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Magneto-optical properties of the UV absorption bands of V_K centres in alkali halides

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Abstract. A new UV absorption band below the original UV band has been discovered through the magnetic circular dichroism of the V_K centre absorption (MCDA) in seven alkali halide crystals. This new band is attributed to the transition $\Sigma_u \rightarrow \Pi_u$ which becomes dipole allowed as a result of a loss of inversion symmetry. We attribute this lowered symmetry to the slow axial oscillation along the V_K axis which results in a momentarily ‘frozen’ geometry of the species at the classical turning point. An approximate estimation of the coupling between the even and odd parity molecular orbitals of Σ and Π symmetry is made in KBr. From this it appears that the coupling between the even and odd parity states is not negligible. Observed experimental trends in the seven crystals are explained from this model.

1. Introduction

V_K centres in alkali halides are trapped hole centres, in which the hole is shared between two adjacent halogen ions along the (110) directions. They have been investigated intensively with optical spectroscopy and electron paramagnetic resonance (EPR) (see e.g. Fowler 1968). V_K centres are created by ionizing radiation and are only stable below room temperature. V_K centres are fundamental hole centres which play a key role in many luminescence processes, for example in scintillator crystals for the detection of x-ray radiation (see e.g. Spaeth *et al* 1994a for the system CsI:Tl). The optical absorption bands of V_K centres are found in the UV and in the IR spectral regions and are explained as $\Sigma_u \rightarrow \Sigma_g$ and $\Sigma_u \rightarrow \Pi_g$ transitions in an X_2^- ($X = \text{halogen}$) molecular model, respectively. Also the EPR of the V_K centres is explained with this model (Schoemaker 1973). There is the general view that V_K centres have a perfect D_{2h} symmetry, in which the halogens have inversion symmetry, i.e. have the same hole charge. Recently for V_K centres in KBr a second absorption band was identified in the UV by means of measuring the magnetic circular dichroism of the absorption (MCDA) and the MCDA-detected EPR spectrum (Spaeth *et al* 1994b). Its MCDA peaks at 2.7 eV, whereas the previously reported absorption band peaks at 3.22 eV (Delbecq *et al* 1961). Only for KI has a second UV transition peaking at 2.12 eV been reported previously by Delbecq *et al* (1961). This second UV transition cannot be explained with the conventional X_2^- molecular model. In KI it was tentatively attributed by Delbecq *et al* (1961) to a $\Sigma_u \rightarrow \Pi_u$ transition, which is forbidden in the X_2^- molecular

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model because of the parity violation, but which could be allowed as a consequence of some distortion, which, however, remained unspecified in Delbecq *et al* (1961). It was speculated by Rogulis *et al* (1993) and Spaeth *et al* (1994b) that the loss of inversion symmetry might arise from a soft axial translational vibrational mode of the V_K centres. It was proposed that the very slow axial oscillations of the centre make the centre seem 'frozen' at the classical turning points during the optical transition, which would be equivalent to having a momentarily off-centre geometry making the $\Sigma_u \rightarrow \Pi_u$ transition allowed.

It is the purpose of this paper to examine whether the occurrence of this second UV absorption band is a common feature to all V_K centres in alkali halides of the NaCl structure. We therefore investigated V_K centres in seven alkali halides with the MCDA technique. We found that indeed the second UV transition is a common feature, which in many cases is only revealed by means of the MCDA and, therefore, has escaped previous investigations of the optical absorption. We tentatively explain the absorption assuming a soft axial translational vibrational mode of the V_K centres, i.e. by a dynamically broken inversion symmetry.

2. Experiment

The alkali halide crystals were grown with the Czochralski method and doped with NO_2^- (0.5 mol% in the melt for NaCl and KCl, 1 mol% for NaBr) or TI (0.5 mol% in the melt for KBr, KI, RbBr and RbI) in order to facilitate the generation of V_K centres by x-irradiation. The crystals were irradiated with x-rays (50 kV, 5 mA) *in situ* in the MCDA spectrometer at 4.2 K for 1–2 hours. The MCDA and MCDA-detected EPR spectra were measured with a custom-built computer-controlled spectrometer working in the K band (24 GHz) between 1.5 K and room temperature in the spectral range between 220 nm and about 1000 nm. Most measurements were performed at 1.8 K.

