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On a structural distortion effect in the NMR-spectrum of alkali fullerides

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Abstract

An investigation is reported on a possible effect in the NMR-spectrum of the fcc-alkali fullerides, caused by the off-centre displacements of the alkali cations. The effect consists in a slight, asymmetrical distortion of the NMR-lines in the direction of lower shift values.

It has been shown recently[1],[2] that the octahedrally-coordinated alkali cations in the fcc-alkali fullerides may acquire off-centre positions, placed along the (111)-symmetry directions.Similar off-centre sites may also appear in other alkali fullerides, ternary compounds included. 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 $\delta \sim 0.3 \; \mathring{A}$ from the centre of the octahedral coordination, along the (111)-symmetry directions, the potential barrier between two adjacent off-centre sits being $\sim 2 \; meV$.[2] The existence of the off-centre sites is well documented for the substitutional impurities in the alkali halides,[3] and their effect on the NMR-spectrum of these compounds has been studied.[4],[5] Generally, the off-centre displacements generate quadrupolar couplings both at the positions of the dispalced nuclei and at the relaxed positions of the neighbouring nuclei; though, usually, these couplings are quadratic in the displacement magnitudes δ , 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-symmertric off-centre sites averages out any observable effect in the NMR-spectrum, in most situations. We shall not be concerned with the quadrupolar coupling in this paper. Instead, a new situation may appear in the alkali fullerides of the K_3C_{60}-type, where a δ-order dipole electric field may change the hyperfine interaction of the (partially) transferred s-orbitals, via a polarization effect. Indeed, the shifts of both ^{39}K- and ^{87}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[6],[7] has been explained as being due to the change in this interaction brought by the tetrahedral vacancies.[8] As a consequence of the octahedral cubic symmetry the dipole electric field at the off-centre positions of the octahedral alkali cations is a δ^3-order contribution;[9] using the small off-centre displacement δ 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 δ-order dipole electric field of the off-centre alkali cations at the positions of the carbon nuclei in the fullerene molecules, due to the absence of highly-polarizable s-orbitals in the outer shells of these atoms. We are left 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 δ^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.
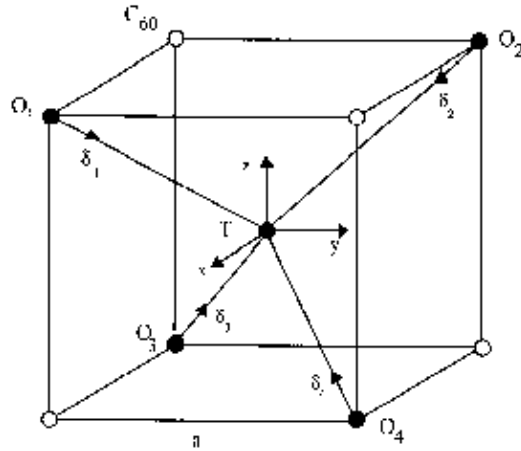
Figure 1: The structural unit of the fcc-alkali fullerides ($a = 7.1$ Å), with the terahedral position T and the octahedral positions $O_{1,2,3,4}$ of the alkali cations, and the centres of the fullerene molecules C_{60} . The projections on the cube diagonals of the off-centre displacements are $\delta_{1,2,3,4}$.

The structural unit employed here for the fcc-alkali fullerides is the body-centered cube shown in $Fig.1$, with the side $a = 7.1$ Å .[10] 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 $2\delta/\sqrt{3}$, centred on the positions $O_{1,2,3,4}$; such a cube 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 δ 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 δ).
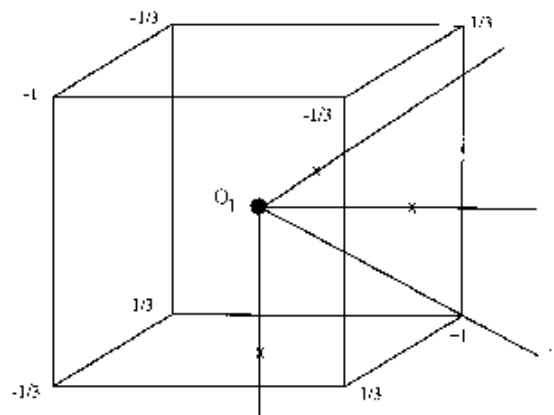

Figure 2: The cube of the off-centre sites of the alkali cation O_1 , with the off-centre site projections $\delta_1/\delta = \pm 1, \pm 1/3$ on the O_1T-diagonal.

