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## Spectral shifts of optical transitions between $F_2^+$ and $F_2^+$ -like colour centres

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**Abstract.** Sennaroglu and Pollock's model, reported in 1991, for the calculation of transition energies of laser-active  $(F_2^+)_H$  centres in NaCl is slightly modified in order to make it applicable to other  $F_2^+$ -like colour centres, without the need for adjusting any parameter. Our version of the model is found to give good results in the cases of  $(F_2^+)_H$  and  $(F_2^+)^*$  centres, where the  $F_2^+$  component of the defect is stabilized by an impurity (or a vacancy) bearing a net electrical charge with respect to the regular lattice ion it replaces. On the other hand, this model is unable to cope with centres such as  $(F_2^+)_A$ , where the stabilizing substitutional impurity bears the same electrical charge as the regular lattice ion.

### 1. Introduction

$F_2^+$ -like centres in alkali-halides are very useful colour-centre-laser materials (see, for instance, Gellermann 1991). Pure  $F_2^+$  centres are rather unstable under intense pump light, but they can be stabilized by several impurities; thus, so-called  $(F_2^+)_A$ ,  $(F_2^+)^*$ ,  $(F_2^+)^{**}$ ,  $(F_2^+)_H$  and  $(F_2^+)_{AH}$  centres have been obtained in various matrices and used in laser work, sometimes with outstanding success, as in the case of  $(F_2^+)_H$  centres in NaCl:O<sup>2-</sup>, discovered by Pinto *et al* (1986). For some  $F_2^+$ -like centres, the location or even the exact nature of the stabilizing impurity is doubtful. However, their kinship with  $F_2^+$  appears clearly from the fact that their absorption and emission spectra are qualitatively very similar to one another, as was shown, for instance, by Mollenauer (1980) for  $(F_2^+)^*$  centres in NaF containing divalent impurities and by Georgiou *et al* (1987) for  $(F_2^+)_H$  in NaCl:O<sup>2-</sup>.

The spectral properties of pure  $F_2^+$  centres can be qualitatively and even semi-quantitatively predicted by using the molecular hydrogen ion model, first introduced by Herman *et al* (1956) and later developed by Aegerter and Lüty (1971) and by Mollenauer (1979). Recently, Sennaroglu and Pollock (1991, referred to as SP for brevity) successfully computed the transition energies of the  $(F_2^+)_H$  centre in NaCl:O<sup>2-</sup>. Their key idea was to add *observed eigen-energies* of the  $F_2^+$  centre in pure NaCl and *corrections, calculated* by first-order perturbation, starting from the wavefunctions of the  $H_2^+$  model. Thus, the rough character of these wavefunctions does not spoil the whole energies of the levels of interest, but only the corrective terms, resulting in a higher overall accuracy.

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SP's calculation is especially attractive for our laboratory: we are currently starting a program on new  $F_2^+$ -like laser materials. Using other alkali-halides and/or other dopants (such as  $S^{2-}$ ), we intend to find colour-centre-laser systems either with a better stability or with a different emission domain (longer wavelengths). This latter quest would obviously be much facilitated by the use of a simple theoretical model allowing a reliable prediction of the spectral positions of absorption and emission for any crystal-plus-impurity system, before undertaking its synthesis.

The aim of the present paper is to describe our investigations concerning SP's model. As we will show, the result is half-satisfactory, half-disappointing. We shall therefore look for an empirical rule stating in which cases SP's model has some predictive value and in which cases it has none.

Although SP state in great detail their hypotheses and calculational methods, we believe it is useful to recall them briefly in section 2, in order to make the present paper more self-contained and, hopefully, easier to read. However, some of our notation differs, for sake of convenience, from that of SP; the differences are given in table 1. In section 3, we shall discuss some of SP's hypotheses and modify them in an attempt to make the calculations more predictive (no adjustable parameter). Section 4 will report on our calculated results for several problems: microscopic configurations of the two varieties of  $(F_2^+)_H$  centres in section 4.1,  $(F_2^+)_H$  centres in various alkali-halides in section 4.2, similar centres with  $S^{2-}$  substituted for  $O^{2-}$  in section 4.3,  $(F_2^+)_A$  centres in section 4.4 and  $(F_2^+)^*$  centres in section 4.5. Finally, section 5 will briefly summarize our results.

Table 1. Differences between our notation and that of Sennaroglu and Pollock (1991).

This paper	SP
$R'$	$R_0$
$E'_i$	$E_{0i}$
$\Delta E'_i$	$\Delta E_0$
$r_a, r_b$	(not named)
$r'_a, r'_b$	$r_a, r_b$
$r'_i, d'_i$	$r_{ion}, d_{ion}$
$r'(\lambda, \mu, \varphi)$	$r_{Ox}(\lambda, \mu, \varphi)$
$d'(\lambda, \mu, \varphi) = d'$	$d(\lambda, \mu, \varphi) = d$
$U(\lambda, \mu, \varphi)$	$(2a_0/e^2)U(\lambda, \mu, \varphi) = \chi_1/R_0^2$
$v(\lambda, \mu, \varphi)$	$v(\lambda, \mu, \varphi)/\kappa_0$

## 2. Sennaroglu and Pollock's model

The  $(F_2^+)_H$  centre consists of two neighbouring anion vacancies, trapping a single electron, in the vicinity of a substitutional  $O^{2-}$  impurity. Figure 1 shows four possible configurations of this centre (Wandt *et al* 1987), along with the coordinate system which we shall use. SP's calculation refers to configuration 1 (i.e. the oxygen ion and the two anionic vacancies forming an equilateral triangle), which is generally assumed to correspond to the laser-active centre. However, in several alkali-halides,  $(F_2^+)_H$  centres are observed to have two varieties (Wandt *et al* 1987), one of which,  $(F_2^+)_H$  (a), is stable at room temperature and metastable at 77 K, while the other,  $(F_2^+)_H$

(b), the laser-active one, is stable at 77 K and unstable at room temperature. Variety (a) does not seem to have been associated with a specific microscopic structure (2, 3 or 4 of figure 1). We shall tackle this point in section 4.1.

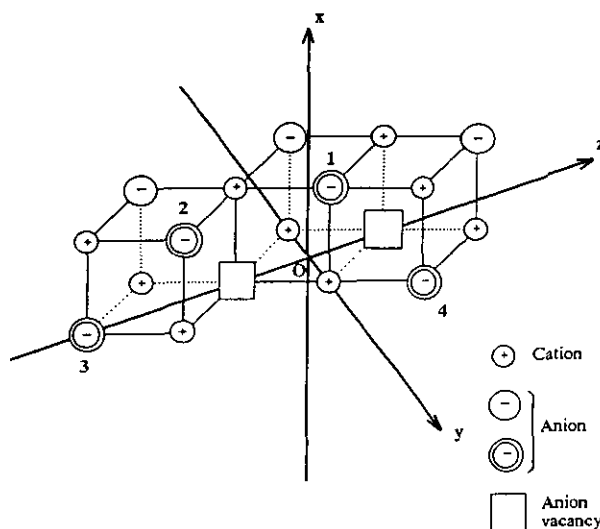


Figure 1. The four possible configurations of  $(F_2^+)_H$  according to Wandt *et al* (1987). The regular anion of site 1, 2, 3 or 4 is replaced by a substitutional  $O^{2-}$ .

In the  $H_2^+$  model, a 'pure'  $F_2^+$  centre is described by the wavefunction of a hydrogen molecular ion with proton distance  $R$ :

$$R = R' / \kappa_0 \quad (1)$$

where  $R'$  is the anion vacancy separation and  $\kappa_0$  the high-frequency dielectric constant of the alkali-halide. Energies  $E'_i$  of the  $F_2^+$  centre are given by

$$E'_i = E_i / \kappa_0^2 \quad (2)$$

where energies  $E_i$  are the eigenvalues of the  $H_2^+$  problem for proton separation  $R$ . In fact, Aegerter and Lüty (1971) and Mollenauer (1979) make slight adjustments of  $R'$  and  $\kappa_0$  to obtain better agreement between calculated and observed spectra. Thus, in the case of the  $F_2^+$  centre of NaCl, Mollenauer uses  $\kappa_0 = 2.23$  instead of the experimental high-frequency dielectric constant 2.34 and  $R' = 2.23 \times 2.95 = 6.58$  au instead of the distance 7.54 au between two neighbouring  $Cl^-$  in the perfect crystal. Moreover, the lattice relaxation when the centre is in its first excited state  $2p\sigma_u$  is taken into account in Mollenauer's calculation by increasing  $R'$  to  $2.23 \times 3.50 = 7.805$  au; this allows the calculation of spectral positions, both of emission and of relaxed excited-state absorption.