3. Experimental results

In figure 1(a) the optical absorption and in figure 1(b) the MCDA of V_K centres in NaBr are shown. The UV absorption band does not have the spectral shape of a single Gaussian, but seems to be a superposition of two Gaussians peaking at 3.3 eV and at 2.6 eV. The decomposition into two Gaussians is indicated in figure 1(a). Figure 1(b) shows the MCDA which is the differential absorption of right and left circularly polarized light measured in a longitudinal static magnetic field. Several positive and negative peaks are resolved. When setting the MCDA to 1.58 eV and inducing microwave transitions (24.09 GHz), the MCDA-detected EPR spectrum of figure 2, curve a, is measured for $B_0 \parallel [100]$. This is the known EPR spectrum of V_K centres in NaBr for those centres which have their molecular axes perpendicular to the field orientation, superimposed on centres with axes under 45° with respect to the field orientation. The simulated spectrum using the g -factors and Br hyperfine (hf) interaction parameters known from conventional EPR experiments (Schoemaker 1973), and assuming a half width of 4 mT for each Br hf transition, is shown in figure 2(b). It agrees very well with the MCDA-detected EPR spectrum (the small isotope differences between ^{79}Br and ^{81}Br are not resolved). It has been shown previously that V_K centres with their axes parallel to the magnetic field have no MCDA and can thus not be detected by MCDA-detected EPR (Spaeth *et al* 1994b).

When measuring the excitation spectrum of the MCDA on setting the magnetic field at one V_K EPR line (e.g. 800 mT for the perpendicular V_K centres), i.e. measuring the

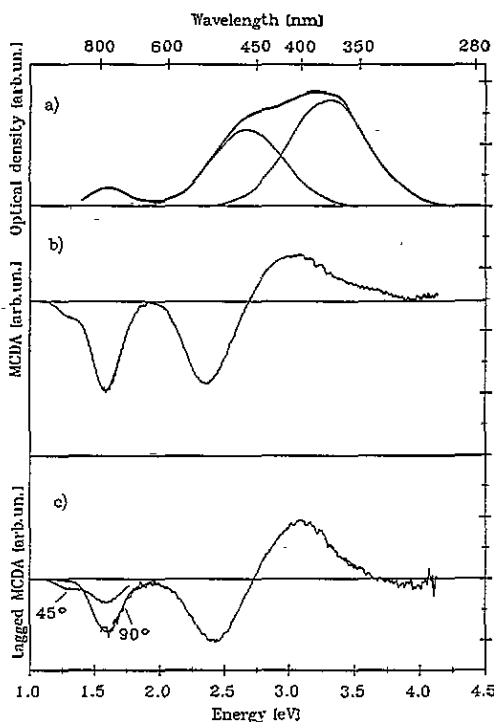


Figure 1. (a) Absorption spectrum of V_K centres in NaBr. (b) MCDA of the absorption spectrum of figure 1(a) measured at 1.8 K and $B = 3$ T. (c) Tagged MCDA of V_K centres with their axes perpendicular to the magnetic field (90°) measured at $B = 800$ mT and of V_K centres under 45° measured at 855 mT. Microwave frequency 24.1 GHz, $T = 1.8$ K, $B \parallel [100]$.

