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## ON A STRUCTURAL DISTORTION EFFECT IN THE NMR-SPECTRUM OF ALKALI FULLERIDES

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An investigation is reported on a possible effect in the NMR-spectrum of the fcc-alkali fullerenes, caused by the off-centre displacements of the alkali cations. The effect consists in a slight, asymmetrical distortion of the NMR-lines of the tetrahedrally-coordinated alkali cations, in the direction of lower shift values. Copyright ©1996 Elsevier Science Ltd

Off-centre sites for the alkali cations A in the alkali fullerenes  $AC_{60}$  and  $A_3C_{60}$  have originally been suggested [1,2], from the analysis of the X-ray and neutron scattering data, as a result of the two competing (tetrahedral and octahedral) coordinations existing in these compounds. Off-centre sites have also been indicated [3,4] in higher-doped alkali fullerenes, as, for instance,  $A_4C_{60}$  and  $A_6C_{60}$ , where the alkali cations may even form clusters of regular geometrical shapes. Evidence for off-centre sites of the octahedrally-coordinated Rb in the ternary compound  $RbK_2C_{60}$  has recently been reported from X-ray studies [5], and recent computations of phonon spectra [6] indicated a central instability of the K-cation in the octahedral coordination in  $K_3C_{60}$ . Such off-centre sites, placed along the (111)-directions, have been confirmed [7,8] for the octahedrally-coordinated alkali cations by the analysis of the inter-atomic potentials in some lightly-doped fcc-alkali fullerenes of the type  $A_nC_{60}$ , with  $n = 1, 2, 3$ .

A typical situation, on which we shall focus in the present paper, refers to the octahedral K-cations in  $K_3C_{60}$ , whose off-centre sites are placed at the distance  $\delta \sim 0.3\text{Å}$  from the centre of the octahedral coordination, along the (111)-symmetry directions, the potential barrier between two adjacent off-centre sites being  $\sim 10\text{ meV}$  [8]. The existence of the off-centre sites is well documented for the substitutional impurities in the alkali halides [9], and their effect on the NMR-spectrum of these compounds has been studied [10,11]. Generally, the off-centre displacements generate quadrupolar couplings, both at the positions of the displaced nuclei and at the relaxed positions of the neighbouring nuclei; though, usually, these couplings are quadratic in the small displacement magni-

tudes  $\delta$ , they may produce sizeable splittings on the NMR-lines, as they affect directly the Zeeman levels. However, the tunneling of the displaced atoms between the highly-symmetric off-centre sites practically averages out any observable effect in the NMR-spectrum. We shall not be concerned in this paper with the quadrupolar coupling generated by the off-centre sites. Instead, a new situation may appear in the alkali fullerenes of the  $K_3C_{60}$ -type, where a  $\delta$ -order dipole electric field may change the hyperfine interaction of the (partially) transferred *s*-electrons of the tetrahedral cations, via a polarization effect. Indeed, the shifts of both  $^{39}\text{K}$ - and  $^{87}\text{Rb}$ -NMR lines in  $K_3C_{60}$  and, respectively,  $Rb_3C_{60}$  have recently been ascribed to this hyperfine interaction, and the well-known splitting of the NMR-line of the tetrahedrally-coordinated alkali cations [12] [13] (known as the  $T - T'$ -splitting) has been explained as being due to the change in this interaction brought about by the tetrahedral vacancies [14,15]. The positive shift values of the alkali-cation NMR lines in these compounds indicate the presence of a superexchange interaction at the positions of the alkali cations, which means that the hyperfine interaction is transferred, to a small extent, to the *s*-orbital of the alkali cations. As is well-known, these compounds are predominantly ionic, but the presence of the paramagnetically shifted NMR-lines of the alkali cations indicate that the outer *s*-wave electrons of the alkali atoms transferred to the fullerenes molecules still spend a certain time around the nuclei of the alkali cations. In other words, the alkali cations in these compounds are not fully ionized, on the average, but they still have an atomic, neutral character. We shall continue to call them alkali "cations", but we shall