$H_2^+$  ion wavefunctions have been studied for a long time (Bates *et al* 1953, and references therein), as the problem of a single electron in a Coulomb field of two fixed protons is separable in spheroidal coordinates  $\lambda, \mu, \varphi$ . Here  $\varphi$  is merely the

polar angle around  $Oz$ , with the origin in the  $xOz$  plane. Let  $r_a$  and  $r_b$  be the distances of the electron to protons a and b (with respective  $z$ -coordinates  $-R/2$  and  $R/2$ ).  $\lambda$  and  $\mu$  are defined by:

$$\lambda = (r_a + r_b)/R \quad (3)$$

$$\mu = (r_a - r_b)/R. \quad (4)$$

Hydrogen ion eigenfunctions are written as:

$$\Psi_0 = L(\lambda)M(\mu) \quad (5)$$

and

$$\Psi_0 = L(\lambda)M(\mu) \begin{cases} \cos \varphi \\ \sin \varphi \end{cases} \quad (6)$$

for molecular  $\sigma$ - and  $\pi$ -states, respectively. Bates *et al* (1953) contains full details about functions  $L(\lambda)$  and  $M(\mu)$ , together with extensive tables giving the energies  $E_i$  and the parameters allowing the calculation of the corresponding wavefunctions. These tables cover a number of values of  $R$ , ranging from 0 to 10 au, for 10 levels:  $1s\sigma_g$ ,  $2s\sigma_g$ ,  $3s\sigma_g$ ,  $2p\sigma_u$ ,  $3p\sigma_u$ ,  $4p\sigma_u$ ,  $3d\sigma_g$ ,  $4f\sigma_u$ ,  $2p\pi_u$  and  $3d\pi_g$ .

Coordinates  $\lambda$ ,  $\mu$  and  $\varphi$  are dimensionless numbers, so that they will remain the same when one goes from the  $H_2^+$  ion problem to the  $F_2^+$  centre problem; if  $r'_a = \kappa_0 r_a$  and  $r'_b = \kappa_0 r_b$  are the distances of the F electron to the centres of the two anion vacancies, (3) and (4) yield:

$$\lambda = (r'_a + r'_b)/R' \quad (3')$$

$$\mu = (r'_a - r'_b)/R' \quad (4')$$

and wavefunctions (5) and (6), as they stand, will describe the properties of the  $F_2^+$  centre.

Let us turn now to the perturbation of the  $F_2^+$  centre by substitution of an  $O^{2-}$  ion for the regular monovalent anion at point C. SP describe it as the coupling of the F electron with the electrostatic potential created by a fixed, uniformly charged sphere, centred at C, with total charge  $-e$  and with radius  $r'_i$  equal to the oxygen ion radius. Let  $r'(\lambda, \mu, \varphi)$  be the distance between point C ( $\lambda_i, \mu_i, \varphi_i$ ) and the F electron ( $\lambda, \mu, \varphi$ ). One introduces the dimensionless quantities:

$$d'(\lambda, \mu, \varphi) = 2r'(\lambda, \mu, \varphi)/R' \quad (7)$$

and

$$d'_i = 2r'_i/R'. \quad (8)$$

Writing  $d'$ , for brevity, instead of  $d'(\lambda, \mu, \varphi)$ , the perturbation is, in Rydbergs:

$$U(\lambda, \mu, \varphi) = 2(2/R')v(\lambda, \mu, \varphi) \quad (9)$$

with

$$\left. \begin{aligned} v(\lambda, \mu, \varphi) &= (3/2\kappa_0 d'_i) \left[ 1 - \frac{1}{3} (d'/d'_i)^2 \right] e^{-\alpha d'} && \text{for } d' \leq d'_i \\ v(\lambda, \mu, \varphi) &= e^{-\alpha d'} / (\kappa_0 d'_i) && \text{for } d' \geq d'_i \end{aligned} \right\} \quad (10)$$

In equation (9), the factor  $2/R'$  arises for the same reason as in equations (7) and (8) and the extra factor 2 from the fact that the chosen energy unit (in this work as well as in the work of SP and Bates *et al*) is the Rydberg, while the energy atomic unit is two Rydbergs. In equations (10),  $e^{-\alpha d'}$  is a screening factor, with an adjustable parameter  $\alpha$ , which was introduced by SP, a procedure which we shall discuss in section 3.3.

From first-order perturbation theory, the energy correction  $\Delta E'_i$  is:

$$\Delta E'_i = \langle \Psi_{0i} | U(\lambda, \mu, \varphi) | \Psi_{0i} \rangle / \langle \Psi_{0i} | \Psi_{0i} \rangle \quad (11)$$

for non-degenerate  $\sigma$ -states. A denominator to equation (11) is needed because the functions of Bates *et al* (5) are unnormalized. Similarly, for doubly degenerate  $\pi$ -states, we have from (6) two orthogonal but unnormalized basis wavefunctions  $|\Psi_{0ic}\rangle$  and  $|\Psi_{0is}\rangle$ , with subscripts c and s standing for  $\cos \varphi$  and  $\sin \varphi$  respectively. Of course:

$$\langle \Psi_{0ic} | \Psi_{0ic} \rangle = \langle \Psi_{0is} | \Psi_{0is} \rangle \quad (12)$$

and

$$\langle \Psi_{0ic} | \Psi_{0is} \rangle = 0. \quad (13)$$

In most cases, the degeneracy is lifted and the energy corrections are obtained by diagonalizing the matrix:

$$\frac{1}{\langle \Psi_{0ic} | \Psi_{0ic} \rangle} \begin{vmatrix} \langle \Psi_{0ic} | U(\lambda, \mu, \varphi) | \Psi_{0ic} \rangle & \langle \Psi_{0ic} | U(\lambda, \mu, \varphi) | \Psi_{0is} \rangle \\ \langle \Psi_{0is} | U(\lambda, \mu, \varphi) | \Psi_{0ic} \rangle & \langle \Psi_{0is} | U(\lambda, \mu, \varphi) | \Psi_{0is} \rangle \end{vmatrix}. \quad (14)$$

SP calculated numerically the matrix elements which appear in (11) and (14) by summing the integrand at approximately  $2 \times 10^6$  points, uniformly spaced in the three-dimensional integration domain (from 1 to 11 for  $\lambda$  and, presumably, from -1 to 1 for  $\mu$  and from 0 to  $2\pi$  for  $\varphi$ ). Finally, the energy shift  $\Delta E'_{ij}$  of the transition between levels  $i$  and  $j$  when going from  $F_2^+$  to  $(F_2^+)_H$  is the difference of the individual energy shifts  $\Delta E'_i$  and  $\Delta E'_j$  of these two levels. SP thus obtained good agreement with experiment (ground-state absorption, excited state absorption, fluorescence) for a range of values of the screening parameter  $\alpha$ . Table 2 shows in column 1 their results, calculated with the best value of  $\alpha$  (0.765), to be compared with the experimental data in the last column. (Actually, SP list in their tables 1 and 3 calculated and observed energies of the  $(F_2^+)_H$  centre transitions, while we choose, throughout the present paper, to compare the theoretical and experimental energy shifts  $\Delta E'_{ij}$  of spectral transitions between  $F_2^+$  and  $F_2^+$ -like centres.)

### 3. Discussion of Sennaroglu and Pollock's hypotheses

#### 3.1. Correction of a numerical error in SP's calculations

In order to ascertain whether we understood everything in SP's work, our first task was to recalculate the various tables and figures of their paper, following as closely as possible their methods, except that our integrations were carried out by summation over  $5.2 \times 10^5$  points only. This reduced number of points was used throughout the

**Table 2.** Spectral shifts (in eV) between corresponding transitions of  $F_2^+$  and  $(F_2^+)_H$  centres in NaCl. Columns 1 to 6, calculations: 1, table 3 of SP ( $\alpha = 0.765$ ); 2,  $\alpha = 0.765$ , omitting the factor  $(\lambda^2 - 1)^{m/2}$  in equation (8) of Bates *et al* (1953), 'floating'  $O^{2-}$  perturber; 3,  $\alpha = 0.765$ , 'floating'  $O^{2-}$  perturber; 4,  $\alpha = 0.765$ , fixed  $O^{2-}$  perturber; 5, equations (16) used instead of (10), fixed  $O^{2-}$  perturber; 6, same as 5, but including higher-order perturbations. Column 7, experiment at 77 K: a, Mollenauer (1979); b, Georgiou *et al* (1987); c, Gellermann (1991).