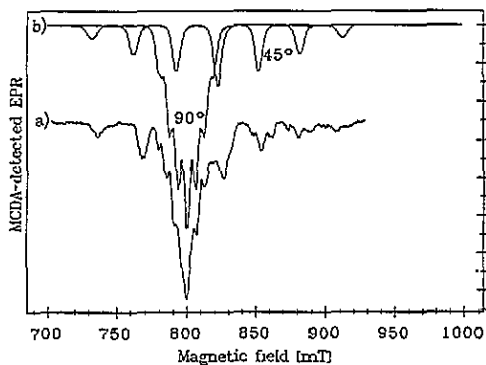


Figure 2. (a) MCDA-detected EPR spectrum of V_K centres in NaBr: $B_0 \parallel [100]$, $\nu = 24.09$ GHz measured at 1.58 eV and 1.8 K. (b) Simulated ESR spectrum of 90° and 45° V_K centres in NaBr using the known g -factors and Br hyperfine interaction parameters from conventional EPR (Schoemaker 1973). A Br line width of 4 mT was assumed; the slight difference between ^{79}Br and ^{81}Br is neglected.

so-called 'tagged' MCDA spectrum (see e.g. Spaeth *et al* 1992), the MCDA spectrum of figure 1(c) is obtained. The MCDA of figure 1(b) between 1 and 4 eV is reproduced. Thus, the MCDA peaks all belong to the V_K centres. The measurement of the tagged MCDA, when setting B_0 into an EPR line of those V_K centres which have an angle of 45° with respect to the field orientation (e.g. 855 mT), gives a slight difference in the IR MCDA (figure 1(c)).

Figure 3 shows the analogous results for NaCl. Also here the tagged MCDA for the 90° V_K centres reproduces the measured MCDA. The measurement of the tagged MCDA for the 45° V_K centres shows a slight shift of the IR MCDA band: its peak is lower by approximately 0.1 eV in energy compared to the perpendicular V_K centres.

From figure 4, representing the optical absorption (taken from Murray and Keller (1967)) and the tagged MCDA for the 90° V_K centres in RbI (measured at 830 mT), it becomes particularly apparent that the MCDA in the UV is measured predominantly from the low-energy side of the UV absorption and that it is very small, if not absent, where the UV absorption has its highest peak. In RbI it was difficult to measure the perpendicular centres

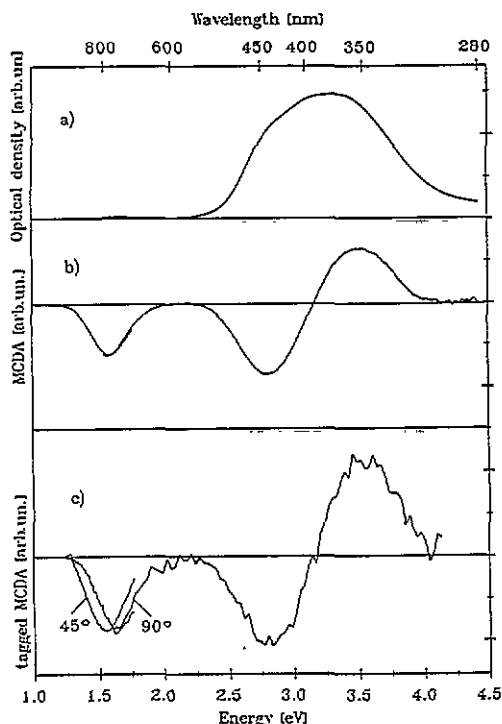


Figure 3. (a) Absorption spectrum of V_K centres in NaCl. (b) MCDA of the absorption spectrum of figure 3(a) measured at 1.8 K and $B = 3$ T. (c) Tagged MCDA of V_K centres with their axes perpendicular to the magnetic field (90°) measured at $B = 850$ mT and of V_K centres under 45° measured at 865 mT. Microwave frequency 24.06 GHz, $T = 1.8$ K, $B \parallel [100]$.