bear in mind that they still have, on the average, a small electronic population on the  $s$ -orbital. It is exactly the change in this electronic population that we compute, as determined by the polarization effects, and it is shown that this change may be related to the polarization of the alkali atoms, i.e. to the polarization corresponding to the full occupancy (one electron) of the  $s$ -orbital of these atoms. The remanent  $s$ -electrons on the alkali "cations" are, in fact, conduction electrons, who spend a certain, small lapse of time on these alkali "cations", and, in this respect, the effect presented here is similar with the Knight shift; however, the off-centre displacements produce a decrease in the small electronic population of the  $s$ -type orbitals, so that the shift is actually diamagnetic.

It is easily to see that, as a consequence of the octahedral cubic symmetry, the dipole electric field at the off-centre positions of the octahedral alkali cations is a  $\delta^3$ -order contribution [16]; using the small off-centre displacement  $\delta$  as a perturbation parameter we shall neglect this third-order effect. We shall also not be concerned with the change in the hyperfine interaction produced by the  $\delta$ -order dipole electric field of the off-centre alkali cations at the positions of the carbon nuclei in the fullerenes molecules, due to the absence of highly-polarizable  $s$ -orbitals in the outer shells of these atoms. It is well-known that the transferred electrons occupy the (hybridized)  $p$ -type carbon orbitals on the fullerene molecules, and, as such, they will not contribute much to the NMR-signal of the carbon atoms, except to the small extent to which they are hybridized with the  $s$ -type orbitals. In addition, the off-centre displacements will excite these electrons to higher atomic orbitals, less of which have  $s$ -character, and even these are placed highly in energy, so that the effect will be extremely small. It is also well-known that the fullerene molecule, and the fullerene anion, are highly polarizable, but the effect we talk about here depends essentially on the change in the population of the  $s$ -type orbitals, under the influence of an external electric field (in our case, the electric field produced by the off-centre displacements), and the two quantities (polarizability and the change in population) differ from each other, as it will be shown below. We are left, therefore, with investigating the effect mentioned above on the alkali cations placed at the tetrahedral positions. We shall see that the off-centre displacements of the neighbouring octahedral alkali cations produce a series of diamagnetic shifts of  $\delta^2$ -order in the NMR-line of the tetrahedral alkali cation. In general, the magnitude of this asymmetrical distortion of the NMR-line is small, as one may expect from a small perturbation acting on a hyperfine coupling of superexchange type.

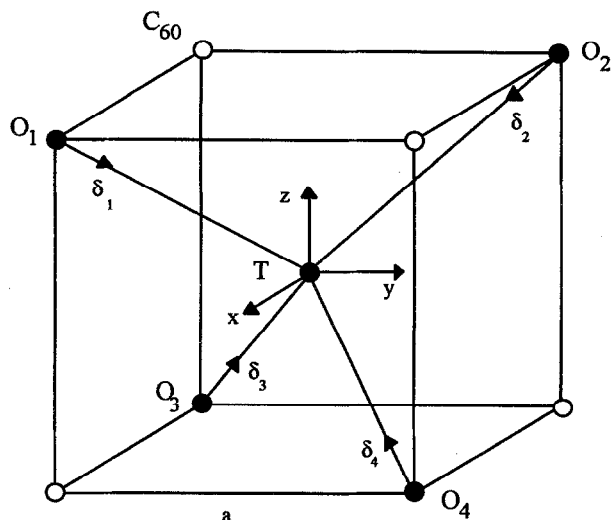


Fig. 1. The structural unit of the fcc-alkali fullerides ( $a = 7.1 \text{ \AA}$ ), with the tetrahedral position  $T$  and the octahedral positions  $O_{1,2,3,4}$  of the alkali cations, and the centres of the fullerene molecules  $C_{60}$ . The projections on the cube diagonals of the off-centre displacements are  $\delta_{1,2,3,4}$ .