	Calculated						Observed
	SP	This work					
	1	2	3	4	5	6	
<b>Unrelaxed centre</b>							
$1s\sigma_g \rightarrow 2p\sigma_u$	-0.12	-0.13	-0.13	-0.09	-0.06	-0.05	-0.06 (a,b)
$1s\sigma_g \rightarrow 2p\pi_u$ (1)	-0.09	-0.09	-0.23	-0.15	-0.13	-0.12	-0.22 (a,b)
$1s\sigma_g \rightarrow 2p\pi_u$ (2)	unlisted	0.24	0.13	0.18	0.04	-0.05	unobserved
<b>Relaxed centre</b>							
$2p\sigma_u \rightarrow 1s\sigma_g$	-0.07	-0.08	-0.08	-0.09	-0.05	-0.05	-0.04 (b) or -0.06 (c)
$2p\sigma_u \rightarrow 2s\sigma_g$	-0.14	-0.13	-0.13	-0.15	-0.15	-0.13	-0.38 (a,b)
$2p\sigma_u \rightarrow 3d\sigma_g$	-0.02	-0.01	-0.01	-0.02	-0.06	0.01	0.19 (a,b)
$2p\sigma_u \rightarrow 3d\pi_g$ (1)	-0.10	-0.10	-0.20	-0.22	-0.19	-0.19	-0.08 (a,b)
$2p\sigma_u \rightarrow 3d\pi_g$ (2)	unlisted	0.03	-0.11	-0.13	-0.14	-0.13	unobserved

present paper. Column 3 of table 2 shows our results for  $\alpha = 0.765$ . We observe a very satisfactory agreement (within 0.01 eV) for all  $\sigma$ -states, but noticeable differences for  $\pi$ -states. After some trials, we guessed that SP had probably omitted the factor  $(\lambda^2 - 1)^{m/2}$  in the expression of  $L(\lambda)$  (equation (8) of Bates *et al* (1953)). Of course, this has no effect for  $\sigma$ -states ( $m = 0$ ), but it alters the results for  $\pi$ -states ( $m = 1$ ). In column 2 of table 2, we list the results we obtain when intentionally omitting the  $(\lambda^2 - 1)^{m/2}$  factor. They compare very favourably with column 1, which supports our hypothesis concerning the omission of factor  $(\lambda^2 - 1)^{m/2}$  in SP's calculation. It is remarkable that SP's model works somewhat better than these authors believed: in column 3, one obtains a much closer agreement with experiment for the  $1s\sigma_g \rightarrow 2p\pi_u$  transition. (The other  $\sigma \rightarrow \pi$  transition,  $2p\sigma_u \rightarrow 3d\pi_g$  is too much shifted, but since experimental data are less accurate, SP attribute a reduced weight to this transition in their  $\alpha$ -fitting procedure.) Moreover, with the correct expression of  $L(\lambda)$ , 0.765 is probably no longer the best choice for  $\alpha$ . However, we did not attempt to further improve the theory-experiment agreement by optimizing  $\alpha$ .

### 3.2. Location of the oxygen impurity

SP's paper tacitly assumes that the two chlorine vacancies and the centre of the oxygen ion always form a perfect equilateral triangle, i.e. that the lattice relaxation occurs in a breathing manner. For the unrelaxed configuration, they suppose  $O^{2-}$  to be  $6.58 \times \sqrt{3}/2 = 5.70$  au from the origin O of coordinates (figure 1), compared with  $7.805 \times \sqrt{3}/2 = 6.76$  au in the relaxed configuration (and  $7.54 \times \sqrt{3}/2 = 6.53$  au for the regular  $Cl^-$  ion in an undisturbed  $ClNa$  lattice). Of course, such oxygen displacements have by no means an incredible magnitude. However, it seems dubious that a breathing-like behaviour of the whole defect should occur whatever the distance between the impurity and the vacancies. As we plan to study defects with more distant perturbers (sections 4.1 and 4.5) or with closer ones (sections 4.4 and 4.5), we look

to see whether predicted transition shifts are altered much by fixing the centre C of the oxygen perturber at the regular anion place of the unperturbed lattice (cartesian coordinates  $a, a/\sqrt{2}, 0$ ; where  $a$  is the nearest-neighbour distance in NaCl, i.e. 2.820 Å or 5.33 au). On the other hand, we continue to use, for the intervacancy distance, the values  $R'$  calculated by Mollenauer (1979) for the unrelaxed or the relaxed centre configurations respectively. Formula (6) of SP must therefore be generalized to yield the dimensionless distance  $d'(\lambda, \mu, \varphi)$  between the F electron  $(\lambda, \mu, \varphi)$  and point C  $(\lambda_i, \mu_i, \varphi_i)$ :

$$d'(\lambda, \mu, \varphi) = \{\lambda^2 + \mu^2 + \lambda_i^2 + \mu_i^2 - 2 - 2\lambda\mu\lambda_i\mu_i - 2[(1 - \mu^2)(\lambda^2 - 1)(1 - \mu_i^2)(\lambda_i^2 - 1)]^{1/2} \cos(\varphi - \varphi_i)\}^{1/2}. \quad (15)$$

Column 4 of table 2 shows the results which differ slightly from those of column 3 and which are not significantly worse in their comparison with experiment.

One consequence of abandoning the breathing relaxation hypothesis for the location of  $O^{2-}$  is to predict nearly equal shifts for the infrared absorption  $1s\sigma_g \rightarrow 2p\sigma_u$  and for the corresponding emission  $2p\sigma_u \rightarrow 1s\sigma_g$ . The difference between these shifts in SP (and in our calculations 2 and 3 of table 2) chiefly arises from the assumed displacement of the oxygen ion between the two configurations, and not from the modification of the  $F_2^+$  wavefunction consecutive to the change of the effective distance  $R'$  between vacancies. Current experimental evidence is rather in favour of nearly equal shifts for  $1s\sigma_g \rightarrow 2p\sigma_u$  (unrelaxed) and for  $2p\sigma_u \rightarrow 1s\sigma_g$  (relaxed). In table 2, one remarks that, for NaCl, the fluorescence shift is either smaller than the absorption one, or equal to it, depending on the authors. In table 5 (later), results for  $(F_2^+)_H$  centres in other alkali-halides confirm that there is no significant difference between fluorescence and absorption shifts, at the present level of accuracy. Therefore, we shall keep below the simplest hypothesis, i.e. that the oxygen perturber sits exactly at the same location as the halogen ion it replaces.

### 3.3. The screening parameter $\alpha$

SP introduce the screening factor  $e^{-\alpha d'}$  of formulae (10) without any comment and we were unable to find a justification for this procedure in the theoretical literature concerning colour centres. Of course, one might argue that it is an empirical way to account for the electric shielding due to polarization of the matter. But this shielding is already described by the dielectric constant  $\kappa_0$  which appears in the denominators of (10). So, in order to avoid counting the same physical effect twice, it seems reasonable to delete the  $e^{-\alpha d'}$  factor, i.e. to choose  $\alpha = 0$ . However, one thus obtains much larger calculated transition shifts than experimental ones (approximately 2.5 too large). This was probably the reason for the introduction of the  $e^{-\alpha d'}$  factor by SP.

However, this factor, apart from the fact that it seems unjustified, spoils the predictive value of the model, as does the introduction of any adjustable parameter when one has few data to fit. The case of NaCl is a favourable one, because the experimental work of Georgiou *et al* (1987) provides a large number of transition energies to be compared with the calculation. But in many other matrices (section 4.2), one only knows one or two absorption bands and one fluorescence transition. Moreover, as stated in the introduction, we are chiefly interested in the *a priori* prediction of pump and emission wavelengths of new laser material candidates



for which experimental data which could allow the determination of  $\alpha$  are evidently lacking. We therefore suggest the replacement of equations (10) by:

$$\left. \begin{aligned} v(\lambda, \mu, \varphi) &= (3/2\kappa_{00}d'_i)[1 - \frac{1}{3}(d'/d'_i)^2] && \text{for } d' \leq d'_i \\ v(\lambda, \mu, \varphi) &= 1/\kappa_{00}d' && \text{for } d' \geq d'_i \end{aligned} \right\} \quad (16)$$

where  $\kappa_{00}$  is the crystal static dielectric constant, 5.90 in the case of NaCl. Thus, we avoid the need of an adjustable parameter, since  $\kappa_{00}$  is tabulated for every material of interest (see, for instance, Appendix A of Fowler 1968).