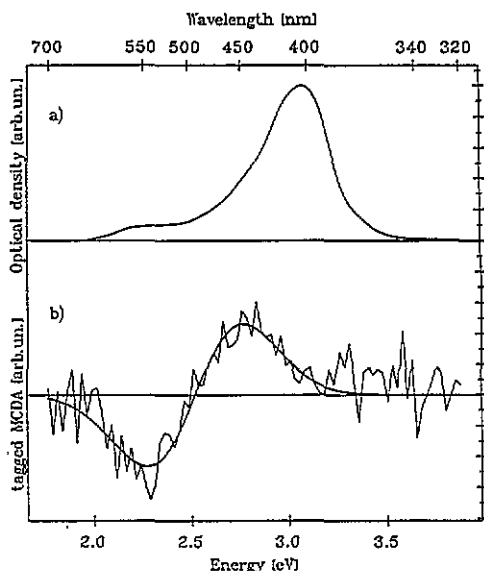


Figure 4. (a) Absorption spectrum of V_K centres in RbI. (b) Tagged MCDA of V_K centres with their axes perpendicular to the magnetic field (90°) measured at $B = 830$ mT. Microwave frequency 23.7 GHz, $T = 1.8$ K, $B \parallel [100]$. The smooth line is a simulation using a derivative of a Gaussian line shape.

due to the overlap with another ODEPR signal. However, as was seen for NaBr and NaCl, the tagged MCDA spectra of the 45° and 90° centres coincide in the UV band. The solid line in figure 4(b) is a simulation assuming a derivative-like spectral shape for the MCDA, being the derivative of a Gaussian absorption line.

In figure 5 a survey of the tagged MCDA spectra for the 90° V_K centres in the UV region is given for seven alkali halides. The vertical bars indicate the positions of the peaks of the UV absorption bands as measured in optical absorption. The solid lines represent simulations of line shapes assuming derivatives of Gaussian bands which describe the experiments rather well. Attempts to measure the MCDA spectra of V_K centres in KF and RbCl, both doped with TI, failed. The signals were too weak.

In none of the alkali halides does the zero transition of the MCDA coincide with the peak position of the UV absorption band. In the bromides and more so in the iodides it is apparent that the MCDA is shifted towards lower energy and must originate in another optical transition than in the known UV (high-energy) absorption band. It thus seems to be a general feature of the V_K centres that they have two UV absorption bands. The high-

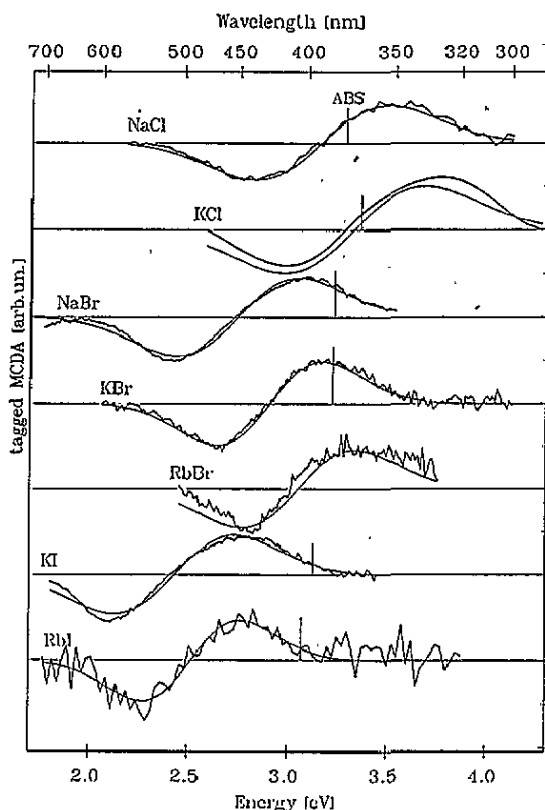


Figure 5. Tagged MCDA spectra of the UV transitions of V_K centres with their axes perpendicular to the magnetic field in seven alkali halides. The positions of the peaks of the UV absorption bands are indicated by vertical bars.

energy band shows no or only a very weak magnetic circular dichroism, while the band at lower energy, although having a comparatively weak absorption band, has a strong MCDA effect. The energy separation between the two UV bands, if one identifies the peak of the low-energy transition with the zero transition of the MCDA signal, increases from the chlorides through the bromides for the same alkali ions. On the other hand, it decreases with increasing alkali ions, for example from NaBr to RbBr or from KI to RbI.

