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# Puzzling absence of hyperfine interaction in the $D_{4h}$ $\text{RhCl}_6^{4-}$ centre: role of the 4d–5s hybridization in $\text{Rh}^{2+}$ centres

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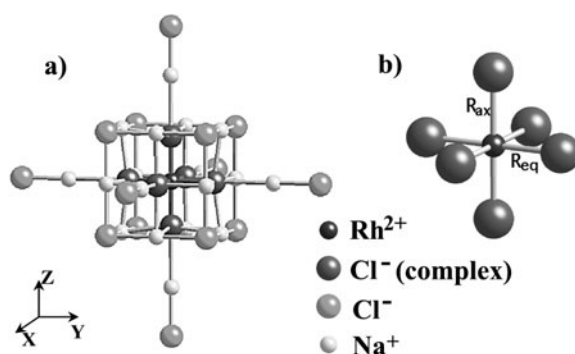
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## Abstract

The amazing absence of hyperfine interaction in EPR spectra of the tetragonally elongated  $\text{RhCl}_6^{4-}$  centre in NaCl is explored through the present work. In addition to the core polarization contribution it is shown that there is another isotropic contribution from the small 5s admixture in the  $a_{1g}^*$  ( $\approx 3z^2 - r^2$ ) level. These two contributions together with the anisotropic ones are shown to lead to a null hyperfine tensor for a 5s admixture of only  $\sim 1.5\%$ . Density functional calculations reveal that such an admixture is strongly sensitive to the tetragonality of the  $\text{RhCl}_6^{4-}$  unit. Writing the axial ( $R_{ax}$ ) and equatorial ( $R_{eq}$ )  $\text{Rh}^{2+}$ – $\text{Cl}^-$  distances as  $R_{ax} = R_0 + 2a$  and  $R_{eq} = R_0 - a$  it is shown that (i) the 5s admixture is proportional to  $a^2$  (for  $a < 25$  pm), a fact which can be accounted for through a simple model; (ii) relative variations of  $R_{eq}$  and  $R_{ax}$  of only  $-0.4$  and  $0.8\%$  lead to a hyperfine constant of 7 MHz. The present results are shown to shed some light on EPR data of the orthorhombic  $\text{RhCl}_6^{4-}$  complex with two *cis*-equatorial  $\text{Na}^+$  vacancies in the fourth shell. It is concluded that the hyperfine interaction measured for this centre can be explained in terms of the small strain induced by equatorial  $\text{Na}^+$  vacancies upon the  $\text{RhCl}_6^{4-}$  unit. This idea can also explain the  $\sim 2\%$  decrement of the isotropic axial superhyperfine constant when compared with that for the tetragonal  $\text{RhCl}_6^{4-}$  centre.

## 1. Introduction

Magnetic resonance techniques (such as EPR or ENDOR) have proven to be quite useful for gaining a better insight into the nature of a given paramagnetic centre formed in insulating or semiconductor materials [1, 2]. This task is greatly helped by the usual observation of hyperfine interactions, which allow one to obtain detailed information about the nature and number of involved nuclei. This relevant information is hard to obtain from optical spectra related to



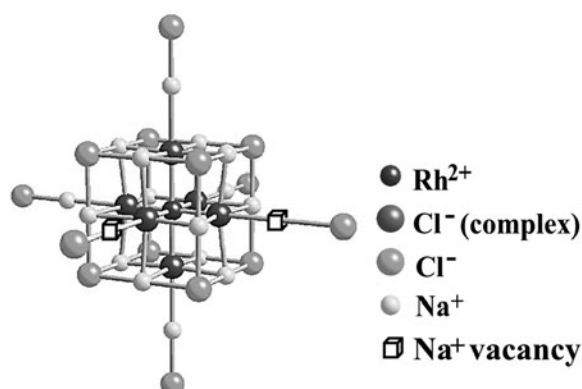
**Figure 1.** (a) Picture of the  $D_{4h}$   $\text{RhCl}_6^{4-}$  centre embedded in NaCl. (b) Detail of the elongated  $\text{RhCl}_6^{4-}$  unit where  $R_{ax} > R_{eq}$ . The principal axis is  $OZ$ .

3d or 4d ions in crystals due to inhomogeneous broadening of zero-phonon lines. Since the discovery of the hyperfine interaction between the unpaired electron and the nucleus of  $\text{Cu}^{2+}$  diluted in Tutton salts made by means of EPR [3], the observation of hyperfine interaction has become a crucial test for relating a given paramagnetic centre to a 3d or 4d impurity.

In recent years a great deal of work has been focused on  $\text{Rh}^{2+}$  centres formed in NaCl or AgCl [4–12]. Among the observed centres in NaCl there is one exhibiting tetragonal symmetry which has been ascribed to *elongated*  $\text{RhCl}_6^{4-}$  Jahn–Teller species (figure 1) with remote charge compensation and an unpaired electron placed in the  $a_{1g}^*$  ( $\approx 3z^2 - r^2$ ) level [5, 7, 9]. The experimental  $g$  tensor ( $g_{\parallel} - g_0 = 0.01$ ;  $g_{\perp} - g_0 = 0.45$ ) and the observation of superhyperfine interaction with the two axial ligands are consistent with this assignment. Moreover, recent density functional (DF) calculations [13] of the adiabatic ground-state energy reveal that the elongated geometry is more stable than the compressed one. The equilibrium axial ( $R_{ax}$ ) and equatorial ( $R_{eq}$ )  $\text{Rh}^{2+}$ – $\text{Cl}^-$  distances are found to be  $R_{ax} = 270.7$  pm and  $R_{eq} = 244.5$  pm. The computed crystal-field transitions and isotropic superhyperfine constants in this geometry reasonably account for experimental values.