At first sight, it may seem awkward to introduce two different dielectric constants in the same problem:  $\kappa_0$  (close to the high-frequency constant) for the calculation of the pure  $F_2^+$  centre eigenfunctions and eigenvalues and the low-frequency constant  $\kappa_{00}$  for the perturbing potential. We can, however, tentatively assume that the presence of a supplementary heavy negative charge (the oxygen ion) *permanently* polarizes, not only the electrons, but also the lattice, so that the static dielectric constant  $\kappa_{00}$  is suitable to describe the ensuing screening. On the other hand, when studying an optical transition of the  $F_2^+$  or  $(F_2^+)_H$  centre, the (heavy) ions do not move according to the Franck-Condon 'principle'; only the (light) electrons of these ions are influenced by the quantum state of the F electron, so that the high-frequency constant  $\kappa_0$  is relevant.

Anyhow, we shall try replacing equations (10) by (16), at least as an empirical way of describing experimental observations. The result, which appears in column 5 of table 2 is rather satisfactory: the agreement with experiment is perfect for infrared  $1s\sigma_g \rightleftharpoons 2p\sigma_u$  absorption and emission (for the latter, within experimental uncertainty). For the visible absorption  $1s\sigma_g \rightarrow 2p\pi_u$ , the agreement with observation is somewhat spoilt in comparison with calculations 3 and 4, but the computed value still accounts for 60% of the observed shift. Concerning excited-state absorptions, predictions are not significantly better or worse than in the previous calculations.

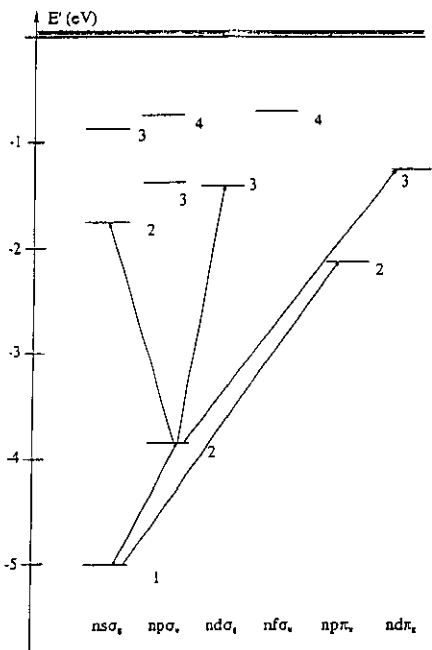
### 3.4. Higher-order perturbations

In table 2 only the differences  $\Delta E'_{ij}$  of energy corrections for two levels  $i$  and  $j$  are tabulated, which somewhat conceals the fact that  $\Delta E'_i$  and  $\Delta E'_j$  themselves are rather large (up to 0.7 eV), quite comparable to the energy differences between consecutive levels of the unperturbed centre. Therefore, one may wonder whether first-order perturbation calculations are sufficient. In order to investigate this point, we took wholly into account the 10  $H_2^+$  levels which have been calculated by Bates *et al* (1953) (see figure 2) and the 12 corresponding wavefunctions  $\Psi_{0i}$  ( $2p\pi_u$  and  $3d\pi_g$  are doubly degenerate). On this basis we calculated the perturbation matrix elements  $U_{ij}$ :

$$U_{ij} = \frac{\langle \Psi_{0i} | U(\lambda, \mu, \varphi) | \Psi_{0j} \rangle}{[\langle \Psi_{0i} | \Psi_{0i} \rangle \langle \Psi_{0j} | \Psi_{0j} \rangle]^{1/2}} \quad (17)$$

with  $U(\lambda, \mu, \varphi)$  given by (9) and (16). We also calculated the energies  $E'_i$  of the unperturbed  $F_2^+$  centre from equation (2) and from table 1 of Bates *et al* (1953). Then, we diagonalized the matrix of elements  $(E'_i\delta_{ij} + U_{ij})$  to get the perturbed eigenenergies  $W'_i$  and the associated wavefunctions. It turns out that the perturbation

is weak enough to allow easy pairing of perturbed and unperturbed eigenstates†: for each of the 12 levels, one of the  $\Psi_{0i}$ s is largely prevailing in the perturbed wavefunction expansion. Thus, without any ambiguity, the difference  $\Delta E'_i = W'_i - E'_i$  is the energy shift under the influence of the oxygen impurity. We plot this in column 6 of table 2.



**Figure 2.** Spectrum of NaCl  $F_2^+$  centre in the hydrogen molecular ion model.  $\kappa_0 = 2.23$ ;  $R = 2.95$  au, i.e.  $R' = 6.58$  au. These parameters are suitable for the unrelaxed lattice configuration. Arrows show all the spectral transitions discussed in section 3, regardless of the configuration in which they are observed.

We remark that low-lying levels  $1s\sigma_g$  and  $2p\sigma_u$  are very weakly affected by higher-order perturbations (compare columns 5 and 6). The state of affairs is less clear-cut for  $2p\pi_u$ , one component (1) of which seems unaffected, while the other (2) is depressed by 0.09 eV with respect to the first-order result. But the apparent insensitivity of component (1) to higher-order corrections arises from the fact that its wavefunction is the only one in our basis set with a symmetry even for reflection in the  $xOy$  plane and odd for reflection in the plane containing the  $Oz$  axis and the  $O^{2-}$  impurity. Thus, this component (1) of  $2p\pi_u$  would probably suffer from higher-order effects comparable to those of component (2), provided one would include other basis wavefunctions with the same symmetry.

One obvious weakness of the calculation which led to column 6 of table 2 is the omission of level  $3p\pi_u$ : a rough estimate locates it in the vicinity of  $-1$  eV, so that it

† Because of the symmetry of the present problem, matrix  $(E'_i\delta_{ij} + U_{ij})$  splits into four submatrices, respectively  $5 \times 5$ ,  $5 \times 5$ ,  $1 \times 1$  and  $1 \times 1$ . This simplification partly disappears for an arbitrary position of  $O^{2-}$ , such as 2 or 4 in figure 1. Then, only two different symmetries remain: wavefunctions are either even or odd with respect to the reflection in the plane containing the two vacancies and the impurity.

may severely perturb both components of  $2p\pi_u$ , as well as  $2s\sigma_g$  and  $3d\sigma_g$ . Thus, part of the discrepancies between theory and experiment for absorptions  $1s\sigma_g \rightarrow 2p\pi_u$  and  $2p\sigma_u \rightarrow 2s\sigma_g$ ,  $3d\sigma_g$ ,  $3d\pi_g$  may well arise from neglect (columns 1 to 5 of table 2) or improper handling (column 6) of higher-order perturbations. In addition to the 10 levels we have here taken into account, a safe higher-order calculation for the six experimentally observed transitions should include in its basis set  $3p\pi_u$ , and also  $4d\sigma_g$ ,  $4p\pi_u$ ,  $4d\pi_g$ ,  $3d\delta_g$ , ... It would, indeed, be rather straightforward to extend the tables of Bates *et al* (1953) to include these levels. But this would require much work for little reward, since we are chiefly interested in the pump and laser transitions  $1s\sigma_g \rightleftharpoons 2p\sigma_u$ , which should be practically unperturbed by these high-lying levels.

#### 4. Other $F_2^+$ -like centres

From section 3, it appears that a modified SP model is both reasonably successful for the  $(F_2^+)_H$  centre in  $\text{NaCl}:\text{O}^{2-}$  and rigid enough (no adjustable parameter) to allow unambiguous tests of its predictive power in the case of other  $F_2^+$ -like centres. Before proceeding to such tests in sections 4.1 to 4.5, let us briefly specify the differences between the current modified model and SP's original one.

(1) The perturbing species is located at a substitutional place of the perfect lattice, instead of a position varying with the intervacancy distance (use of equation (15)).

(2) In the perturbation potential, SP's screening factor  $e^{-\alpha d'}/\kappa_0$  is replaced by  $1/\kappa_{00}$ , where  $\kappa_{00}$  is the crystal static dielectric constant (use of equations (16)).

On the other hand, we limit ourselves, like SP, to first-order perturbation calculations, because higher-order corrections are negligible for the two lowest-lying levels which are of greatest practical importance for laser work, whereas a proper higher-order calculation for the levels involved in excited-state absorption would require a previous extension of the tables of Bates *et al*. Thus our results for  $1s\sigma_g \rightarrow 2p\pi_u$  (unrelaxed) and for  $2p\sigma_u \rightarrow 2s\sigma_g$ ,  $3d\sigma_g$  and  $3d\pi_g$  (relaxed) should be viewed as more tentative than those concerning  $1s\sigma_g \rightleftharpoons 2p\sigma_u$ .