In table 1 the positions of the UV absorption peaks ('ABS'), the zero transitions of the UV MCDAs (MCD_0) and the energy separation of the positive and negative MCDA peaks ($MCD_+ - MCD_-$) as well as E_{11} , the average energy separation between the Σ_u and Π_u levels, derived from EPR (Schoemaker 1973) are collected. The shifts between ABS and MCD_0 are also listed.

4. Discussion

Our experiments have shown that the second UV transition at lower energy compared to the known UV band must be a common feature to all V_K centres in the alkali halides. It therefore seems unlikely that its occurrence is attributable to a distortion by another defect as was tentatively proposed by Delbecq *et al* (1961) for their observation of this extra

Table 1. UV absorption and MCDA data of V_K centres in alkali halides (in eV). ABS = peak of the UV absorption band; MCD_0 is the zero transition of the MCDA bands; MCD_+ , MCD_- are the energy positions of the positive and negative MCDA peaks; E_{\perp} : average of the $\Sigma_u - \Pi_u$ energy separation (after Schoemaker 1973).

		Na	K	Rb
Cl	ABS	3.28 ^a	3.40 ^a	
	MCD_0	3.17	3.35	
	$ABS - MCD_0$	0.11	0.05	
	$(MCD_+) - (MCD_-)$	0.7	0.75	
	E_{\perp}	2.28	2.42	
	ABS	3.22 ^b	3.22 ^a	
Br	MCD_0	2.75	2.91	3.06
	$ABS - MCD_0$	0.47	0.31	
	$(MCD_+) - (MCD_-)$	0.67	0.52	0.53
	E_{\perp}	1.95	2.19	2.23
	ABS		3.10 ^a	3.06 ^c
			2.12	2.21
I	MCD_0		2.43	2.50
	$ABS - MCD_0$		0.67	0.56
	$(MCD_+) - (MCD_-)$		0.66	0.55
	E_{\perp}		2.03	2.12

^a Delbecq *et al* 1961.

^b Schoemaker 1973.

^c Murray and Keller 1967.

band in KI. The question arises, therefore, of what could be the reason for this additional UV band. In principle, one could think that it arises from a charge transfer transition from the neighbouring alkali ions into the X_2^- molecule. However, one would then expect a stronger dependence of the MCDA effects on the alkalis, which is not observed. The MCDA intensity, i.e. $I_+ - I_-$, is rather similar in all the alkali halides observed. Since the X_2^- molecular model has been successful so far in explaining the EPR results and other optical properties, it is tempting to seek explanation within this model. In order to explain a second UV band, it is necessary to find a 'mechanism' which would make the $\Sigma_u \rightarrow \Pi_u$ transition dipole allowed by removing the inversion symmetry. In our previous paper on MCDA measurements of V_K centres in KBr and KI, we suggested that there is a soft axial translational mode of vibration along the $\langle 110 \rangle$ directions and that this slow axial oscillation of the centre makes the centre seem 'frozen' at the classical turning points during the optical transition. This is equivalent to having a momentary off-centre geometry of the V_K centre, thereby making the $\Sigma_u - \Pi_u$ transition allowed. Since the oscillation is fast compared to 10 GHz normally used in EPR, this symmetry breaking is not seen in the EPR experiments.

Regarding the nature of the 'frozen' motion at the classical turning points, we can offer the following qualitative comments. Considering that the V_K centre can be formed along the $\langle 110 \rangle$ axis at equally spaced intervals, it is to be expected that the soft axial mode would deviate from a simple harmonic potential as it approaches the mid-point to the next site. Indeed, an approximate calculation based on the CNDO code embedded in an ionic lattice suggests a flattening of the potential around 1 Å off the centre. This would enhance the 'freezing' effect near the classical turning points. The broad bandwidth (about 0.5 eV) of the new UV band (figure 1(a)) seems to indicate that the absorption is not between a pair

of vibronic states differing by one quantum of the axial mode phonon.