Despite these facts no experimental evidence of hyperfine interaction with the Rh nucleus for any orientation of the  $\text{RhCl}_6^{4-}$  species has been obtained [5, 9]. This experimental fact is certainly puzzling as it means that the two components,  $A_{\parallel}$  and  $A_{\perp}$ , of the hyperfine tensor for the  $D_{4h}$   $\text{RhCl}_6^{4-}$  centre should be *both* equal to zero. This circumstance is far from being observed for tetragonal elongated centres of  $d^9$  ions (like  $\text{Cu}^{2+}$  or  $\text{Ag}^{2+}$ ) in chlorides or fluorides where the unpaired electron resides however in the  $b_{1g}^*$  ( $\approx x^2 - y^2$ ) orbital [1, 14–17]. In these cases at least the  $A_{\parallel}$  component is well detected experimentally. On these grounds a main reason for rejecting the ascription to  $\text{Ag}^{2+}$  of a centre formed in  $\text{Ag}^+$ -doped  $\text{CaF}_2$  under X-irradiation was the lack of silver hyperfine structure in the associated EPR spectra [18].

The absence of hyperfine structure in EPR spectra of the  $D_{4h}$   $\text{RhCl}_6^{4-}$  centre in NaCl cannot be attributed to the smallness of the nuclear magnetic moment of  $\text{Rh}^{103}$  ( $\mu = -0.088\beta_N$ ) as it is about only 80% of the value corresponding to the two isotopes of silver and  $|A_{\parallel}|$  lies between 60 and 125 MHz for  $\text{Ag}^{2+}$  in chlorides and fluorides [14–17]. Neither can it be attributed to a huge delocalization of the unpaired electron lying in the  $a_{1g}^*$  ( $\approx 3z^2 - r^2$ ) level as DFT calculations performed on a  $\text{RhCl}_6\text{Na}_{12}\text{Cl}_8\text{Na}_6\text{Cl}_6$  cluster indicate [13] that only 2% of the unpaired electron in this centre lies *outside* the  $\text{RhCl}_6^{4-}$  complex, while about 65% of the charge is found to be on the  $3z^2 - r^2$  orbital of Rh. Moreover, when one or two vacancies are introduced [7, 9, 12] in the fourth shell of  $\text{Na}^+$  ions along  $X$  or  $Y$  directions (figure 2), hyperfine interaction is already detected in the associated centres (table 1). For instance when



**Figure 2.** Pictorial description of the  $\text{RhCl}_6^{4-} \cdot 2\text{vac}$  centre. The two  $\text{Na}^+$  vacancies are placed in the *cis* position.

**Table 1.** Principal values of gyromagnetic, hyperfine and superhyperfine (of axial ligands) parameters for three  $\text{Rh}^{2+}$  centres depicted in figure 1. For the  $D_{4h}$  centre the principal directions  $x, y, z$  coincide with  $X, Y, Z$  directions of figures 1 and 2. This is however no longer true for the other centres involving a lower symmetry [11]. Hyperfine and superhyperfine tensors are given in MHz.

Centre	$\text{Rh}^{2+}$			$\text{Cl}^{35}$			$g_x$	$g_y$	$g_z$	References
	$A_x$	$A_y$	$A_z$	$A_x$	$A_y$	$A_z$				
$D_{4h} \text{RhCl}_6^{4-}$	—	—	—	33.9	33.9	75.5	2.451	2.451	2.019	[9]
$\text{RhCl}_6^{4-} \cdot 2\text{vac}$	14.26	14.26	11.10	33.9	33.9	72.7	2.4797	2.4712	2.0118	[7, 9, 11]
$\text{RhCl}_6^{4-} \cdot 1\text{vac}$	8.01	9.74	8.18	35	35	73	2.4779	2.4301	2.0154	[7, 9, 11]

two vacancies are present the isotropic hyperfine constant is about 12 MHz. Nevertheless, the addition of one or two vacancies to the  $D_{4h}$   $\text{RhCl}_6^{4-}$  centre is not likely to lead to strong modifications of the electronic structure, as reflected by the experimental values of the  $g$  and superhyperfine tensor of axial ligands for the three centres gathered in table 1. This fact is consistent with the location of vacancies *outside* the  $\text{RhCl}_6^{4-}$  complex and suggests that the absence of hyperfine interaction in the  $D_{4h}$   $\text{RhCl}_6^{4-}$  centre may be a subtle phenomenon indeed.