##### 4.1. What is the microscopic structure of the high-temperature variety of $(F_2^+)_H$ centres?

As mentioned at the beginning of section 2, there are two varieties of  $(F_2^+)_H$  centres in NaCl, as well as in several other alkali-halides. One of them,  $(F_2^+)_H$  (b), is the subject of the calculations of SP and of section 3 above. The other one,  $(F_2^+)_H$  (a), should correspond to one of the geometries 2, 3 or 4 of figure 1. In order to choose among these three geometries, we have calculated the energy shifts of  $1s\sigma_g \rightarrow 2p\pi_u$ ,  $1s\sigma_g \rightarrow 2p\pi_u$  and  $2p\sigma_u \rightarrow 1s\sigma_g$  when the  $\text{O}^{2-}$  ion is in each of the four positions of figure 1. The results, given in table 3, strongly suggest that  $(F_2^+)_H$  (a) has configuration 4 rather than 2 or 3†. This is not surprising: it means that the two most stable configurations of  $(F_2^+)_H$  are precisely those for which  $\text{O}^{2-}$  is nearest to the centre O of the anion divacancy. For configuration 1,  $(F_2^+)_H$  (b), this distance is  $(3/2)^{1/2}a$ ; for configuration 4,  $(F_2^+)_H$  (a), it is  $(5/2)^{1/2}a$ ; whereas for the

† Similar calculations, performed for the other alkali-halides considered in section 4.2, led to the same conclusion: configurations 1 and 4 should respectively correspond to the observed strongly and weakly perturbed  $(F_2^+)_H$  varieties (when both exist).

unobserved configurations 2 and 3, this distance would be  $(7/2)^{1/2}a$  and  $(9/2)^{1/2}a$  respectively. It seems reasonable that the excess negative charge of  $O^{2-}$  should sit as close as possible to the excess positive charge. (In an alkali-halide lattice, an  $F_2^+$  centre behaves like a unit positive charge.) However, one may wonder why configuration 4 is more stable at room temperature than the closer packed configuration 1. Obviously this problem cannot be solved in the crude electrostatic frame of the present model.

**Table 3.** Configurations of  $(F_2^+)_H$  centres in  $NaCl:O^{2-}$ . In the first three rows, the assumed coordinates of the perturbing oxygen are given as functions of the distance  $a = 5.33$  au between neighbouring anion and cation in the perfect lattice. In the four lower rows, experimental transition energy shifts (in eV) are compared with calculated shifts for the four configurations of figure 1. a, Mollenauer (1979); b, Georgiou *et al* (1987); c, Gellermann (1991).

	Observed		Calculated			
	$(F_2^+)_H$ (a)	$(F_2^+)_H$ (b)	1	2	3	4
Impurity cartesian coordinates						
$x_i$			$a$	$a$	0	0
$y_i$			$a/\sqrt{2}$	$a/\sqrt{2}$	0	$a\sqrt{2}$
$z_i$			0	$-a\sqrt{2}$	$-3a/\sqrt{2}$	$a/\sqrt{2}$
Spectral shift of transitions						
Unrelaxed centre						
$1s\sigma_g \rightarrow 2p\sigma_u$	-0.02 (a,c) or -0.03 (c)	-0.06 (a,b) or -0.08 (c)	-0.06	0.01	0.03	-0.02
$1s\sigma_g \rightarrow 2p\pi_u$ (1)		-0.22 (a,b)	-0.13	-0.06	-0.05	-0.08
$1s\sigma_g \rightarrow 2p\pi_u$ (2)			0.04	-0.01	-0.05	0.04
Relaxed centre						
$2p\sigma_u \rightarrow 1s\sigma_g$	-0.01 (c)	-0.04 (b) or -0.06 (c)	-0.05	0.01	0.03	-0.02

#### 4.2. $(F_2^+)_H$ centres in other alkali-halides

For each crystal, we must first determine the values of parameters  $\kappa_0$ ,  $R'_u$  and  $R'_r$  (subscripts u and r stand respectively for unrelaxed and relaxed configurations) by fitting  $F_2^+$  optical spectra to formulae (1) and (2), with the help of table 1 of Bates *et al* (1953). Two cases are possible:

(i) When we have experimental information concerning the three transitions  $1s\sigma_g \rightarrow 2p\sigma_u$ ,  $1s\sigma_g \rightarrow 2p\pi_u$  and  $2p\sigma_u \rightarrow 1s\sigma_g$ , the task is easy: three data to determine three parameters. Subsequently, we verify that the values thus obtained for  $\kappa_0$ ,  $R'_u$  and  $R'_r$  also yield calculated spectral positions in reasonable agreement with experiment for other transitions in the same crystal (when they have been reported).

(ii) For a number of crystals, we only found in the literature the positions of  $1s\sigma_g \rightleftharpoons 2p\sigma_u$ , so that we lacked one result for determining the three parameters. We then made the calculations successively in two hypotheses: (a)  $\kappa_0$  is the high-frequency dielectric constant  $\epsilon_\infty$  of the pure lattice, as tabulated in Appendix A of Fowler (1968); (b)  $\kappa_0$  is 1.06 times  $\epsilon_\infty$ . The empirical factor 1.06 has been chosen because, for NaF, KF, NaCl and KCl, procedure (i) leads to 1.06, on average, for the ratio of  $\kappa_0$  to tabulated  $\epsilon_\infty$ .

Table 4 gives, for seven alkali-halides, the values of  $\kappa_0$ ,  $R_u = R'_u/\kappa_0$  and  $R_r = R'_r/\kappa_0$  thus obtained, along with parameters  $\kappa_{00}$  and  $a$ , which are also necessary for calculating the spectral shifts. One observes that  $R'_u$  and  $R'_r$  remain close to (and generally slightly smaller than)  $a\sqrt{2}$ , the unperturbed distance between neighbouring anions. In the case of KCl, Aegerter and Lüty (1971) have observed emission from the  $2p\pi_u$  state of  $F_2^+$  centres and Wandt *et al* (1987) from the corresponding state of  $(F_2^+)_{\text{H}}$  centres. For this particular crystal, it is therefore of interest to consider also a second relaxed lattice configuration, corresponding to the  $F$ -electron in the  $2p\pi_u$  state. We shall call  $R_{r2} = R'_{r2}/\kappa_0$  the proton distance corresponding to this configuration. From table 4, one sees that  $R'_{r2}$  is noticeably larger than  $a\sqrt{2}$  and one may have some doubts concerning the applicability of the hydrogen molecular ion model in this case. It should also be mentioned that, for NaCl, our estimated values of  $\kappa_0$  and  $R'_r$  differ slightly from those of Mollenauer (1979). Throughout this paper, we use Mollenauer's values, in order to remain as consistent as possible with SP's calculations. However, we have verified that the results would be very slightly modified if we used  $\kappa_0 = 2.22$  (instead of 2.23) and  $R'_r = 3.44$  (instead of 3.50), as suggested by table 4.

Table 5 compares the transition shifts of  $(F_2^+)_{\text{H}}$  centres observed experimentally by different authors and those we have calculated using the parameters of table 4. Several observations may be made.

(i) In the case of KBr, KI and RbI, our uncertainty concerning the exact choice of  $\kappa_0$  ( $\epsilon_\infty$  or  $1.06 \epsilon_\infty$ ) has a negligible influence on the final results.

(ii) The various  $\Delta E'_{ij}$  are predicted to depend weakly on the crystalline matrix, with a tendency to decrease when the alkali-halide becomes heavier. This agrees with experiment for the best-known cases of NaCl, KCl and KBr. For KI, the only available  $(F_2^+)_{\text{H}}$  data are the preliminary ones obtained in our group. They are somewhat at variance with the theoretical predictions, but we do not take this too seriously since we are not sure that the observed defects are really  $(F_2^+)_{\text{H}}$  centres: the chief problem is that, in the KI matrix, it is very difficult, or perhaps impossible (Gümmer 1968), to obtain  $O^{2-}$ -vacancy complexes, which is usually the first step in the synthesis of  $(F_2^+)_{\text{H}}$  centres.