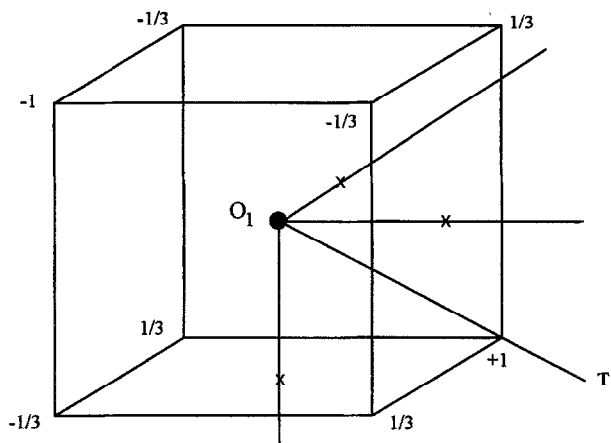


Fig. 2. The cube of the off-centre sites of the alkali cation  $O_1$ , with the off-centre site projections  $\delta_1/\delta = \pm 1, \pm 1/3$  on the  $O_1T$ -diagonal.

The structural unit employed here for the fcc-alkali fullerides is the body-centered cube shown in Fig. 1, with the side  $a = 7.1 \text{ \AA}$  [17]. One can see in Fig. 1 the tetrahedral position  $T$  of the alkali cations, the four octahedral alkali cations  $O_{1,2,3,4}$ , as well as the centres of the fullerene molecules  $C_{60}$ . The off-centre sites of the octahedral alkali cations are placed at the corners of small cubes of side  $2\delta/\sqrt{3}$ , centered on the positions  $O_{1,2,3,4}$ ; such a cube, on a larger scale, is shown in Fig. 2, for the octahedral alkali cation  $O_1$ . Since we are interested only in the first-order effects of the off-centre displacement  $\delta$  we consider only the

projections of these displacements on the  $O_{1,2,3,4} - T$  diagonals; they are denoted by  $\delta_{1,2,3,4}$  in Fig. 1. One can easily check that these projections may only take the values  $\pm\delta$ ,  $\pm\delta/3$ , as shown in Fig. 2 (in units of  $\delta$ ).

The dipole electric potential produced at the point  $\vec{r} = (x, y, z)$  in Fig. 1 by the displacement  $\delta$  of an octahedral alkali cation  $O$  is given by

$$\Phi = e\delta \frac{a\sqrt{3}/2 + r \cos \theta}{\left[ (a\sqrt{3}/2 + r \cos \theta)^2 + r^2 \sin^2 \theta \right]^{3/2}}, \quad (1)$$

where  $e$  is the absolute value of the electron charge (the proton charge), and, at the same time, the charge of the octahedral alkali cation; here, we neglect the small deviation from the full ionization of this cation, since it would only bring a second-order effect in (1). The angle between  $\vec{r}$  and the cube diagonal  $OT$  is denoted by  $\theta$  in (1). The total potential at  $\vec{r}$  is obtained by summing up the contributions of the type (1) of all the neighbouring octahedral alkali cations  $O_{1,2,3,4}$ . Up to a constant term, this potential generates at the point  $\vec{r}$  in the neighbourhood of the tetrahedral alkali cation  $T$  ( $r \ll a$ ) a potential energy

$$V_T = -\frac{16e^2}{3\sqrt{3}a^3} \sum_{i=1}^4 \vec{\delta}_i \vec{r}, \quad (2)$$

where the vectorial notation has been introduced for the displacements  $\delta_i$ . Added to the inter-molecular potential energy [8] the interaction given by (2) produces a change in the position of the tetrahedral alkali cation of the order  $\delta$ . However, averaging over the off-centre displacements this change in position vanishes [18]. To the first-order in  $\delta$  the interaction energy produced by (1) for an electron of the tetrahedral alkali cation is, therefore,  $u = -e\Phi$ .