In the off-centre geometry, the two halogens will have unequal hole charges. In the on-centre position, both halogens are relaxed inwards. As a consequence of the axial motion (e.g. for the turning points), one halogen moves towards the halogen lattice site which has the full positive Madelung potential, which is repulsive for the hole, while the other moves further away from this repulsive potential. Consequently, the latter halogen will acquire more hole charge than the former. This can be formally expressed by mixing the Σ_g and Σ_u molecular orbitals. The electrostatic lattice potential thus causes a charge transfer between the two halogen components of the V_K centre for an 'asymmetric' position of the V_K centre. As will be discussed below, this makes the $\Sigma_u \rightarrow \Pi_u$ transition dipole allowed.

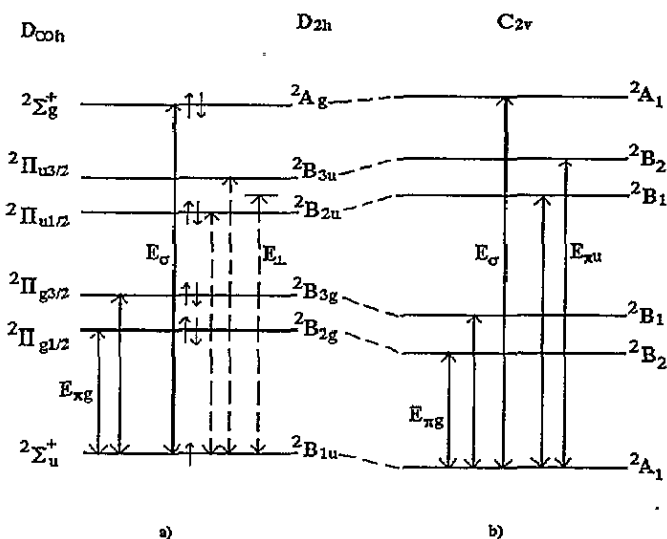


Figure 6. Schematic representation of the energy level changes for the X_2^- molecular model caused by the slow axial centre oscillation: (a) on-centre X_2^- (D_{2h}); (b) off-centre X_2^- (C_{2v}).

It is possible to give a general qualitative discussion on the MO energy levels as the inversion symmetry is broken. Figure 6 shows schematic changes, in particular the level repulsion between Σ_u and Σ_g , and Π_u and Π_g . This is the direct consequence of mixing of above pairs of states through the odd-parity potential term introduced by loss of inversion. It is likely that the effect is larger for the second than for the first. At static equilibrium, $\Sigma_u \rightarrow \Sigma_g$ and $\Sigma_u \rightarrow \Pi_g$ transitions are optically allowed and correspond, respectively, to the UV and IR bands. We propose that the new UV band observed by MCDA corresponds to $\Sigma_u \rightarrow \Pi_u$ transition which becomes allowed because of the loss of inversion symmetry at the classical turning point. It can be seen that the two UV band energies tend to be larger than in the on-centre geometry, while the IR band changes less. Such absorption energy changes have been noted in alkaline earth fluorides between the V_K and H centres, oriented respectively along the $\langle 100 \rangle$ and $\langle 111 \rangle$ axes (Parker *et al* 1981). It is therefore interesting to examine whether such variation is present in the data obtained in the present work by MCDA and earlier works by EPR (Schoemaker 1973). As shown in table 1, E_{\perp} (the average of $\Sigma_u \rightarrow \Pi_u$), derived from the g shifts observed in EPR, is systematically smaller than the new UV band peaks, identified as the zero of the MCDA (MCD_0 in table 1). There are some interesting and systematic trends among the crystals studied. They are discussed

below.

Qualitatively, in this model one can also understand the trends we have observed in the various alkali halides. For example, the new band shifts to lower energy for the same halogen when the alkali ion becomes smaller, i.e. the lattice constant decreases (e.g. on going from RbBr to NaBr, it varies from 3.06 eV to 2.75 eV).

Since there is less space in NaBr than in RbBr for the off-centre motion, the Π_u level moves less upwards and Σ_u moves less downwards (see figure 6(b)). Therefore, the new UV band in NaBr peaks at lower energy than in RbBr.