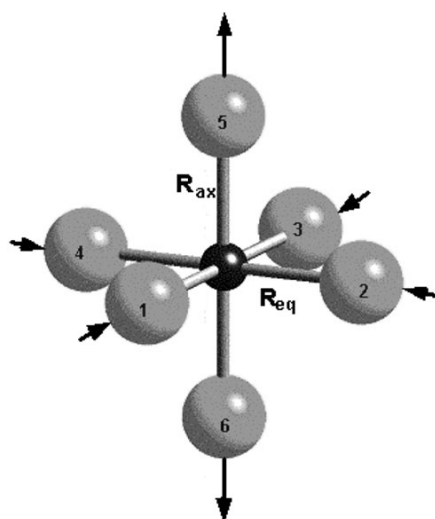
Searching to explain this attractive feature the contributions to  $A_{\parallel}$  and  $A_{\perp}$  for a  $d^7$  elongated  $D_{4h}$  complex with an unpaired electron in the  $a_{1g}^*$  ( $\approx 3z^2 - r^2$ ) level are first considered. Similar to what is found in the case of  $d^9$  ions in a compressed tetragonal symmetry [19, 20], attention has been paid to the contribution from the  $4d-5s$  hybridization allowed in the  $a_{1g}^*$  ( $\approx 3z^2 - r^2$ ) level but usually ignored in crystal-field-like models [1].

In a second step the amount of such  $4d-5s$  hybridization is calculated within the DF framework for different values of the vibrational  $Q_{\theta}$  ( $\approx 3z^2 - r^2$ ) coordinate of the  $\text{RhCl}_6^{4-}$  complex pictured in figure 3.

## 2. Analysis of the hyperfine tensor for the tetragonal $\text{RhCl}_6^{4-}$ complex

The hyperfine coupling in the  $\text{RhCl}_6^{4-}$  centre is directly or indirectly due to the unpaired electron located in the  $a_{1g}^*$  orbital. Ignoring in a first step the spin-orbit coupling, the associated wavefunction can briefly be described as

$$|a_{1g}^*\rangle = \alpha_d |3z^2 - r^2\rangle + \alpha_{5s} |5s\rangle - \lambda_{p\sigma}^{ax} |\chi_{p\sigma}^{ax}\rangle - \lambda_s^{ax} |\chi_s^{ax}\rangle - \lambda_{p\sigma}^{eq} |\chi_{p\sigma}^{eq}\rangle - \lambda_s^{eq} |\chi_s^{eq}\rangle \quad (1)$$



**Figure 3.** Pictorial description of the  $Q_\theta (\sim 3z^2 - r^2)$  distortion coordinate.

where, for instance,  $|\chi_{p\sigma}^{ax}\rangle$  and  $|\chi_s^{ax}\rangle$  mean suitable linear combinations of 3p and 3s wavefunctions of axial ligands, respectively. Of course,  $\alpha_{5s}$  should be zero if  $R_{ax} = R_{eq}$ .

The two components describing the diagonal hyperfine tensor of the  $D_{4h}$   $\text{RhCl}_6^{4-}$  centre can simply be written as

$$A_i = A_i^{an} + A^{is} \quad (i = \parallel \text{ or } \perp) \quad (2)$$

where the first and second terms refer to the anisotropic and isotropic contributions, respectively. Considering only the admixture via spin-orbit coupling (up to second-order perturbations) of  $a_{1g}^*$  with the crystal-field level  $e_g^*$ , the expressions for  $A_{\parallel}^{an}$  and  $A_{\perp}^{an}$  can be written as

$$A_{\parallel}^{an} = P\left(\frac{4}{7}\alpha_d^2 - \frac{1}{7}\Delta g_{\perp}\right) \quad A_{\perp}^{an} = P\left(-\frac{2}{7}\alpha_d^2 + \frac{15}{14}\Delta g_{\perp}\right) \quad (3)$$

where  $P = 2\beta g_N \beta_N \langle r^{-3} \rangle_{4d}$  [1]. The first term arises from the first-order contribution due to the anisotropic dipolar interaction,  $H_D$ , between the electron spin and that of the Rh nucleus

$$H_D = 2\beta g_N \beta_N \left\{ \frac{3(\mathbf{r} \cdot \mathbf{s})(\mathbf{r} \cdot \mathbf{I})}{r^5} - \frac{\mathbf{s} \cdot \mathbf{I}}{r^3} \right\}. \quad (4)$$

Due to the  $r^{-3}$  dependence of  $H_D$  such a contribution reflects the fractional charge on the  $|3z^2 - r^2\rangle$  orbital in (1) due to covalency. As  $\langle L_z \rangle \approx 0$ , the second term in  $A_{\parallel}^{an}$  reflects the influence of the  $e_g^*$  admixture upon the expected value of  $H_D$ . In the case of  $A_{\perp}^{an}$  the influence of such an admixture upon *both*  $H_D$  and  $H_L$  interactions has to be considered, where  $H_L$  is given by

$$H_L = 2\beta g_N \beta_N \frac{\mathbf{l} \cdot \mathbf{I}}{r^3}. \quad (5)$$

Equation (3) contains covalency effects involved in the reduction of  $\Delta g_{\perp}$  and leads to the expressions by the crystal-field model when covalency is ignored.