As we have said above, the shifts in the NMR-lines of the tetrahedral alkali: "cations" in  $K_3C_{60}$  and  $Rb_3C_{60}$  are assumed to arise from a remanent spin density in the  $s$ -orbital, which generates a hyperfine coupling (via a superexchange type of interaction). [12–15] These lines are positioned at  $\sim 200$  ppm with respect to the reference NMR-signal of  $^{87}Rb^+$  in the gas phase, for example [12]. We estimate here the change brought about by the interaction  $u$  in this  $s$ -wave electron density at the tetrahedral position of the nucleus of the alkali "cation"; specifically, we carry out the computations for K. We assume a mean-field single-electron picture for the electron orbitals of the K-atom, with hydrogen-like electron wavefunctions, and estimate the first-order correction to, the  $4s$ -wavefunction brought by the perturbation  $u$ . The effective nuclear charge for this orbital is taken as equal to  $Z^* = 3.5$ , corresponding to an orbital expo-

nent  $Z^*/4 = 0.87$  [19]. We shall limit ourselves to the  $4p_z$ -orbital as the first excited orbital, since it lies closest in energy to the  $4s$ -orbital, and use for the latter the same orbital exponent. The matrix element of  $u$  between these two orbitals is then readily obtained as

$$u_{sp} = \frac{\sqrt{5}e^2\delta}{18a^2} I_M, \quad (3)$$

where

$$I_M = \int_0^\infty d\rho f_M(\rho) \rho^3 \exp(-\rho) \left( 1 - 2\rho + \frac{13}{10}\rho^2 - \frac{11}{30}\rho^3 + \frac{11}{240}\rho^4 - \frac{1}{480}\rho^5 \right); \quad (4)$$

the function  $f_M(\rho)$  is given by

$$f_M(\rho) = \begin{cases} \rho/M - 3M/\rho, & \text{for } \rho < M, \\ 3 + M^2/\rho^2, & \text{for } \rho > M, \end{cases} \quad (5)$$

where  $M = \sqrt{3}Z^*a/4a_H$ ,  $a_H$  being the Bohr radius. With a difference in energy between the two orbitals denoted by  $\Delta$  we obtain easily, by using the first-order perturbation theory, a change  $-u_{sp}/2\Delta$  in the energy of the  $s$ -orbital, and a relative content  $(u_{sp}/2\Delta)^2$  of  $p$ -orbital in the perturbed wavefunction. We emphasize here that this is the fraction of  $p$ -orbital contained in the perturbed wavefunction, i.e. contained in the perturbed mixture of  $s$ - and  $p$ -orbitals, and both the unperturbed  $s$ -orbital and the perturbed mixture are normalized to the small electronic occupancy, as discussed above. In other words,  $(u_{sp}/2\Delta)^2$  is the mixing coefficient between the  $s$ -orbital and the  $p$ -orbital, and it does not depend on the electronic content of the unperturbed orbital, as it is well-known from the standard first-order perturbation calculations. This fraction gives the relative change in the small electronic population of the  $s$ -orbital, as a result of the polarization effects. The relative shift in the corresponding NMR-line is therefore given by  $-(u_{sp}/2\Delta)^2$ . Taking into account the contributions of the type (1) coming from all the neighbouring octahedral alkali cations we may write the relative shift of the NMR-line of the tetrahedral alkali cation as

$$S = -S_0\sigma^2, \quad (6)$$

where

$$S_0 = \left( \frac{\sqrt{5}e^2\delta}{36a^2\Delta} \cdot I_M \right)^2 \quad (7)$$

and  $\sigma = (\delta_1 + \delta_2 + \delta_3 + \delta_4)/\delta$ . We emphasize that the displacement given by (6) is computed with respect of the shift of the tetrahedral NMR-line (i.e., with respect to 200 ppm, for example).