The other trend, i.e. the lower energy of the new band, when varying the halogens from smaller to larger ones, can be understood as follows. Owing to the smaller size of Cl_2^- compared with those of Br_2^- or I_2^- , there is relatively more space in NaCl to induce larger off-centre axial motion. Several basic properties of the self-trapped excitons in alkali halides depend in a sensitive way on this geometric relation (Song and Williams 1993). Therefore, the effect of the off-centre motion, i.e. a higher energy for the $\Sigma_u \rightarrow \Pi_u$ transition, is less on going from the chlorides to the iodides in agreement with the observed trends.

In the ideal case of a single Gaussian absorption band, there are simple relations between the optical absorption and MCDA spectra (see e.g. Spaeth *et al* 1992). If the absorption coefficient α can be represented by a Gaussian: $\alpha_0 e^{-(E - E_0)^2/W^2}$, the MCDA signal, which is proportional to the first derivative of α , consists of two parts, one negative and the other positive. The peak-to-peak energy separation is given by $W\sqrt{2}$ and equal to $0.85W_{1/2}$, where $W_{1/2}$ is the half-width. Also, the absorption band peak E_0 is given by the zero of MCDA, represented by MCD_0 in table 1. In an ideal case, the two parts of the MCDA signal are symmetrical, except for the signs. In the above discussion, W represents the absorption band width originating from electron-phonon coupling and we have assumed that it is larger than the splitting between $\Pi_{1/2}$ and $\Pi_{3/2}$.

One of the striking observations made in the present work is the absent or very weak MCDA signal from the strong UV band, and the much stronger MCDA from the generally weak lower-energy UV band. In the following, we present a qualitative discussion of this observation based on the assumption that the new lower-energy UV band originates from the $\Sigma_u \rightarrow \Pi_u$ transition, which becomes allowed as a result of the relaxation of the parity selection rule at the classical turning point of the axial oscillation along $\langle 110 \rangle$. Lifting of the inversion symmetry, without changing other symmetries, will promote mixing of Σ_u and Σ_g states as well as Π_u and Π_g states. This is described below:

$$|\Sigma_{u'}\rangle = |\Sigma_u\rangle + a|\Sigma_g\rangle \quad |\Sigma_{g'}\rangle = |\Sigma_g\rangle - a'|\Sigma_u\rangle. \quad (1)$$

Because of the orthogonality between $|\Sigma_{u'}\rangle$ and $|\Sigma_{g'}\rangle$, which now belong to the same irreducible representation, $a = a'$. This mixing coefficient is determined either by perturbation theory or by solving a secular determinant involving the pair of interacting states.

A semi-quantitative estimate of the mixing coefficients is made in the appendix. It shows that the mixing is not negligible and lends support to the model presented here to explain the observed results. The MCDA signal is obtained by calculating the difference of the left and right circularly polarized absorptions. From this it follows that

$$I_+ - I_- = (I_+^0 - I_-^0)(1 - a^2) \quad a \leq 1. \quad (2)$$

Here, the I^0 are the intensities before mixing and have been shown to be non-zero for the V_K axis perpendicular to the static magnetic field (Spaeth *et al* 1994b, Meise 1993). It follows that the new MCDA signal is reduced by a factor $(1 - a^2)^2$ which is generally smaller than unity.

The MCDA signal associated with the new UV band can be analysed in a similar way after the perturbed states $|\Sigma_u'\rangle$ and $|\Pi_u'\rangle$ are described as

$$|\Sigma_u'\rangle = |\Sigma_u\rangle + a|\Sigma_g\rangle \quad (3)$$

$$|\Pi_u'\rangle = |\Pi_u\rangle + b|\Pi_g\rangle. \quad (4)$$

In this case, a is the same as a above, but b is unrelated to a . A simple consideration based on perturbation theory indicates that a and b are of the same sign, but b is expected to be larger than a . Using the above vectors, one can find

$$I_+ - I_- = a^2[I_+ - I_-]_1 + b^2[I_+ - I_-]_2 + 2ab[\text{cross terms}] \quad (5)$$

with

$$[I_+ - I_-]_1 = |\langle \Sigma_g | I_+ | \Pi_u \rangle|^2 - |\langle \Sigma_g | I_- | \Pi_u \rangle|^2 \quad (6)$$

$$[I_+ - I_-]_2 = |\langle \Sigma_u | I_+ | \Pi_g \rangle|^2 - |\langle \Sigma_u | I_- | \Pi_g \rangle|^2. \quad (7)$$