In addition to the usual contribution from the polarization of 1s, 2s, 3s and 4s inner closed shells of Rh by the external unpaired electron [1], the 4d-5s admixture in (1) leads to *another* contribution to  $A^{is}$ , which is absent from  $O_h$  geometry as well as from tetragonal symmetry when the unpaired electron lies in the  $b_{1g}^*$  ( $\approx x^2 - y^2$ ) orbital. Therefore,  $A^{is}$  can be written as

$$A^{is} = (2\beta g_N \beta_N) \left\{ -\frac{2}{3}\chi + \frac{8\pi}{3} |\psi_{5s}(0)|^2 \alpha_{5s}^2 \right\} \quad (6)$$

where the core polarization contribution  $\chi$  usually lies between 7 and 9.5 au for 4d ions [21], and thus it is about three times bigger than that for 3d ions. The origin of this large difference is quite subtle and was satisfactorily accounted for by Watson and Freeman [21]. The dominant contribution to  $\chi$  for 4d ions originates from 4s electrons whose wavefunction has a maximum at  $r_{4s}(\text{max})$  lying *below the second* maximum of the radial 4d wavefunction, thus giving rise to a negative contribution to  $\chi$ . By contrast, for 3d ions  $r_{3s}(\text{max})$  is higher than  $r_{3d}(\text{max})$ , corresponding to the *only* maximum of the radial 3d wavefunction. As expected the  $\chi$  value depends on the covalency of the complex [22, 23]. For  $\text{Ag}^{2+}$  in different environments it has been reported that  $\chi$  decreases when covalency increases,  $\chi$  being always in the range 7–9.3 au [24].

The  $|\psi_{5s}(0)|^2$  quantity involved in equation (6) corresponds to a virtual 5s orbital of  $\text{Rh}^{2+}$  and can in principle be estimated by the value  $|\psi_{5s}(0)|_{HF}^2$  derived within the Hartree–Fock approximation. It is worth noting however that in the case of the silver atom  $|\psi_{5s}(0)|_{HF}^2$  leads to a serious *underestimation* of  $|\psi_{5s}(0)|^2$ . In fact the calculated Hartree–Fock value for  $\text{Ag}^0$ ,  $|\psi_{5s}(0)|_{HF}^2 = 4.81$  au [25], leads to an isotopic hyperfine constant  $A^{is} = 928$  MHz, which is about half the experimental value,  $A^{is} = 1845$  MHz [26]. Therefore, correlation effects between the valence electron and inner ones lead to a higher probability for the presence of the former on the nucleus than expected from the mean-field approximation. A similar situation also holds for the  $\text{Cu}^0$  atom [20]. In view of these facts  $|\psi_{5s}(0)|^2$  is written as

$$|\psi_{5s}(0)|^2 = \gamma |\psi_{5s}(0)|_{HF}^2 \quad (7)$$

where  $\gamma \approx 2$  is an amplification factor.

Now using the quantities

$$\kappa = \frac{2}{3} \frac{\chi}{\langle r^{-3} \rangle_{4d}} \quad \kappa_{5s} = \frac{|\psi_{5s}(0)|_{HF}^2}{\langle r^{-3} \rangle_{4d}} \quad (8)$$

$A^{is}/P$  can be expressed in terms of dimensionless quantities as follows:

$$A^{is} = P \left\{ -\kappa + \frac{8\pi}{3} \gamma \kappa_{5s} \alpha_{5s}^2 \right\}. \quad (9)$$

By means of equations (3) and (9), the hyperfine tensor for the  $D_{4h}$   $\text{RhCl}_6^{4-}$  centre in NaCl can now be analysed. Using the experimental  $g_{\perp} - g_0 = 0.45$  value [5, 9] and the calculated  $\alpha_d^2 = 0.65$ , we obtain  $A_{\parallel}^{an}/P \approx A_{\perp}^{an}/P = 0.30$ . This result is certainly relevant as it implies that if  $A^{is}/P = -0.30$  *both* components  $A_{\parallel}$  and  $A_{\perp}$  can *simultaneously* be equal to zero.

Bearing in mind the calculated  $\langle r^{-3} \rangle_{4d}$  values for  $\text{Rh}^{2+}$  ( $\langle r^{-3} \rangle_{4d} = 6.8$  au) and  $\text{Rh}^+$  ( $\langle r^{-3} \rangle_{4d} = 6.2$  au) [25], the value  $\langle r^{-3} \rangle_{4d} = 6.5$  au will be employed, implying  $P = -109$  MHz. From  $|\psi_{5s}(0)|_{HF}^2 = 4.7$  au calculated for the  $4d^8 5s^1$  configuration of  $\text{Rh}^0$  and  $|\psi_{5s}(0)|_{HF}^2 = 7.9$  au computed for the  $4d^7 5s^1$  configuration of  $\text{Rh}^+$  [25], a value  $|\psi_{5s}(0)|_{HF}^2 \approx 11$  au can be estimated for the virtual 5s orbital of  $\text{Rh}^{2+}$ . Now assuming  $\chi \approx 7.5$  au and  $\gamma \approx 2$ , it is found that  $\kappa \approx 0.77$ ,  $\kappa_{5s} \approx 1.7$  and  $\frac{8\pi}{3} \gamma \kappa_{5s} \approx 30$ .