It is easy to see that  $S_0$  can be expressed in terms of the polarizability  $\alpha$  of the alkali atom. Indeed, by a similar perturbation calculation we get the polarizability (in an external, uniform electric field)

$$\alpha = \left( \frac{\sqrt{5} e a_H}{6 Z^*} \cdot I \right)^2 \cdot \frac{1}{\Delta}, \quad (8)$$

where  $I$  denotes the integral

$$I = \int d\rho \cdot \rho^4 \exp(-\rho) (1 - 2\rho + \frac{13}{10}\rho^2 - \frac{11}{30}\rho^3 + \frac{11}{240}\rho^4 - \frac{1}{480}\rho^5). \quad (9)$$

This integral is straightforwardly computed, and we obtain  $I = -36$ ; whence, eliminating  $\Delta$  between (7) and (8), we get

$$S_0 = \left( \frac{\sqrt{5} Z^{*2}}{6480} \frac{\alpha}{a^2 a_H} \frac{\delta}{a_H} I_M \right)^2. \quad (10)$$

We remark here that the polarizability is obtained from the shift in energy  $-u_{sp}^2/2\Delta$  while the relative change in the population of the  $s$ -type orbital that gives the distortion effect is  $-(u_{sp}/2\Delta)^2$ ; this is the difference we have spoken about before. It follows, from what we have said above, that for any configuration  $(\delta_1, \delta_2, \delta_3, \delta_4)/\delta$  of off-centre displacements there is a diamagnetically shifted NMR-line of the tetrahedral alkali cation, whose shift is given by (6). In the remaining of this paper we compute the intensities of these lines.

Looking at Fig. 2 we can see that the probabilities of the off-centre sites  $\delta_1/\delta = \pm 1$  are  $1/8$ , while the probabilities of the off-centre sites  $\delta_1/\delta = \pm 1/3$  are  $3/8$ . The probability of a configuration  $(\delta_1, \delta_2, \delta_3, \delta_4)/\delta$  of the four independent octahedral alkali cations can therefore be obtained by a multiple binomial distribution; for example, the probability of the configuration  $(1, -1, -1/3, -1/3)$  is  $C_4^2 C_2^1 (1/8)^2 (3/8)^2$ , etc. These probabilities, together with the corresponding reduced shifts  $\sigma^2$ , are given in Table 1 for any configuration. Summing up the probabilities for the same value of  $\sigma^2$  we obtain the relative intensities of the lines, included in Table 2. As one can see, there are 6 lines diamagnetically shifted with respect to the normal line ( $\sigma = 0$ ), due to various configurations of the off-centre displacements. Using the intensities given in Table 2 we obtain the average (reduced) shift  $\bar{\sigma}^2 = 1.3$ . The magnitude of the effect is easily estimated from (10). Using  $Z^* = 3.5$ ,  $\delta \simeq a_H = 0.53 \text{ \AA}$  and  $a = 7.1 \text{ \AA}$  the integral given by (4) is  $I_M \approx 16.5$  ( $M = 20.3$ ); making use of the polarizability  $\alpha \sim 50 \text{ \AA}^3$  of atomic K, [20] [21] we obtain from (10)  $S_0 \sim 1.7 \cdot 10^{-2}$ , i.e. an

Table 1. Probabilities and the reduced shifts  $\sigma^2$  for the off-centre configurations  $(\delta_1, \delta_2, \delta_3, \delta_4)/\delta$

