.1) is very small. From a crude approximation, it can be estimated to be two or three orders of magnitude smaller than for the Br$^-$ (second-nearest neighbour) of an F centre, which in NaBr is estimated to be about 2.5 to 3 mT by extrapolation from the known values in KBr and RbBr (Seidel and Wolf 1968).

Thus, we conclude, although a number of parameters are not quantitatively known and had to be estimated crudely, that our overall analysis explains the observed zero-field splitting and HF interaction reasonably well with an off-centre model and an off-centre shift Q_2 by about 1 Å. Not only can the on-centre model not explain D and A_{zz}, but it also fails to account for the lifetime of the π luminescence.

Thus, the conclusion is that the type I STE is not truly of on-centre geometry, but of split electron–hole geometry as in types II and III. The magnitude of axial shift is much smaller, however.

Acknowledgments

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