Therefore, a value  $A^{is}/P = -0.30$  can be reached if  $\alpha_{5s}^2$  is equal *only* to  $\approx 1.5\%$ , which means a very small 5s admixture into the  $a_{1g}^*$  wavefunction (1).

### 3. Calculation of the 5s admixture as a function of the $Q_{\theta}$ distortion

Following a previous study [13], the value of  $\alpha_{5s}^2$  corresponding to the  $D_{4h}$   $\text{RhCl}_6^{4-}$  centre in NaCl has been calculated by means of DF calculations. For this goal a 39-atom

$\text{RhCl}_6\text{Na}_{12}\text{Cl}_8\text{Na}_6\text{Cl}_6$  cluster has been used where the  $\text{RhCl}_6^{4-}$  centre is embedded (figure 1). In the calculations, carried out using the Amsterdam DF (ADF) code [27] and the generalized gradient approximation (GGA), the effects of the electrostatic potential due to the rest of the ions in the NaCl host lattice not included in the studied cluster have been considered. In these calculations, Rh electrons lying below the 3d shell are included in a frozen core, while 1s, 2s and 2p electrons form the frozen core for Cl and Na. A basis set of the best quality in the ADF code has been used. More details on the calculations are offered elsewhere [13, 28].

By means of this kind of calculation on the  $D_{4h}$   $\text{RhCl}_6^{4-}$  centre in NaCl it has been possible to explain [13]

- (i) why the isotropic superhyperfine constant of axial ligands is much larger than that associated with equatorial ones, although  $R_{ax} > R_{eq}$  [5, 9], and
- (ii) the nature of two experimentally observed crystal-field transitions [9].

In the present calculations attention has been paid not only to the  $\alpha_{5s}^2$  value computed at the calculated equilibrium distance of the ground state but also to the dependence of  $\alpha_{5s}^2$  upon the  $Q_\theta$  distortion (depicted in figure 3) for  $Q_\theta > 0$ . Such a dependence reflects the sensitivity of the 5s admixture to variations of both  $R_{ax}$  and  $R_{eq}$  distances. Writing

$$R_{ax} = R_0 + 2a \quad R_{eq} = R_0 - a \quad (10)$$

the  $Q_\theta$  normal coordinate is just given by  $Q_\theta = \sqrt{12}a$ , while  $R_0$  means the equilibrium metal–ligand distance for a hypothetical  $\text{RhCl}_6^{4-}$  centre in NaCl with octahedral symmetry. This distance,  $R_0$ , can be derived through a DF calculation for a  $(3z^2 - r^2)^{0.5}(x^2 - y^2)^{0.5}$  ground-state configuration whose associated density exhibits the required orbital  $A_{1g}$  symmetry. For the present case, the computed value is  $R_0 = 2.53 \text{ \AA}$  [13]. This value is found to be practically independent of the employed cluster size.

Results on the obtained  $Q_\theta$  dependence of both  $\alpha_d^2$  and  $\alpha_{5s}^2$  quantities are collected in figure 4. It can first be noted that  $\alpha_d^2$  is only slightly dependent upon  $a$  in the  $0 < a < 25 \text{ pm}$  range as the obtained variations are about 3% compared with the value computed for  $O_h$  geometry. This result is quite comparable to that found for 3d complexes with octahedral symmetry and also to tetragonal complexes of  $d^9$  ions where the unpaired electron lies in the  $b_{1g}^*$  ( $\approx x^2 - y^2$ ) orbital. An explanation of the small dependence of covalency on metal–ligand distance is given in [29].

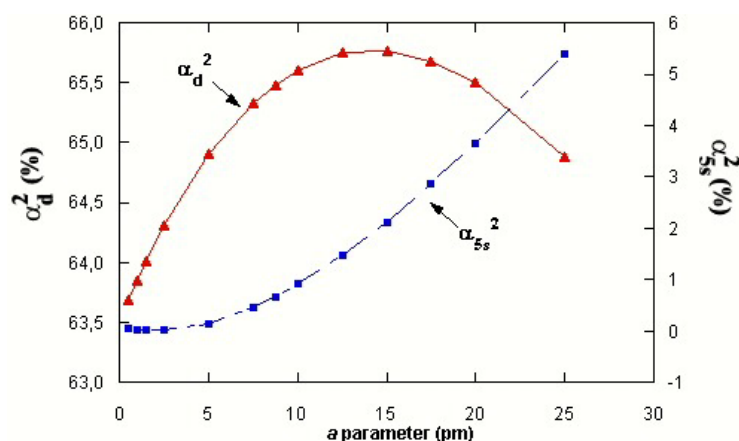
The sensitivity of  $\alpha_{5s}^2$  to changes of the tetragonality parameter  $a$  is found, however, to be quite different to that displayed by  $\alpha_d^2$ . Although, obeying symmetry requirements,  $\alpha_{5s}^2 = 0$  for the octahedral geometry, the  $\alpha_{5s}^2$  value increases very rapidly following the increase of the parameter  $a$ . Therefore,  $\alpha_{5s}^2 = 1\%$  is found for  $a = 10 \text{ pm}$  ( $R_{ax} = 273 \text{ pm}$  and  $R_{eq} = 243 \text{ pm}$ ) while  $\alpha_{5s}^2 = 4\%$  for  $a = 21 \text{ pm}$ , which means an increase of about 300%. For a value  $a = 12 \text{ pm}$ ,  $\alpha_{5s}^2$  is found to be equal to 1.5%. Bearing in mind the difficulties for a precise calculation of small quantities such as  $\alpha_{5s}^2$  and the approximations involved in the analysis of section 2, it can reasonably be concluded that the tiny 5s admixture plays a key role in explaining the lack of hyperfine interaction in EPR spectra of the  $D_{4h}$   $\text{RhCl}_6^{4-}$  centre in NaCl.