(iii) We compare our theoretical values for the light halides NaF and KF with experimental data for so-called  $(F_2^+)_{\text{H}}$ \*\* centres (Mollenauer 1981, Volkova *et al* 1987, Gellermann 1991).  $(F_2^+)_{\text{H}}$ \*\* centres were first observed by Mollenauer in NaF:OH<sup>-</sup> coloured by heavy electron irradiation at low temperature, followed by annealing during a few hours at room temperature. This is rather different from the usual production method of  $(F_2^+)_{\text{H}}$  centres (additive coloration of  $O^{2-}$ -doped alkali-halides, followed by two irradiations in the F-band spectral region, one at  $\approx -10^\circ\text{C}$  and the other at 77 K). However, in the case of KCl:OH<sup>-</sup>,  $(F_2^+)_{\text{H}}$ \*\* absorption and emission wavelengths coincide with those of  $(F_2^+)_{\text{H}}$  (b) centres† obtained by the usual technique. This is why Gellermann (1991) suggests that  $(F_2^+)_{\text{H}}$ \*\* centres in NaF and KF could well be  $(F_2^+)_{\text{H}}$ . Our calculation disagrees with this hypothesis: the spectral shift of  $1s\sigma_g \rightleftharpoons 2p\sigma_u$  transitions from those of  $F_2^+$  centres is observed to be significantly higher than those expected from a substitutional oxygen ion at distance  $(3/2)^{1/2}a$  from the centre of the anion divacancy.

† We call  $(F_2^+)_{\text{H}}$  (b) the stable variety of centres in KCl, because they show large spectral transition shifts, like the (b) centres of other halides (table 5). On the other hand, Wandt *et al* (1987) call the same centres  $(F_2^+)_{\text{H}}$  (a), because they are directly formed by F-light irradiation at  $\approx -10^\circ\text{C}$ .



(iv) In the case of the  $2p\pi_u \rightarrow 1s\sigma_g$  fluorescence of KCl, the model correctly predicts a larger shift than for the  $2p\sigma_u \rightarrow 1s\sigma_g$  emission, but noticeably underestimates it. Two reasons could explain this quantitative discrepancy: omission of higher-order corrections (section 3.4), which may not be negligible in that case; and inadequacy of the hydrogen molecular ion model for this 'second relaxed' configuration, as already suspected in section 4.2.1, when discussing the value of  $R_{r2}$ .

(v) It will be interesting to obtain new reliable experimental data both for  $F_2^+$  and for  $(F_2^+)_H$  centres in different alkali-halides, in order to verify whether the good agreement between experiment and theory for NaCl, KCl and KBr is a mere whim of fate or if it is really significant.

(vi) There is no particular 'accident' of calculated shifts for the four configurations of  $(F_2^+)_H$  centres in  $KCl:O^{2-}$ . Therefore, the present model does not explain why these centres are observed only under one variety, contrary to the cases of NaCl, KBr, RbCl and RbBr. Maybe the weakly coupled  $(F_2^+)_H$  centres in KCl really exist, but with absorption and emission bands indistinguishable from those of  $F_2^+$  centres. This would not be so different from our prediction ( $-0.02$  eV for both transitions).

#### 4.3. $(F_2^+)_H$ -like centres in sulphur-doped crystals

Some work has been performed on the stabilization of  $F_2^+$  centres by sulphur instead of oxygen (Gellermann 1991, Suzuki *et al* 1992). The  $S^{2-}$  ion is assumed to take the place of  $O^{2-}$  in position 1 or 4 of figure 1. We calculate the  $\Delta E'_{ij}$  of such centres in the case of NaCl merely by changing  $r'_i$  from 2.494 au for  $O^{2-}$  to 3.477 au for  $S^{2-}$ . Table 6 shows that the result is rather disappointing: both oxygen- and sulphur  $(F_2^+)_H$ -like centres are predicted to absorb and emit at the same energies.

The reason is very simple: in the present model, the perturbing potential is the same as the one of a point charge outside a sphere ( $\Sigma$ ) of radius  $r'_i$  centred on the same point C as the impurity. However, the wavefunctions of the ground and first excited states of  $F_2^+$  centres in the  $H_2^+$  model are rather compact and they nearly vanish before reaching ( $\Sigma$ ). Thus, only the coulombic part  $1/(\kappa_{00}d')$  of potential  $v(\lambda, \mu, \varphi)$  in equations (16) plays a significant role and the final result is calculated to be independent of the radius of the perturbing ion. In order to test this explanation dramatically, we performed a calculation with a mere point-ion perturbation potential. We used, instead of (16):

$$v(\lambda, \mu, \varphi) = 1/\kappa_{00}d' \quad \text{for every } d', \text{ except } d' = 0. \quad (18)$$

The result appears in the third column of table 6. Differences are indeed very small between this column and the two previous ones, which confirms that it was pointless, for SP's calculations and for ours, to use a 'complicated' potential like (10) or (16);  $e^{-\alpha d'}/(\kappa_0 d')$  or  $1/(\kappa_{00}d')$  respectively would have yielded practically the same results.

Thus, the original as well as the modified SP models clearly predict that  $(F_2^+)_H$  centres should have essentially the same absorption and emission maxima both with sulphur and with oxygen impurity. Currently, experimental results for sulphur-doped samples are scarce, but those available are in fair agreement with the prediction above: Gellermann (1991) mentions a  $-0.02$  eV shift of the  $2p\sigma_u \rightarrow 1s\sigma_g$  emission in  $NaCl:S^{2-}$  with respect to  $NaCl:O^{2-}$ . Suzuki *et al* (1992) have measured positions for  $1s\sigma_g \rightleftharpoons 2p\sigma_u$  both in  $(F_2^+)_H$  (a) and  $(F_2^+)_H$  (b) centres of  $NaCl:S^{2-}$ . They are found

Table 5. Comparison of experimental and calculated transition energy shifts (eV) in  $(F_2^+)_H$  centres. Calculation (a) corresponds to  $\kappa_0 = \epsilon_\infty$  and calculation (b) to  $\kappa_0 = 1.06\epsilon_\infty$ . Experimental data at 77 K (except † at  $\approx 13$  K): a, Mollenauer (1981); b, Nahum (1968); c, Mollenauer (1979); d, Gellermann (1991); e, Mollenauer *et al.* (1978); f, Georgiou *et al.* (1987); g, Wandt *et al.* (1987); h, Aegerter and Lüty (1971); i, Lifante *et al.* (1990); j, Foster and Schneider (1986); k, our experimental unpublished results.

	$(F_2^+)_H$ (b)				$(F_2^+)_H$ (a)			
	Unrelaxed		Relaxed	Second relaxed	Unrelaxed		Relaxed	Second relaxed
	$1s\sigma_g \rightarrow 2p\sigma_u$	$1s\sigma_g \rightarrow 2p\pi_u$	$2p\sigma_u \rightarrow 1s\sigma_g$	$2p\pi_u \rightarrow 1s\sigma_g$	$1s\sigma_g \rightarrow 2p\sigma_u$	$1s\sigma_g \rightarrow 2p\sigma_u$	$2p\sigma_u \rightarrow 1s\sigma_g$	$2p\sigma_u \rightarrow 1s\sigma_g$
NaF	Obs. ( $F_2^+$ )**		-0.31 (a)					
	Calc.		-0.08				-0.03	
KF	Obs. ( $F_2^+$ )**		-0.13 (c,d)					
	Calc.		-0.06				-0.02	
NaCl	Obs.		-0.06 (c,f)					
	Calc.		or -0.08 (d)				or -0.03 (d)	
KCl	Calc.		-0.13				-0.02	
	Obs.		-0.04 (g)				-0.02	
KBr	Calc.		-0.14				-0.03 (g)	
	Obs.		-0.06 (g)				-0.01	
KI	Calc. (a)		-0.05				-0.02	
	Calc. (b)		-0.05				-0.02	
RbI	Obs. (?)		-0.08 (j,k)				0.04 (j,k)	
	Calc. (a)		-0.05				-0.01	
	Calc. (b)		-0.05				-0.02	
	Calc. (a)		-0.04				-0.01	
	Calc. (b)		-0.05				-0.01	



**Table 6.** Influence of the radius of the perturbing charge on spectral shifts  $\Delta E'_{ij}$  (in eV) of  $(F_2^+)_{\text{H}}$  centres.