The dipole electric potential produced at the point $\overrightarrow{r} = (x, y, z)$ in $Fig.1$ by the displacement

δ of an octahedral alkali cation O is given by

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

where e is the electron (and alkali cation) charge and θ is the angle between $\overrightarrow{r}$ and the cube diagonal OT. The total potential at $\overrightarrow{r}$ 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 $\overrightarrow{r}$ in the vicinity of the tetrahedral alkali cation T a potential energy

$$V_T = -\frac{16e^2}{3\sqrt{3}a^3}\sum_{i=1}^{4}\overrightarrow{\delta_i}\,\overrightarrow{r}, \tag{2}$$

where the vectorial notation has been introduced for the displacements δ_i. Added to the inter-molecular potential energy[2] the interaction given by (2) produces a change in the position of the tetrahedral alkali cation of the order δ. However, averaging over the off-centre displacements this change in position vanishes.[11] To the first-order in δ the interaction energy produced by (1) for an electron of the tetrahedral alkali cation is, therefore, $u = -e\Phi$.

The shifts in the NMR-lines of the tetrahedral alkali cationsin 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).[6]−[8] These lines are positioned at ~ 200 *ppm* with respect to the reference NMR-signal of $^{87}Rb^+$ in the gas phase, for example.[6] We estimate here the change brought by the interaction u in this s-wave electron density at the tetrahedral position of the nucleus of 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 charge for this orbital is taken as equal to $Z^* = 3.5$, corresponding to an orbital exponent $Z^*/4 = 0.87$.[12] We shall limit ourselves to the $4p_z$-orbital, as lying closest in energy to the $4s$-orbital, and use the same orbital exponent. The matrix element of u between these two orbitals is then readily obtained as

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

where

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

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

$$f_M(\rho) = \Big\langle \begin{array}{ll} \rho/M - 3M/\rho, & , for\ \rho < M, \\ 3 + M^2/\rho^2, & for\ \rho > M, \end{array} \tag{5}$$

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 Δ we obtain easily, by using the first-order perturbation theory, a change $-u_{sp}^2/2\Delta$ in the energy of the s-orbital, and a relative content $(u_{sp}/2\Delta)^2$ of p-orbital in the perturbed wavefunction. 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

$$S = -S_0\sigma^2, \tag{6}$$

where

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

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 easily to see that S_0 can be expressed in terms of the polarizability α of the alkali cation. Indeed, by a similar perturbation calculation we get the polarizability

$$\alpha = 180 \frac{e^2 a_H^2}{Z^{*2}\Delta} , \tag{8}$$

whence, eliminating Δ between (7) and (8) , we obtain

$$S_0 = \left(\frac{\sqrt{5}Z^{*2}}{6480} \frac{\alpha}{a^2 a_H} \frac{\delta}{a_H} I_M \right)^2 . \tag{9}$$

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 σ^2 , are given in Table 1 for any configuration. Summing up the probabilities for the same value of σ^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 $\overline{\sigma^2} = 1.3$. The magnitude of the effect is easily estimated from (9). Using $Z^* = 3.5$, $\delta \simeq a_H = 0.53$ $\mathring{A}$ and $a = 7.1$ $\mathring{A}$ the integral given by (4) is $I_M = 16.5$ ($M = 20.3$); making use of the polarizability $\alpha \sim 50$ $\mathring{A}^3$ of (atomic) K,[13][14] we obtain from (9) $S_0 \sim 1.7 \cdot 10^{-2}$, i.e. an average diamagnetic shift ~ 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 ,[1][2] would also cause such an asymmetrical distortion. The effect is, however, insignificant for low polarizable atoms, as, for example, carbon.