The present results strongly suggest that tiny changes of the tetragonality parameter  $a$  can lead to significant variations of  $A^{is}$ . For  $a < 0.25 \text{ \AA}$  the results of figure 4 are well represented by the law

$$\alpha_{5s}^2 (\%) = 89.1 [a (\text{\AA})]^2. \quad (11)$$

Let us denote by  $A_{5s}^{is}$  the contribution to  $A^{is}$  in equation (9) from the 5s admixture

$$A_{5s}^{is} = P \frac{8\pi}{3} \gamma \kappa_{5s} \alpha_{5s}^2. \quad (12)$$



**Figure 4.** Calculated dependence of  $\alpha_d^2$  and  $\alpha_{5s}^2$  upon the tetragonality parameter  $a$  in the range  $0 < a < 25$  pm.

(This figure is in colour only in the electronic version)

It turns out that if  $a$  is increased by a quantity  $\Delta a$  equal *only* to 1 pm then  $A_{5s}^{is}$  would experience an increase  $\Delta A_{5s}^{is} = 7$  MHz. This result means that if initially  $A_{\parallel} = A_{\perp} = 0$ , a small strain involving  $\Delta R_{eq} = -1$  pm and  $\Delta R_{ax} = +2$  pm would lead to a positive hyperfine constant which is already detectable. It is worth noting that the changes for other contributions in equations (3) and (9) induced by  $\Delta a = 1$  pm are expected to be much smaller. According to figure 4 the change undergone by the quantity  $\frac{4}{7}\alpha_d^2 P$  would be smaller than 0.1 MHz. Following the dependence of  $\Delta g_{\perp}$  on  $R_{eq}$  and  $R_{ax}$  studied for  $\text{AgX}_6^{4-}$  ( $X = \text{Cl}, \text{F}$ ) [29, 31] one can estimate that the change experienced by the quantity  $P\Delta g_{\perp}$  is smaller than 1 MHz, while from the analysis carried out on  $\text{MnF}_6^{4-}$  [20, 23] the variation of  $\kappa \cdot P$  would be  $< 0.1$  MHz. This simple analysis thus stresses that observed variations on hyperfine constants due to a small strain described by  $\Delta a$  has to be related mainly to  $\Delta A_{5s}^{is}$  and thus to the small changes undergone by the weak 5s admixture in (1).

#### 4. Tentative explanation of the hyperfine interaction in $\text{RhCl}_6^{4-} \cdot 1\text{vac}$ or $\text{RhCl}_6^{4-} \cdot 2\text{vac}$ centres

The present results could also shed some light on the influence of fourth-shell  $\text{Na}^+$  vacancies upon the experimental hyperfine tensor. First DF calculations carried out on clusters involving up to 87 atoms reveal that the  $D_{4h}$   $\text{RhCl}_6^{4-}$  centre in NaCl is decoupled to a good extent from the rest of the lattice [13]. In this sense the computed value  $R_0 = 2.53$  Å is about 10% smaller than the distance ( $= 2.82$  Å) corresponding to the perfect NaCl lattice. By contrast,  $\text{Na}^+$  ions of the fourth shell are found to lie at 5.8 Å, involving a small outwards relaxation due to the increase of positive charge from the  $\text{Na}^+ \rightarrow \text{Rh}^{2+}$  substitution.

Bearing in mind these facts, it can be guessed that the main role of equatorial vacancies present in  $\text{RhCl}_6^{4-} \cdot 1\text{vac}$  or  $\text{RhCl}_6^{4-} \cdot 2\text{vac}$  centres (figure 2) is to produce a strain upon the  $\text{RhCl}_6^{4-}$  complex. As in such centres  $\text{Na}^+$  vacancies are formed in the equatorial plane they favour a diminution of the *average*  $R_{eq}$  distance and thus an increase of  $R_{ax}$  and  $A_{5s}^{is}$ . This idea is supported by the fact that in both centres the experimental hyperfine tensor is essentially isotropic (table 1). Moreover, if the present interpretation is right one would expect that the



sign of hyperfine constants for  $\text{RhCl}_6^{4-} \cdot 1\text{vac}$  or  $\text{RhCl}_6^{4-} \cdot 2\text{vac}$  centres is negative and not positive as would occur when core polarization effects were dominant. This issue has not yet been clarified through experiments [32].