	$(F_2^+)_{\text{H}}$ in NaCl:O <sup>2-</sup>	$(F_2^+)_{\text{H}}$ in NaCl:S <sup>2-</sup>	Point-charge perturbation
$(F_2^+)_{\text{H}}$ (b)			
Unrelaxed centre			
$1s\sigma_g \rightarrow 2p\sigma_u$	-0.06	-0.05	-0.06
$1s\sigma_g \rightarrow 2p\pi_u$ (1)	-0.13	-0.13	-0.13
$1s\sigma_g \rightarrow 2p\pi_u$ (2)	0.04	0.02	0.06
Relaxed centre			
$2p\sigma_u \rightarrow 1s\sigma_g$	-0.05	-0.05	-0.05
$2p\sigma_u \rightarrow 2s\sigma_g$	-0.15	-0.15	-0.15
$2p\sigma_u \rightarrow 3d\sigma_g$	-0.06	-0.07	-0.06
$2p\sigma_u \rightarrow 3d\pi_g$ (1)	-0.19	-0.19	-0.19
$2p\sigma_u \rightarrow 3d\pi_g$ (2)	-0.14	-0.14	-0.14
$(F_2^+)_{\text{H}}$ (a)			
Unrelaxed centre			
$1s\sigma_g \rightarrow 2p\sigma_u$	-0.02	-0.02	-0.02
$1s\sigma_g \rightarrow 2p\pi_u$ (1)	-0.08	-0.08	-0.08
$1s\sigma_g \rightarrow 2p\pi_u$ (2)	0.04	0.03	0.05
Relaxed centre			
$2p\sigma_u \rightarrow 1s\sigma_g$	-0.02	-0.02	-0.02
$2p\sigma_u \rightarrow 2s\sigma_g$	-0.10	-0.10	-0.10
$2p\sigma_u \rightarrow 3d\sigma_g$	-0.06	-0.06	-0.06
$2p\sigma_u \rightarrow 3d\pi_g$ (1)	-0.14	-0.14	-0.14
$2p\sigma_u \rightarrow 3d\pi_g$ (2)	-0.06	-0.07	-0.05

either identical or very close (less than 0.02 eV shift) to the locations reported for the corresponding centres of NaCl:O<sup>2-</sup> by Georgiou *et al* (1987) and by Gellermann (1991). Of course, more numerous data are necessary to decide whether the present model is really reliable or if its success in the cases of NaCl:O<sup>2-</sup>, KCl:O<sup>2-</sup>, KBr:O<sup>2-</sup> and NaCl:S<sup>2-</sup> arises merely from a deceptive coincidence.

#### 4.4. $(F_2^+)_{\text{A}}$ centres

The previous section shows that SP's model will most probably be unable to cope with  $(F_2^+)_{\text{A}}$  centres, where one regular alkaline cation is replaced by a smaller one: contrary to the O<sup>2-</sup> of  $(F_2^+)_{\text{H}}$  centres, this substitution introduces no long-range coulombic field, so that the calculation will yield very small energy shifts. On the other hand, experimental data show large shifts. Moreover, significant differences are observed between infrared absorption and emission shifts (see, for instance, Schneider 1981), whereas our calculations lead to nearly identical shifts for  $1s\sigma_g \rightarrow 2p\sigma_u$  and for  $2p\sigma_u \rightarrow 1s\sigma_g$  (section 3.2).

In spite of these bad auspices, we attempted a calculation of the  $\Delta E'_{ij}$  for  $(F_2^+)_{\text{A}}$  centres in KCl:Na<sup>+</sup> and in KCl:Li<sup>+</sup>. With the axes of figure 1, the cartesian coordinates of the perturbing ion centre C are (0,  $a/\sqrt{2}$ , 0); i.e. the perturber is nearer to 0 than in the case of  $(F_2^+)_{\text{H}}$ . This should somewhat increase the overlap of the  $F_2^+$  electron wavefunction with the core of the perturber. Let us call  $r'_k$  the ionic radius of potassium (2.513 au) and  $r'_i$  the impurity radius (1.833 and 1.285 au respectively for Na<sup>+</sup> and Li<sup>+</sup>). By analogy with equation (8), we introduce:

$$d'_K = 2r'_K / R'. \quad (19)$$

The electrostatic potential perturbing the  $F_2^+$  centre will be assumed to be the difference between those created by a uniformly charged sphere (total charge  $+e$ ) centred at C, with radius  $r'_i$ , accounting for the impurity, and by another uniformly charged sphere (same total charge), also centred at C, with radius  $r'_K$ , accounting for the missing  $K^+$  ion. Thus, we replace equations (16) by†:

$$\left. \begin{aligned} v(\lambda, \mu, \varphi) &= -\frac{3}{2\kappa_{00}d'_i} \left[ 1 - \frac{1}{3} \left( \frac{d'}{d'_i} \right)^2 \right] + \frac{3}{2\kappa_{00}d'_K} \left[ 1 - \frac{1}{3} \left( \frac{d'}{d'_K} \right)^2 \right] && \text{for } d' \leq d'_i \\ v(\lambda, \mu, \varphi) &= -\frac{1}{\kappa_{00}d'} + \frac{3}{2\kappa_{00}d'_K} \left[ 1 - \frac{1}{3} \left( \frac{d'}{d'_K} \right)^2 \right] && \text{for } d'_i \leq d' \leq d'_K \\ v(\lambda, \mu, \varphi) &= 0 && \text{for } d' \geq d'_K \end{aligned} \right\} \quad (20)$$

Table 7 contains the calculated results which confirm our expectation: the present model is unable to explain experimental results for  $(F_2^+)_A$  centres in KCl and, quite probably, in any other matrix. The rather large  $\Delta E'_{ij}$ s observed for  $(F_2^+)_A$  centres are obviously caused by a mechanism other than the electrostatic perturbation which works well for  $(F_2^+)_H$  centres. Probably, the important point for  $(F_2^+)_A$  centres is that the impurity does not occupy a regular cation site, but is displaced away from the vacancies. Thus, Schneider (1981) attributes the large Stokes shift observed in lithium  $(F_2^+)_A$  centres to a motion of the small  $Li^+$  ion during lattice relaxation, following excitation into the  $2p\sigma_u$  state. Such displacements could rather easily be included in the framework of SP's model by a procedure similar to that of equations (20), but at the cost of introducing new adjustable parameter(s) describing the position of the impurity. Thus, the predictive ability of the calculation would be lost, which would make it nearly useless.

Table 7. Theoretical and experimental values of  $\Delta E'_{ij}$  (in eV) for  $(F_2^+)_A$  centres in KCl. a, Gellermann (1991); b, Schneider and Marquardt (1980).

	KCl:Na <sup>+</sup>		KCl:Li <sup>+</sup>	
	Calculated	Observed (a)	Calculated	Observed (a,b)
Unrelaxed centre				
$1s\sigma_g \rightarrow 2p\sigma_u$	0.008	0.10	0.012	0.02
$1s\sigma_g \rightarrow 2p\pi_u(1)$	-0.008		-0.014	
$1s\sigma_g \rightarrow 2p\pi_u(2)$	0.008		0.013	
Relaxed centre				
$2p\sigma_u \rightarrow 1s\sigma_g$	0.007	-0.03	0.011	-0.18

† To be self-consistent, our  $(F_2^+)_H$  centre calculations above should also have used such a 'composite potential': a uniformly charged sphere (total charge  $-2e$ ), centred at C, with radius  $r'_i$ , accounting for the oxygen impurity and a uniformly charged sphere (total charge  $+e$ ), also centred at C, with radius  $r'_R$ , accounting for the missing halogen ion of radius  $r'_R = R'd'_R/2$ . But this composite potential has exactly the same value as equations (16) for  $d' > d'_R$ , i.e. for the only important contributions to the perturbation matrix elements. Therefore we thought it pointless to complicate the calculation by using a composite potential for  $(F_2^+)_H$  centres.

Since the present model fails for  $(F_2^+)_{\text{A}}$  centres, it is quite hopeless to use it for  $(F_2^+)_{\text{AH}}$ , with both  $O^{2-}$  and alkaline ion impurities. It would predict practically the same absorption or emission wavelengths for  $(F_2^+)_{\text{H}}$  and for  $(F_2^+)_{\text{AH}}$  in a given matrix, which is contradicted by experiment (see, for instance, Gellermann 1991).