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Table 1

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

$Configuration$	$Probability$	σ^2
(1111)	$(1/8)^4$	16
(1111/3)	$C_4^1(1/8)^3(3/8)$	100/9
$(111-1/3)$	$C_4^1(1/8)^3(3/8)$	64/9
$(111-1)$	$C_4^1(1/8)^4$	4
(111/31/3)	$C_4^2(1/8)^2(3/8)^2$	64/9
$(111/3-1/3)$	$C_4^2C_2^1(1/8)^2(3/8)^2$	4
$(111/3-1)$	$C_4^2C_2^1(1/8)^3(3/8)$	16/9
$(11-1/3-1/3)$	$C_4^2(1/8)^2(3/8)^2$	16/9
$(11-1/3-1)$	$C_4^2C_2^1(1/8)^3(3/8)$	4/9
$(11-1-1)$	$C_4^2(1/8)^4$	0
(11/31/31/3)	$C_4^1(1/8)(3/8)^3$	4
$(11/31/3-1/3)$	$C_4^1C_3^1(1/8)(3/8)^3$	16/9
$(11/31/3-1)$	$C_4^1C_3^1(1/8)^2(3/8)^2$	4/9
$(11/3-1/3-1/3)$	$C_4^1C_3^1(1/8)(3/8)^3$	4/9
$(11/3-1/3-1)$	$C_4^1C_3^1(C_2^11/8)^2(3/8)^2$	0
$(11/3-1-1)$	$C_4^1C_3^1(1/8)^3(3/8)$	4/9
$(1-1/3-1/3-1/3)$	$C_4^1(1/8)(3/8)^3$	0
$(1-1/3-1/3-1)$	$C_4^1C_3^1(1/8)^2(3/8)^2$	4/9
$(1-1/3-1-1)$	$C_4^1C_3^1(1/8)^3(3/8)$	16/9
$(1-1-1-1)$	$C_4^1(1/8)^4$	4
(1/31/31/31/3)	$(3/8)^4$	16/9
$(1/31/31/3-1/3)$	$C_4^1(3/8)^4$	4/9
$(1/31/31/3-1)$	$C_4^1(1/8)(3/8)^3$	0
$(1/31/3-1/3-1/3)$	$C_4^2(3/8)^4$	0
$(1/31/3-1/3-1)$	$C_4^2C_2^1(1/8)(3/8)^3$	4/9
$(1/31/3-1-1)$	$C_4^2(1/8)^2(3/8)^2$	16/9

$$(1/3 - 1/3 - 1/3 - 1/3) \qquad C_4^1(3/8)^4 \qquad 4/9$$
$$(1/3 - 1/3 - 1/3 - 1) \qquad C_4^1 C_3^1 (1/8)(3/8)^3 \qquad 16/9$$
$$(1/3 - 1/3 - 1 - 1) \qquad C_4^1 C_3^1 (1/8)^2(3/8)^2 \qquad 4$$
$$(1/3 - 1 - 1 - 1) \qquad C_4^1 (1/8)^3(3/8) \qquad 64/9$$

$$(-1/3 - 1/3 - 1/3 - 1/3) \qquad (3/8)^4 \qquad 16/9$$
$$(-1/3 - 1/3 - 1/3 - 1) \qquad C_4^1 (1/8)(3/8)^3 \qquad 4$$
$$(-1/3 - 1/3 - 1 - 1) \qquad C_4^2 (1/8)^2(3/8)^2 \qquad 64/9$$
$$(-1/3 - 1 - 1 - 1) \qquad C_4^1 (1/8)^3(3/8) \qquad 100/9$$

$$(-1 - 1 - 1 - 1) \qquad (1/8)^4 \qquad 16$$

Table 2
Relative intensities and the reduced shifts σ^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