Configuration	Probability	$\sigma^2$
(1,1,1,1)	$(1/8)^4$	16
(1,1,1,1/3)	$C_4^1 (1/8)^3 (3/8)$	100/9
(1, 1, 1, -1/3)	$C_4^1 (1/8)^3 (3/8)$	64/9
(1, 1, 1, -1)	$C_4^1 (1/8)^4$	4
(1,1,1/3,1/3)	$C_4^2 (1/8)^2 (3/8)^2$	64/9
(1, 1, 1/3, -1/3)	$C_4^2 C_2^1 (1/8)^2 (3/8)^2$	4
(1, 1, 1/3, -1)	$C_4^2 C_2^1 (1/8)^2 (3/8)^2$	16/9
(1, 1, -1/3, -1/3)	$C_4^2 (1/8)^2 (3/8)^2$	16/9
(1, 1, -1/3, -1)	$C_4^2 C_2^1 (1/8)^2 (3/8)$	4/9
(1, 1, -1, -1)	$C_4^2 (1/8)^4$	0
(1,1/3,1/3,1/3)	$C_4^1 (1/8) (3/8)^3$	4
(1, 1/3, 1/3, -1/3)	$C_4^1 C_3^1 (1/8) (3/8)^3$	16/9
(1, 1/3, 1/3, -1)	$C_4^1 C_3^1 (1/8)^2 (3/8)^2$	4/9
(1, 1/3, -1/3, -1/3)	$C_4^1 C_3^1 (1/8) (3/8)^3$	4/9
(1, 1/3, -1/3, -1)	$C_4^1 C_3^1 (C_2^1 1/8)^2 (3/8)^2$	0
(1, 1/3, -1, -1)	$C_4^1 C_3^1 (1/8)^3 (3/8)$	4/9
(1, -1/3, -1/3, -1/3)	$C_4^1 (1/8) (3/8)^3$	0
(1, -1/3, -1/3, -1)	$C_4^1 C_3^1 (1/8)^2 (3/8)^2$	4/9
(1, -1/3, -1, -1)	$C_4^1 C_3^1 (1/8)^3 (3/8)$	16/9
(1, -1, -1, -1)	$C_4^1 (1/8)^4$	4
(1/3,1/3,1/3,1/3)	$(3/8)^4$	16/9
(1/3, 1/3, 1/3, -1/3)	$C_4^1 (3/8)^4$	4/9
(1/3, 1/3, 1/3, -1)	$C_4^1 (1/8) (3/8)^3$	0
(1/3, 1/3, -1/3, -1/3)	$C_4^2 (3/8)^4$	0
(1/3, 1/3, -1/3, -1)	$C_4^2 C_2^1 (1/8) (3/8)^3$	4/9
(1/3, 1/3, -1, -1)	$C_4^2 (1/8)^2 (3/8)^2$	16/9
(1/3, -1/3, -1/3, -1/3)	$C_4^1 (3/8)^4$	4/9
(1/3, -1/3, -1/3, -1)	$C_4^1 C_3^1 (1/8) (3/8)^3$	16/9
(1/3, -1/3, -1, -1)	$C_4^1 C_3^1 (1/8)^2 (3/8)^2$	4
(1/3, -1, -1, -1)	$C_4^1 (1/8)^3 (3/8)$	64/9
(-1/3, -1/3, -1/3, -1/3)	$(3/8)^4$	16/9
(-1/3, -1/3, -1/3, -1)	$C_4^1 (1/8) (3/8)^3$	4
(-1/3, -1/3, -1, -1)	$C_4^1 (1/8)^2 (3/8)^2$	64/9
(-1/3, -1, -1, -1)	$C_4^1 (1/8)^3 (3/8)$	100/9
(-1, -1, -1, -1)	$(1/8)^4$	16

Table 2. Relative intensities and the reduced shifts  $\sigma^2$  of the off-centre NMR-multiplet

$9\sigma^2$	144	100	64	36	16	4	0
Intensity	1	12	66	220	495	832	462

average diamagnetic shift  $\sim 2.2\%$ ; for 200 ppm it corresponds to  $\sim 4-5$  ppm. The effect would, however, be easier observable in a static, broad NMR-spectrum, which would acquire a largely asymmetrical shape. It is also worth mentioning that a flat potential energy

curve around the octahedral positions, as in the case of Rb [7, 8], would also cause such an asymmetrical distortion. The effect is, however, insignificant for weakly-polarizable atoms, as, for example, carbon.

In conclusion, one may say that a small, diamagnetic distortion of the NMR-lines of the tetrahedrally-coordinated alkali "cations" may appear in some alkali fullerenes, as a result of the change in the remanent population of the outer *s*-orbital of these "cations", change determined by the off-centre octahedrally-coordinated alkali cations via polarization effects.

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