The second term (7) represents the MCDA due to the IR band, derived in Meise (1993), and does not vanish. The first term has not been completely derived and is expected not to vanish. The cross term is made of products of different matrix elements instead of squares of the same matrix as above. Although it is not simple to show that the sum of all three terms is large, it seems fair to say that generally it would not vanish.

When setting $a = 0$, a limiting case, we are left with the term of (7), of which we know that it does not vanish from the observation of an MCDA in the IR bands. Thus, with the assumption of the off-centre oscillation, one is able to explain both the appearance of the new UV band and the fact that it has an MCDA which is stronger than that of the UV band coming from the $\Sigma_u \rightarrow \Sigma_g$ transition.

Appendix. Mixing of even and odd parity states

Here, we present the results of a semi-quantitative estimation of the mixing coefficients coupling the even and odd parity states of the V_K centre which is realized by the soft translational mode Q_2 . First, we studied the potential energy variation of the V_K centre in the KBr crystal. This was obtained by embedding a CNDO code in the point charge lattice, with Born-Mayer-type short-range interaction in the same way as in earlier studies of the self-trapped excitons. According to this approximate calculation, the translational motion is, indeed, very soft. For a shift of 0.8 Å, the energy rises by about 0.14 eV. We also observed that around 1 Å the potential flattens, suggesting a deviation from harmonic potential.

At several values of the axial shift Q_2 , we have examined the variation of the even and odd parity molecular orbital (MO) energies. As expected, the energy difference between the even (gerade) and odd (ungerade) parity states increases for both Σ and Π MOs as a result of the coupling. We attribute the new UV band to the $\Sigma_u - \Pi_u$ transition. Therefore, we consider the mixing in both states with their respective even parity MO. The example described below is at a shift of $Q_2 \cong 1.3$ Å. Following an approach already used in an earlier study of the V_K and H centres in CaF_2 (Parker *et al* 1981), we solve a secular determinant of the following form for both Σ and Π states.

$$\begin{vmatrix} -\Delta - E & V \\ V & \Delta - E \end{vmatrix} = 0$$

As in Parker *et al* (1981), it is more convenient to express the Σ (or Π) MOs in terms of atomic bases z_1 and z_2 (or y_1 and y_2) on the pair of bromines. $2V$ gives the UV (or IR) transition energy at $Q_2 = 0$. 2Δ describes the potential (mostly the Madelung potential)

difference between the two atoms at finite Q_2 . The two parameters Δ and V are deduced from the MO energies obtained from the CNDO calculation. The UV energy varies between 4.7 eV and 5.0 eV (and the IR between 0.42 to 0.56 eV) for the on-centre and off-centre geometries. (The UV energies are somewhat larger than the observed one around 3 eV and the IR smaller compared to 1.2 eV experimentally. The CNDO parameters used were fitted mainly to the equilibrium bond length and stretching mode frequency. Also, the above energies are one-electron energies.)

Finally, the new eigenvectors are obtained:

$$\begin{aligned} |\Sigma_{u'}\rangle &= 0.96|\Sigma_u\rangle + 0.26|\Sigma_g\rangle \\ |\Pi_{u'}\rangle &= 0.33|\Pi_g\rangle + 0.93|\Pi_u\rangle. \end{aligned}$$

This shows that the mixing is not negligible around this region of Q_2 . It is clear that the precise magnitude of the mixing depends on the amplitude of the low-frequency vibration. A more reliable determination of these parameters would be desirable, but is beyond the scope of this paper.

Acknowledgments

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