The present interpretation is reinforced when looking at the experimental  $\Delta g_{\perp}$  value of the  $\text{RhCl}_6^{4-} \cdot 2\text{vac}$  centre. In fact, the referred strain would decrease the energy of the  $a_{1g}^*$  orbital and in principle the separation between this level and the crystal-field level  $e_g^*$ , leading to an increase of  $\Delta g_{\perp}$  such as is observed (table 1). Moreover, the strain in the  $\text{RhCl}_6^{4-} \cdot 2\text{vac}$  centre would also lead to a decrement of the isotropic superhyperfine constant,  $A_{ax}^{is}$ , of axial ligands when compared with that for the  $D_{4h}$   $\text{RhCl}_6^{4-}$  centre in NaCl. From data gathered in table 1  $A_{ax}^{is} = 47.8$  MHz for the  $D_{4h}$  centre while  $A_{ax}^{is} = 46.8$  MHz for the  $\text{RhCl}_6^{4-} \cdot 2\text{vac}$  centre. According to previous results [13] on the  $D_{4h}$  centre in NaCl,  $\partial A_{ax}^{is}/\partial a = -1.6$  MHz  $\text{pm}^{-1}$ . Therefore, a variation  $\Delta A_{ax}^{is} = -1$  MHz on the  $D_{4h}$  centre would imply a small change  $\Delta a \approx 1$  pm of the tetragonality parameter. The present reasoning thus suggests that changes  $\delta R_{ax} > 0$  and  $\delta R_{eq} < 0$  of the *average*  $R_{ax}$  and  $R_{eq}$  distances induced by the presence of one or two equatorial vacancies can be smaller than  $\sim 5$  pm. Despite this fact, however, the obtained results on the  $D_{4h}$  centre cannot be directly transferred to  $\text{RhCl}_6^{4-} \cdot 1\text{vac}$  or  $\text{RhCl}_6^{4-} \cdot 2\text{vac}$  centres where a lower symmetry is involved. Additional work on the  $\text{RhCl}_6^{4-} \cdot 2\text{vac}$   $C_{2v}$  centre is thus necessary.

### 5. Origin of the strong $Q_{\theta}$ dependence of $\alpha_{5s}^2$ through a simple model

A deep understanding of  $\alpha_{5s}^2(Q_{\theta})$  is not yet fulfilled only by the calculation of  $\alpha_{5s}^2$  for different  $Q_{\theta}$  values. In fact, it is also required to clarify the *main reason* for the strong dependence of  $\alpha_{5s}^2$  upon  $Q_{\theta}$  displayed in figure 4.

Let us first consider the limit when  $R_{ax} = R_{eq}$  (octahedral symmetry). The wavefunction of the  $a_{1g}^*$  orbital of the  $D_{4h}$   $\text{RhCl}_6^{4-}$  centre can be written in a simple molecular orbital description [33] as

$$|a_{1g}^*(O)\rangle = N\{|3z^2 - r^2\rangle - \lambda_{p\sigma}|\phi_{p\sigma}\rangle\} \quad (13)$$

where the linear combination  $|\phi_{p\sigma}\rangle$  involving 3p levels of six Cl ligands (figure 3) is given by

$$|\phi_{p\sigma}\rangle = \frac{1}{\sqrt{12}}\{2(|p_z(5)\rangle + |p_z(6)\rangle) - (|p_x(1)\rangle + |p_y(2)\rangle - |p_x(3)\rangle - |p_y(4)\rangle)\}. \quad (14)$$

For simplicity the additional contribution arising from 3s levels of six Cl ligands is not included in (13). Such an admixture is much smaller than that for 3p(Cl) levels and reflects the large separation (15.5 eV) between 3p(Cl) and 3s(Cl) levels of free  $\text{Cl}^-$  and  $\text{Cl}^0$  species [34]. A similar situation is encountered for other halides and the oxygen as well [34].

If  $h$  denotes the one-electron Hamiltonian, a 5s admixture into the wavefunction (13) is governed by the matrix element  $\langle 5s|h|a_{1g}^*(O)\rangle$  which is just proportional to the overlap integral  $\langle 5s|a_{1g}^*(O)\rangle$  if the Wolfsberg–Helmholz approximation [33] is used. Of course, this integral is strictly equal to zero if  $R_{ax} = R_{eq} = R_0$ . When  $a/R_0 \ll 1$ , equation (13) can however be used as a reasonable first-order approximation of the  $a_{1g}^*$  wavefunction. In such a case, using second-order perturbation,  $\alpha_{5s}^2$  is related to  $\langle 5s|a_{1g}^*(O)\rangle$  by

$$\alpha_{5s}^2 \propto \frac{\langle 5s|a_{1g}^*(O)\rangle^2}{[\varepsilon(5s) - \varepsilon(a_{1g}^*)]^2}. \quad (15)$$

Assuming that the dependence of  $\alpha_{5s}^2$  upon  $a$  is governed by the square of the overlap integral  $\langle 5s|a_{1g}^*(O)\rangle$ , this quantity can be expressed according to (14), as follows:

$$\langle 5s|a_{1g}^*(O)\rangle = \frac{4}{\sqrt{12}}\{S_{5s}(R_{ax}) - S_{5s}(R_{eq})\}. \quad (16)$$