#### 4.5. $(F_2^+)^*$ centre in NaF

Mollenauer (1980) discovered a new laser-active  $F_2^+$ -like centre in NaF doped with divalent impurities and he named it  $(F_2^+)^*$ . The optical spectrum of this defect does not depend on the exact nature of the impurity ( $Mg^{2+}$ ,  $Ca^{2+}$ ,  $Cr^{2+}$ ,  $Mn^{2+}$ ,  $Ni^{2+}$ , ...). A few years later, the microscopic structure of  $(F_2^+)^*$  was established by EPR measurements with optical detection (Hofmann *et al* 1985), see figure 3. The cartesian coordinates of the two perturbers are here  $(0, a/\sqrt{2}, 0)$  for  $C_1$  (centre of the cation vacancy) and  $(0, 3a/\sqrt{2}, -a/\sqrt{2})$  for  $C_2$  (centre of the divalent impurity). Let  $r_1'(\lambda, \mu, \varphi)$  and  $r_2'(\lambda, \mu, \varphi)$  be respectively the distances of these two points to the F-electron (spheroidal coordinates  $\lambda, \mu, \varphi$ ); and let us introduce, as above,  $d_1' = 2r_1'/R'$ ,  $d_2' = 2r_2'/R'$ ,  $d'_{\text{Na}} = 2r'_{\text{Na}}/R'$ , where  $r'_{\text{Na}}$  is the ionic radius of  $\text{Na}^+$ . The perturbation potential is now

$$U(\lambda, \mu, \varphi) = (4/R')v(\lambda, \mu, \varphi) = (4/R')[v_1(\lambda, \mu, \varphi) + v_2(\lambda, \mu, \varphi)]. \quad (21)$$

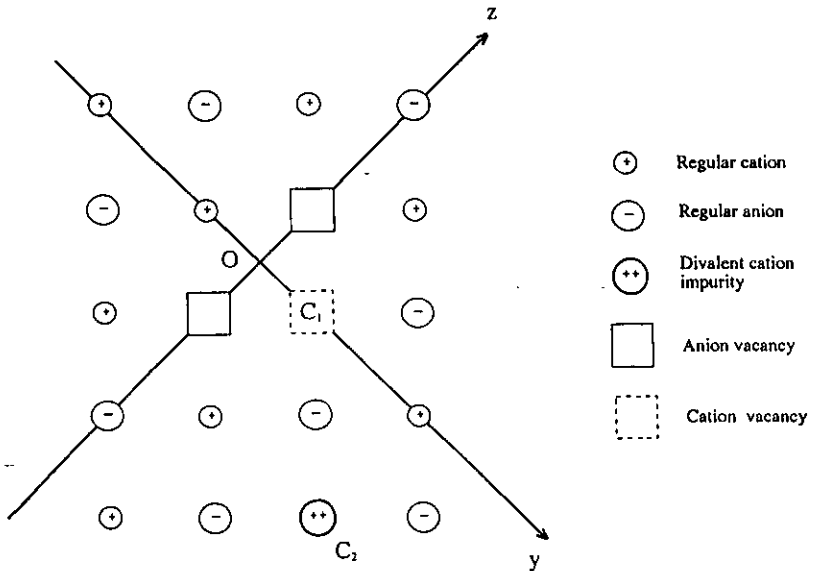


Figure 3. Microscopic structure of the  $(F_2^+)^*$  centre in NaF according to Hofmann *et al* (1985).

Here,  $v_1(\lambda, \mu, \varphi)$ , which represents the effect of the cation vacancy, is:

$$\left. \begin{aligned} v_1(\lambda, \mu, \varphi) &= (3/2\kappa_{00}d'_{\text{Na}})[1 - \frac{1}{3}(d_1'/d'_{\text{Na}})^2] & \text{for } d_1' \leq d'_{\text{Na}} \\ v_1(\lambda, \mu, \varphi) &= 1/\kappa_{00}d_1' & \text{for } d_1' \geq d'_{\text{Na}} \end{aligned} \right\} \quad (22)$$

Similarly,  $v_2(\lambda, \mu, \varphi)$  accounts for the effect of the divalent cationic impurity and is written as:

$$\left. \begin{aligned} v_2(\lambda, \mu, \varphi) &= -(3/2\kappa_{00}d'_i)\left[1 - \frac{1}{3}(d'_2/d'_i)^2\right] & \text{for } d'_2 \leq d'_i \\ v_2(\lambda, \mu, \varphi) &= -1/\kappa_{00}d'_2 & \text{for } d'_2 \geq d'_i \end{aligned} \right\} \quad (23)$$

The calculation was performed with  $r'_{Na} = 1.833$  au and  $r'_i = 1.247$  au ( $Mg^{2+}$ ) or 1.871 au ( $Ca^{2+}$ ), which are respectively the smallest and biggest impurities with which the observation of an  $(F_2^+)^*$  centre has been reported. Table 8 compares the results with experiment. The agreement is as good as in the case of  $(F_2^+)_H$  centres, which supports the model of Hofmann *et al.* There is no significant difference between the predicted positions of absorption or emission bands for  $Mg^{2+}$  and  $Ca^{2+}$  impurities, just as observed experimentally. This was expected, since we found in section 4.3 that SP's model is nearly equivalent to a point-charge calculation. Moreover, the foreign divalent ion of  $(F_2^+)^*$  is farther from the divacancy than the  $O^{2-}$  ion of the  $(F_2^+)_H$  (b) centre, so that its size is of even smaller consequence.

**Table 8.** Theoretical and experimental values of  $\Delta E'_{ij}$  (in eV) for  $(F_2^+)^*$  centres in NaF. a, Mollenauer (1980); b, Nahum (1968). Experimental values for  $2p\sigma_u \rightarrow 2s\sigma_g$  and  $2p\sigma_u \rightarrow 3d\sigma_g$  may be inverted since figure 2 of Mollenauer (1980) does not differentiate between the two possible identifications of the observed absorption bands.

	Calculated (NaF:Mg <sup>2+</sup> )	Calculated (NaF:Ca <sup>2+</sup> )	Observed
Unrelaxed centre			
$1s\sigma_g \rightarrow 2p\sigma_u$	-0.21	-0.21	-0.26 (a)
$1s\sigma_g \rightarrow 2p\pi_u$ (1)	-0.44	-0.44	-0.52 (a)
$1s\sigma_g \rightarrow 2p\pi_u$ (2)	-0.32	-0.32	unobserved
Relaxed centre			
$2p\sigma_u \rightarrow 1s\sigma_g$	-0.19	-0.19	-0.16 (a,b)
$2p\sigma_u \rightarrow 2s\sigma_g$	-0.43	-0.43	-0.19 (a)
$2p\sigma_u \rightarrow 3d\sigma_g$	-0.29	-0.29	-0.30 (a)
$2p\sigma_u \rightarrow 3p\pi_g$ (1)	-0.51	-0.50	-0.41 (a)
$2p\sigma_u \rightarrow 3p\pi_g$ (2)	-0.44	-0.44	unobserved

Let us now return to the case of the  $(F_2^+)^{**}$  centres in NaF. Experimentally, they are  $F_2^+$ -like defects, more perturbed than  $(F_2^+)^*$ , as evidenced by greater shifts, both in absorption and emission. On the other hand, the  $(F_2^+)_H$  model we tried for  $(F_2^+)^{**}$  in section 4.2.2 was less perturbed: an excess negative charge at distance  $(3/2)^{1/2}a$  from the origin O, as compared with a missing positive charge at distance  $(1/2)^{1/2}a$  in the present  $(F_2^+)^*$  calculation. It is therefore not astonishing that we failed to explain the  $\Delta E'_{ij}$  of  $(F_2^+)^{**}$  by using an  $(F_2^+)_H$  hypothesis. If the transition shifts of  $(F_2^+)^{**}$  are explainable in the electrostatic framework of the present model, without requiring consideration of off-site impurities, as for  $(F_2^+)_A$  centres, we must look for a microscopic structure with stronger negative perturbers than those of  $(F_2^+)^*$ . This could be, for instance, an  $F_2^+$  centre, perturbed both by a first-neighbour cation vacancy, as in  $(F_2^+)^*$ , and by a second-neighbour substitutional oxygen ion, as in  $(F_2^+)_H$ . Unfortunately, such a configuration for the defect seems rather unlikely from the electrostatic point of view, and we did not calculate the corresponding  $\Delta E'_{ij}$ .

## 5. Conclusion

In this paper, we have explored the successes and failures of Sennaroglu and Pollock (1991)'s model for predicting the spectra of  $F_2^+$ -like centres in alkali-halides. To this end, we introduced two modifications into the original model, in the hope of allowing it to yield *a priori* predictions on still unknown centres:

- (i) the impurity or vacancy is centred at the exact location that the ion it replaces would occupy in the unperturbed lattice;
- (ii) instead of SP's  $e^{-\alpha d} / \kappa_0$  screening factor, with adjustable constant  $\alpha$ , we used  $1/\kappa_{00}$ , where  $\kappa_{00}$  is the low-frequency dielectric constant of the crystal.

It turns out that SP's model is practically a point-charge one. Thus, with the two strict rules above, it is quite unable to explain observed results for colour centres where  $F_2^+$  is perturbed by a substitutional impurity with the same charge as the regular ion. On the other hand, it yields good results for vacancies or foreign ions with an electrical charge different from the regular one, at least in the cases where unambiguous experimental results are at hand. If this agreement between calculation and observation persists when a greater number of reliable experimental data become available, this modified SP model will prove to be a simple and useful tool for the research of new  $F_2^+$ -like laser materials.

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