Here  $S_{5s}(R)$  denotes the diatomic overlap integral (always taken as positive) between the 5s wavefunction of the central ion and the  $3p_\sigma$  wavefunction of a ligand. In the limit  $a/R_0 \ll 1$  the difference  $S_{5s}(R_{ax}) - S_{5s}(R_{eq})$  can be approximated by

$$\{S_{5s}(R_{ax}) - S_{5s}(R_{eq})\} \approx \left( \frac{\partial S_{5s}}{\partial R} \right)_{R_0} 3a. \quad (17)$$

Then, in view of (15) we can write

$$\alpha_s^2 \propto \langle 5s | a_{1g}^*(O) \rangle^2 \propto a^2 \quad (18)$$

explaining in a simple way the parabolic dependence of  $\alpha_{5s}^2$  upon  $a$  displayed by figure 4 when  $a < 25$  pm, and thus the sensitivity of  $A_{5s}^{is}$  to the tetragonality of the  $RhCl_6^{4-}$  centre. This dependence is not altered by considering the covalency in the mainly 5s level or by adding the contribution of 3s(Cl) orbitals in (13).

## 6. Final remarks

According to present results *fine details* of the wavefunction can be responsible for relevant properties of a given system. This situation is thus similar to that encountered in the explanation of the strong dependence of the cubic field splitting parameter, 10 Dq, on the metal–ligand distance. It was shown that, in a case like the  $O_h$   $CrF_6^{3-}$  complex, such a dependence arises mainly from the *weak admixture* of 2s(F) orbitals into the antibonding  $e_g^*$  orbital [35].

It has reasonably been shown that a value of  $\alpha_{5s}^2$  around only 1% can explain the amazing absence of hyperfine structure from EPR spectra of the  $D_{4h}$   $RhCl_6^{4-}$  centre in NaCl. Furthermore, the present results indicate that a very small tetragonal strain described by  $\Delta R_{eq}/R_0 = -0.4\%$  and  $\Delta R_{ax}/R_0 = 0.8\%$  would already lead to an isotropic hyperfine interaction around 7 MHz. This situation is thus comparable to that found for  $D_{4h}$  complexes of  $Cu^{2+}$  with an unpaired electron in the  $a_{1g}^*$  ( $\approx 3z^2 - r^2$ ) level such as occurs for  $CuX_4(NH_3)_2^{2-}$  complexes ( $X = Cl, Br$ ) or  $BaZnF_4:Cu^{2+}$  [19, 20]. In all these cases the experimental variations of  $A^{is}$  induced by either external or internal stresses can be used as a sensitive parameter for monitoring the associated changes of tetragonality.

When the unpaired electron of a  $Cu^{2+}$  complex resides in the  $b_{1g}^*$  ( $\approx x^2 - y^2$ ) level the 4s admixture in that level is symmetry forbidden, but allowed if a small orthorhombicity occurs. It has recently been discovered [36] that the experimental hyperfine constant  $A_{||}$  of  $D_{2h}$   $CuCl_6^{4-}$  units is significantly smaller than that corresponding to tetragonal  $CuCl_6^{4-}$  complexes. This discrepancy has also been related to the 4s admixture in the electronic level where the unpaired electron is placed. The importance of the 4d–5s hybridization was already underlined by Muniz *et al* [37] on  $Rh(CN)_2Cl_4^{4-}$  in KCl. These authors pointed out that the experimental values  $|A_{||}| = 123$  MHz,  $|A_{\perp}| = 111$  MHz can only be explained assuming that  $A_{||}$  and  $A_{\perp}$  are both negative. A similar analysis to that carried out in section 2 leads to  $\alpha_{5s}^2 \approx 6\%$  consistent with the higher tetragonality expected for  $Rh(CN)_2Cl_4^{4-}$  in comparison with that of  $RhCl_6^{4-}$  where all ligands are  $Cl^-$ .

The analysis of section 2 outlines that  $|\psi_{5s}(0)|^2$  is substantially higher than that predicted through the Hartree–Fock approximation, a fact which reflects important correlation effects in the core region. Although expressions (2), (6) and (9) are able to explain why *both*  $A_{||}$  and  $A_{\perp}$  can become equal to zero, they only include partially the effects of covalent bonding. Inclusion of admixture (via spin–orbit coupling) of charge transfer excitations into the ground state [30] will lead to additional contributions to  $A_{||}^{an}$  and  $A_{\perp}^{an}$ . This work is likely to be more necessary for studying  $RhBr_6^{4-}$  centres.

The analysis carried out in section 4 indicates that EPR parameters due to  $\text{RhCl}_6^{4-} \cdot 1 \text{ vac}$  or  $\text{RhCl}_6^{4-} \cdot 2 \text{ vac}$  centres can simply be understood in terms of the  $D_{4h}$   $\text{RhCl}_6^{4-}$  centre *but* perturbed by a small strain induced by equatorial  $\text{Na}^+$  vacancies. Despite this promising view, calculations of such centres including their actual symmetry become necessary for achieving a detailed description of their structural and electronic properties. Work along this line is now under way.

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